

## FREE RADICAL POLYMERIZATION KINETICS - REVISITED

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Abstract Recent developments in the kinetic modelling of free radical polymerization are reviewed with an emphasis on work in the author's laboratory. At low conversions the chain length dependence of the termination rate constant has been experimentally demonstrated and theoretically modelled. The impact of this chain length dependence on other aspects of free radical polymerization kinetics has also been explored both theoretically and experimentally. At higher conversions the gel effect has been modelled with some success by using the concept of chain entanglement to describe the influence of high polymer concentration on the termination reaction rate. The state of knowledge concerning copolymerization kinetics is briefly discussed.

### INTRODUCTION

The free radical polymerization of vinyl monomers is probably the most common synthetic reaction carried out by man. As such, it has been studied long and well. In broad outline the nature of the reactions involved has been well understood for more than three decades, and this has led many to believe that the subject is one in which there is not much new to be found. However, interest does continue in this area because its complexity has so far prevented anyone from giving a complete description of the course of a polymerization in quantitative terms. Interest in modelling free radical polymerization kinetics has also received added stimulus in recent years because of the need for kinetic models for computer control of processes (1).

A complete kinetic model must be able to describe the individual reaction rates for initiation, propagation, chain transfer and termination of the propagating chain. Only from such information can one deduce the molecular weight distribution or other important properties of the polymer chain. Conversely, only by using the molecular weight distribution (MWD) or at least averages of it can one hope to sort out the highly coupled influences of the various elementary reactions on the overall rate and extent of polymerization.

The common use of gel permeation chromatography (GPC) to determine MWD in the last decade has provided the polymerization kineticist with what is now an indispensable tool for experimental work. As a result of its use the "classical" kinetic model, based almost exclusively on rates and number average degrees of polymerization, must be modified. In this paper, the work done toward such a modification during the last six years in the author's laboratory is reviewed and summarized.

When a vinyl monomer undergoes free radical polymerization the simplest possible system consists of an initiator which is soluble in the monomer and a resultant polymer which is also soluble in its monomer. A wide variety of techniques have been employed to measure the kinetics of polymerization for such systems using characteristics such as shrinkage,

temperature rise, refractive index change, etc. which occur as polymerization does. Necessarily, the techniques are different for different extents and degrees of polymerization. One can, however, use the results of investigations from many different laboratories to synthesize a composite view of a simple polymerization. Such a description is given in Figure 1.

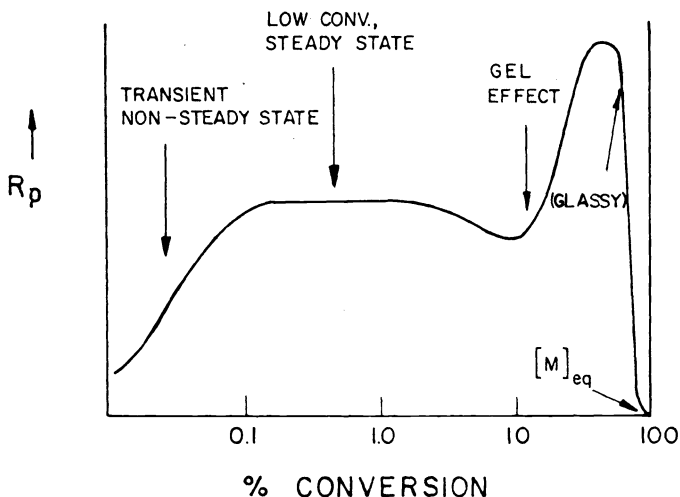


Fig. 1. Rate of Polymerization as a function of conversion

At the beginning there is a short period when the rate is changing and then the reaction reaches a steady state; as the reaction advances to 10% or so, both the rate and degree of polymerization are observed to pass through minima. This is regarded as the onset of the "gel effect" a period when the increasing viscosity of the polymerizing system causes the reaction to accelerate. The rate acceleration is matched by an increase in the cumulative molecular weight of the polymer (especially the weight average) and there is a concomitant broadening of the MWD. Ultimately, the rate of polymerization passes through a maximum and, as the mixture becomes glassy, the rate falls to nearly zero. Since there exists an equilibrium monomer concentration the rate must go to zero at some conversion less than 100%. This description is semi-quantitative at best and some features of it may be missing or difficult to observe in a given polymerization. We shall however employ it for discussion purposes and use the words "low" and "high" to refer to conversion (of monomer to polymer) before and after the onset of the gel effect, respectively.

#### THE SIMPLEST KINETIC MODEL

What has come to be called the "classical" kinetic model of free radical polymerization kinetics involves the unimolecular decomposition of initiator,  $I$ , to produce two free radicals,  $R\cdot$ , a fraction of which,  $f$ , then add monomer,  $M$ , to initiate the active polymer chain,  $P\cdot$ . The active chain either propagates and grows by adding more monomer or stops its growth by undergoing chain transfer with some species  $Y$  or by terminating in a bimolecular reaction with another active chain. These reactions and associated rate expressions are set forth in Scheme 1. Note that species  $Y$  may be initiator, monomer, polymer, solvent, impurity, or deliberately added chain transfer agent.

Scheme 1

	Reaction	Rate expression
Initiation	$I \rightarrow 2R\cdot$	$k_d[I]$
	$R\cdot + M \rightarrow P_1\cdot$	$k_i[R\cdot][M]$
Propagation	$P_n\cdot + M \rightarrow P_{n+1}\cdot$	$k_p[P_n\cdot][M]$
Transfer	$P_n\cdot + Y \rightarrow P_n + R\cdot$	$k_{tr,Y}[P_n\cdot][Y]$
Termination	$P_n\cdot + P_m\cdot \rightarrow P_{n+m}$	$k_{tc}[P_n\cdot][P_m\cdot]$
	$\rightarrow P_n + P_m$	$k_{td}[P_n\cdot][P_m\cdot]$

To solve this simplest model of polymerization for useful kinetic expressions it is commonly assumed that:

- i, the radical reactivity is independent of chain length,
- ii, the rate at which chains are initiated equals the rate at which they are terminated,
- iii, radicals generated in chain transfer rapidly reinitiate propagating chains, and
- iv, chains are very long so that the amount of monomer consumed in initiation and chain transfer reactions is small compared to that in propagation.

Using these assumptions the rate and degree of polymerization are given by (2)

$$-d[M]/dt = (k_p^2 k_d [I] / k_t)^{1/2} [M] \quad (1)$$

$$1/\bar{P}_n = \sum_Y k_{tr,y} / k_p [Y] / [M] + k_p^2 R_p / [M]^2 \quad (2)$$

The predictions of these and other equations which can be derived for the classical mode, have been sustained in many investigations carried out at low conversions and over some concentration variation. However, there exist many reported instances where the predictions of the classical model have failed (3). In particular this is true at high initiator concentration, in solution polymerization and, as expected, at high conversion of monomer to polymer. Some of these failures are readily attributed to the need for inclusion of, e.g., primary radical termination at high initiator concentration, or specific complex formation not included in the simple model. However, a combination of theoretical and experimental work in our laboratory has shown that a more fundamental problem is the first assumption above: the termination rate constant is a function of chain length.

#### LOW CONVERSION KINETICS

A number of earlier workers had suspected that  $k_t$  was a function of chain length, but their experiments were either done where the dependency was weak or their tools were not adequate to the task. In particular, one might have expected that some of the chain lifetime measuring techniques, such as the rotating sector, might have revealed the chain length dependence. However, it is the case for all such techniques that the measurement of chain lifetime gives only the ratio  $k_p/k_t$ , and separation of these two variables is usually done using a value of  $k_p^2/k_t$ , determined in a separate set of experiments - often done in a separate laboratory. Therefore, if chain length dependence does exist, such experiments will not reveal it; instead the data from them ought to be quite scattered and may explain the enormous scatter of results one sees in literature tabulations (4).

The experimental work which has established the chain length dependence of the  $k_t$  is based on a linear analog of the rotating sector measurement, which we call spatially intermittent polymerization (SIP) (5). In the SIP apparatus the monomer plus photoinitiator is pumped at a measured speed through a glass capillary onto which UV light shines through a set of evenly placed slits in a mask. Thus the monomer passes alternately through light and dark regions in which the radical concentration rises and falls. By controlling the pump speed, the rate of polymerization is varied. A mathematical description of this process is formally identical to that of the rotating sector experiment, with the pump speed replacing the (inverse) frequency of rotation. The major advantage of the SIP technique is that the effluent from the reactor may be collected, at very low conversion, thus providing a sample large enough for use in a GPC directly for the determination of both conversion and MWD.

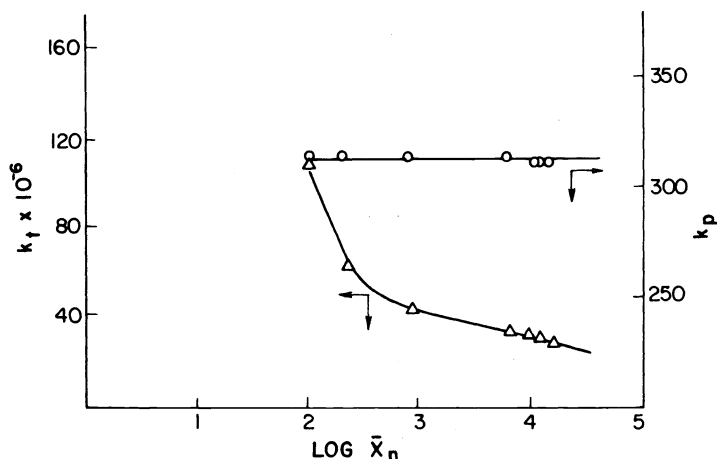


Fig. 2 Effect of chain length on  $k_p$  and  $k_t$  for methylmethacrylate at 25°C (5)

Results typical of those we have obtained using the SIP are shown in Figure 2. It should be noted that the chain length dependence is quite strong below a chain length of 100, but is almost negligible above 1000. Given that most polymerizations yield a degree of polymerization averaging 1000 or more the question might be asked, is the chain length dependence unimportant? To answer this it must be remembered that every chain that grows to be 1000 units in length spends 10% of its time being less than 100 units long; during that time, its probability of terminating is much higher and therefore the distribution of lengths of active chains is skewed, as is the final MWD, and the rate of polymerization is also affected.

To explore further the phenomena affected by the chain length dependence of  $k_t$ , we developed a model whose roots can be traced to the work of Benson and North (6) and, more recently Horie *et al.* (7). This model begins with the premise that two radical containing polymer coils (which will ultimately react to form dead polymer) must first undergo translational diffusion to collide and then must undergo segmental diffusion to bring the chain ends into a very small volume element where reaction (combination or disproportionation) takes place. The results of this model (slightly simplified) are expressed in the following equations:

$$k_t = F_1(\xi, T) F_2(\alpha, N) \quad (3)$$

where  $\xi$  is the segmental friction coefficient,  $\alpha$  is the linear chain expansion coefficient and  $N$  is the radical chain length. The detailed form of  $F_1$  works out to be approximately

$$F_1 = 1/(a_m N_o \eta) \quad (4)$$

at 300 K while  $F_2$  is more complicated:

$$F_2 = (1 - 0.37/\alpha^{0.74} (1 - 1.84 N_o^{1/2}/\alpha N^{1/2})) \alpha^{2.6} \quad (5)$$

In eqn. 4  $a_m$  is the hydrodynamic radius of a segment,  $N_o$  is the chain stiffness and  $\eta$  is the solvent viscosity.

Since the parameters in eqns 4 and 5 are either known or experimentally accessible, it is possible to use the model to test experimental data for conformity and, finding this to be true, to design and interpret further experiments. For example, the data in Table 1 show a dependence of  $k_t$  on the ester length for a number of alkyl methacrylates which is completely predicted by the variance in  $F_1$  calculable from known (or estimated) values of the parameters of eqn. 4(8).

TABLE 1  
Comparison of Experimental and  
Calculated Termination Rate Constants of Alkyl Methacrylates (8)

Monomer Ester of AMA	$\eta_o$ [poise]	$a_m$ AMA/ $a_m$ MMA	$N_o$ AMA/ $N_o$ MMA	$K_t$ AMA/ $K_t$ MMA x 10 <sup>2</sup>	
				Expt'l	Calcd
Methyl (MMA)	0.53	1.0	1.0	100.0	100.0
Butyl	0.91	1.60	0.911	47.6	40.0
Octyl	1.92	1.96	1.093	12.45±4.25	12.88
Dodecyl	3.96	2.84	1.62	2.86±0.9	2.91
Cetyl	7.52	3.95	2.35	0.762±0.19	0.76

The conversion dependence of  $k_t$  is also predictable by this model in terms of the influence of polymer on the coil sizer as expressed by the chain expansion coefficient, (9, 10). In general, anything which reduces the solvent's thermodynamic quality towards the polymer will cause the coil to shrink. In the smaller coil, the chain end will be found more easily by the other chain end, and therefore  $k_t$  will be larger. Therefore any reduction in solvent quality should result in a reduced rate of polymerization. As a polymerization advances the presence of more polymer makes the solution a thermodynamically poorer one and therefore produces a slower rate and a lower degree of polymerization. The latter was first noted experimentally by Schulz and Harborth more than 30 years ago (11), while North and Reed observed the decrease in  $k_t$  20 years ago (12); the latter's data are quantitatively interpreted by an extension of eqn 3 as shown in Figure 3. Furthermore, the linear dependence of  $k_t$  on polymer concentration seen in Figure 3 is quite general at low polymer concentrations, and the experimentally observed slopes of the line are predicted to be simply proportional to chain length. Verification of this prediction has been seen for methylmethacrylate and, as shown in Figure 4, also for styrene.

Other applications of this model have shed some light on the importance of primary radical termination (13), the influence of pressure on the termination reaction (14, 15) and the influence of the chain length dependence of  $k_t$  on the quantitative measurement of chain transfer coefficients (16). From this work has arisen the appreciation of a somewhat disturbing fact: the use of experimental variables in free radical polymerization is not as simple as we once thought it was! Whenever a variable is changed (such as the initiator or chain transfer agent concentration) the rate of polymerization is changed; this causes a change in the degree of polymerization which in turn causes a change in  $k_t$ .

Therefore the interpretation of the effect of the change in the original variable is confounded by the change in  $k_t$ . Separating these two concurrent changes is possible but requires more care than has usually been given to the interpretation of results using the "classical" model or variants on it.

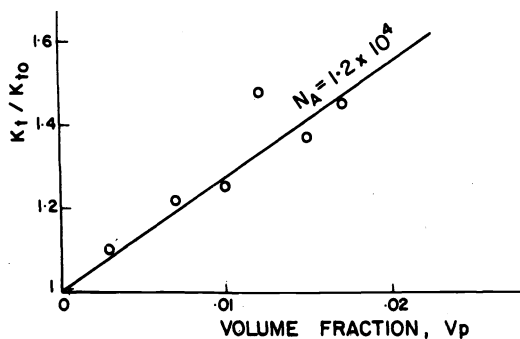


Fig. 3 Effect of polymer on  $k_t$  in MMA polymerization. Solid line predicted by theory (9).

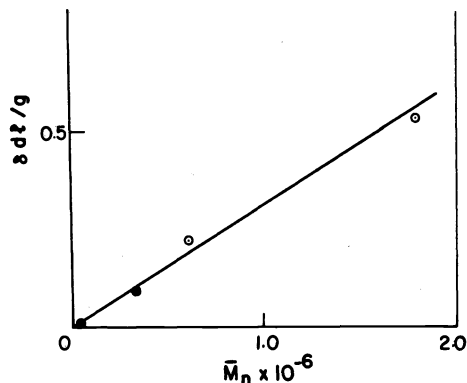


Fig. 4 Effect of polymer molecular weight on slopes of plots such as Fig. 3 for styrene (10).

If one takes care to do all experiments at similar degrees of polymerization or to correct data for changes in chain length then results which are both accurate and precise can be obtained (17). Figure 5 for example shows the temperature dependence of  $k_p$  and  $k_t$  for the two most studied monomers, styrene and methylmethacrylate (MMA), which may be compared with the enormous scatter seen in the tabulated literature (4). Another example may be seen in Figure 6 where the lumped rate constant for primary radical concentration obtained with experiments done at similar degrees of polymerization shows the expected Arrhenius dependence, whereas those data obtained with no attention to chain length gave a curvature which led to a qualitative misunderstanding of the termination process.

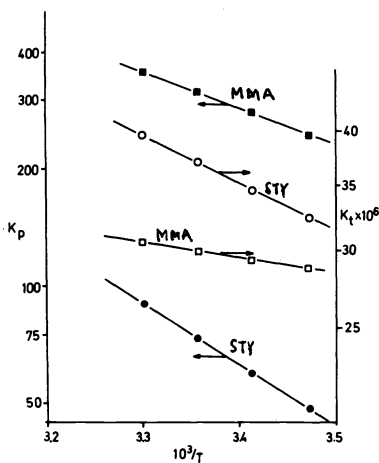


Fig. 5 Variation of  $k_p$  and  $k_t$  with temperature for styrene and MMA at constant chain length (17).

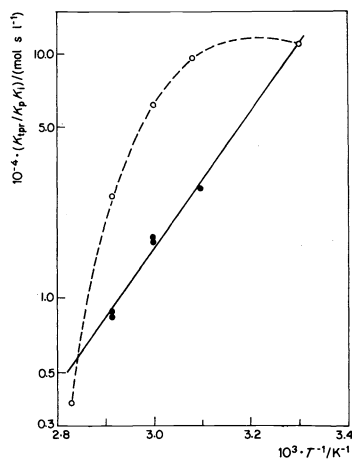


Fig. 6 Variation of PRT constant with temperature at constant (filled circles) and variable (open circles) chain length (13)

## HIGH CONVERSION KINETICS

Given the quantitative understanding of the influence of segmental mobility and polymer coil size on the kinetics of low conversion polymerization, the question then arises can we develop a similar understanding of the nature of the gel effect, the autoacceleration that appears as the reaction mixture becomes viscous and leads rapidly to high conversion. To do so we begin by recognizing that the onset of the gel effect represents a change in the nature of the diffusion process which is the rate controlling step in the termination reaction (18). This is shown schematically in Figure 7 where the rate constant for the overall process of termination,  $k_t$ , is viewed as a sum of the constants describing segmental diffusion,  $k_s$ , and translational diffusion,  $k_T$ . As described above,  $k_s$  is expected to increase linearly with conversion, conversely translational diffusion is expected to decrease with increasing reaction viscosity and, when chain entanglement becomes dominant, will do so in an explosive manner. This leads to the observed maximum in  $k_t$ .

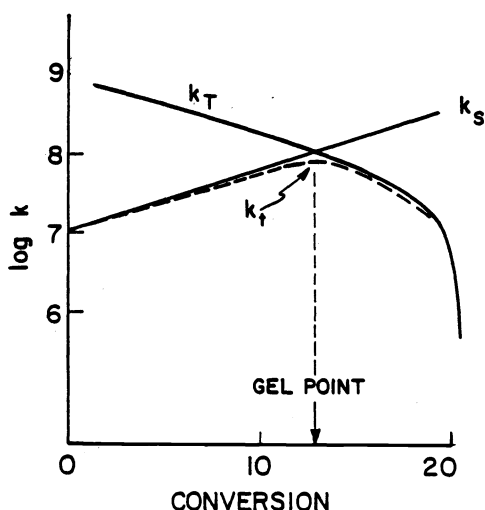


Fig. 7 Schematic showing combined effects of segmental and translational diffusion processes on  $k_t$  as function of conversion.

To model this phenomenon, we have proposed (19) that the active polymer chains in moderately concentrated solution are either small enough to be regarded as mobile or large enough to be regarded as entangled and thus of restricted mobility. The small chains are regarded as having the same value of  $k_t$  as in more dilute solution, while the large entangled chains terminate with a rate constant  $k_{te}$ . Cross termination between large and small chains is regarded as occurring with a rate constant which is the geometric mean of  $k_t$  and  $k_{te}$ . The chain size which separates "small" from "large" is  $n_c$  and given by

$$K_c = \phi_p n_c^{\frac{1}{2}} \quad (6)$$

where  $K_c$  is a chain entanglement constant, familiar to those who study concentrated polymer solutions and polymer melts, and  $\phi_p$  is the volume fraction of polymer in the reaction mixture. Applying conventional steady state approximations this model yields for the rate of polymerization,  $R_p$ ,

$$\frac{R_p}{R_{p,0}} - 1 = ((1/\beta) - 1) \exp(-n_c v) \quad (7)$$

where  $R_{p,0}$  is the rate of polymerization (given in eqn 1) and  $v$  is the kinetic chain length, both of which would be obtained in the absence of the gel effect and

$$\beta = (k_{te}/k_t)^{1/2} \quad (8)$$

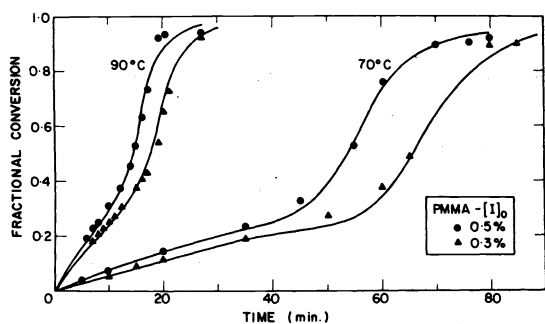


Fig. 8 Bulk polymerization of methyl methacrylate; solid line predicted by eqn. 7.

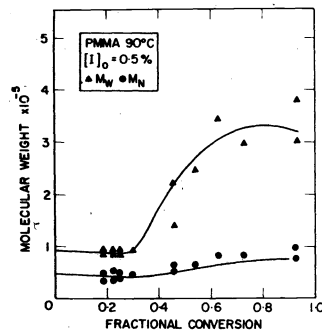


Fig. 9 Molecular weight variation with conversion in polymerization of methyl methacrylate. Solid line predicted by theory (19).

Using the same parameters the leading moments of the MWD can also be described. Figures 8 and 9 show typical examples of the success of this model, which has only the two adjustable parameters  $K_c$  and  $\beta$  in describing the gel effect quantitatively. The temperature dependence of these two parameters has been measured and the model rewritten in a somewhat more convenient form so that non-isothermal polymerizations could be described (20). To do so, two other parameters were defined in terms of the existing kinetic constants:

$$C_1 = [((1 + e)/\alpha_o^2 K_c) ([M]_o / -2e)^{1/2}]^{1/2} \quad (9)$$

$$C_2 = (2k_t^{1/2}/k_p [M]_o) K_c / (1 + e) \quad (10)$$

where  $e$  is the fractional shrinkage accompanying polymerization. In these terms the rate of polymerization becomes

$$R_p/R_{p0} - 1 = (C_1 g_1 - 1) \exp(-C_2 g_2) \quad (11)$$

where  $g_1$  and  $g_2$  are functions only of conversion; it should be emphasized that  $C_1$  and  $C_2$  are not functions of anything except the physical and chemical characteristics of the monomer.

An interesting consequence of eqn. 11 is that it can be used to understand why styrene has so much weaker a gel effect than methylmethacrylate does. Note that  $C_2$  appears in a negative exponential term and that the experimental value for  $k_t^{1/2}/k_p$  is about six-fold smaller for styrene than for MMA. In plain language this means that if a polymerization of styrene is carried out at the same initial rate as one for MMA the latter will produce a higher molecular weight polymer and thus become entangled at a lower conversion the gel effect will start sooner and be more pronounced because of the greater entanglement.

Useful though these equations have been, the model has proved to have some very real limitations. It does not properly describe polymerizations carried out in solution, probably because it does not incorporate any measure of the free volume change which occurs during the polymerization. Such a change must be different in solution polymerization from what it is in bulk. Also the model ignores any contribution from primary radical termination which has been calculated to become of importance as the chain end



concentration increases and the monomer concentration decreases during the advanced stages of the gel effect.

A major limitation of the model, one which it was never intended to handle, is the highest level of conversion where, if the temperature is low enough, the monomer-polymer mixture becomes glassy. Under such conditions, the propagation and initiation reactions become diffusion controlled. An approach to treating this problem has been presented by Hamielec (21). Even if the reaction temperature is higher than the polymer glass transition temperature, the highest level of conversion must ultimately involve the reversibility of the propagation reaction. Little work has been done in this area where the kinetics are controlled by the thermodynamics. However, in an era when trace amounts of suspect chemicals are of concern in our environment, more attention must be given to polymerization at the highest possible level of conversion.

#### COPOLYMERIZATION KINETICS

If our quantitative understanding of the details of homopolymerization kinetics is as limited as outlined above, that of copolymerization is woeful. Relative rates of copolymerization have usually been expressed in terms of reactivity ratios, thousands of which have been measured and tabulated. Unfortunately, most of the measurements have been done with a complete disregard for the non-linear character of the equations used and the statistical validity of most methods for deriving the reactivity ratios is poor. This problem, it has been recently shown (22), can easily be overcome by proper design of experiments. Unfortunately, this realization does nothing to improve the quality of the many data in the literature.

Absolute rates of free radical copolymerization have been described using equations analogous to homopolymerization, the major difficulty being how to describe the termination reaction. Rudin has surveyed the various treatments (23). It is clear that, whichever may be the proper way to describe the termination reaction in copolymerization, it must recognize the diffusion control in the process. For this reason, the use of a phi factor, which implies chemical control, is not acceptable. The problem of finding a correct description at low conversion which embodies the segmental motion of a chain of variable and random composition remains unsolved (24).

At high conversion, recent work by Johnson, Karmo and Smith (25) has shown that the simple Mayo-Lewis model of four propagation reactions, each with its own propagation rate constant, may not be able to explain the drift of composition with conversion in the copolymerization of styrene with methylmethacrylate. This observation has been confirmed in our laboratory (26) and also noted in the copolymerization of styrene with butylmethacrylate (27). It also appears in terpolymerizations of similar monomers. Pichot *et al.* have shown that a similar problem exists in acrylonitrile-styrene copolymerization (28) and have suggested that selective solvation may be the cause. Whatever the cause may prove to be it appears that there is still a lot to learn about free radical polymerization kinetics.

#### ACKNOWLEDGEMENT

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