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The Failure of Terminal-Model Kinetics of Free-Radical Copolymerization

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Summary

The validity of terminal-model kinetics of free-radical copolymerization was examined by a complete set of experiments carried out on the bulk-copolymerization of styrene and methyl methacrylate at 40°C. The copolymer composition conforms to the model within experimental error, whereas the measured propagation rate constant is entirely different from what the model predicts. The termination rate constant is close to the composition average of those of the homopolymerizations.

The composition curves of most free-radical copolymerizations are well explained by terminal-model kinetics (1). This is equivalent to saying that the ratios of the propagation rate constants (reactivity ratios) are effectively constant, independent of composition. However, it is obvious that constancy of the ratios does not necessarily imply constancy of the individual rate constants. Curiously, the terminal model has never been critically tested in this respect, except for a few limited cases (2-4). We have doubted the general validity of the terminal model (5,6), and for some years, have been collecting basic experimental data (5-7) to make a stringent test of the model. Here, we briefly report results of such a test which was made on the bulk-copolymerization of styrene (S, monomer 1) and methyl methacrylate (MMA, monomer 2) at 40°C.

The copolymer composition , the initiation rate, the volume contraction factor (conversion factor), and the polymerization rate R_p were all measured as a function of feed-monomer composition f. The radical lifetime was measured by the rotating sector method at several different compositions including $f_1 = 0$ and 1. The validity of this method for copolymerization systems has already been demonstrated (4,8). In order to decrease experimental errors, in each experiment we carried out as many independent runs as possible. Using this method, the composition of a p-chlorostyrene-methyl acrylate system was found to deviate slightly from the terminal-model curve (5). In the present system, no such deviation was detectable. Details of the experiments and numerical results will be reported elsewhere (7,9).

The rate constants of propagation, k_p, and termination, k_t, for a copolymerization system are defined by

$$R_p = k_p[P^{\cdot}][M] \tag{1}$$

$$R_t = k_t[P^{\cdot}]^2 \tag{2}$$

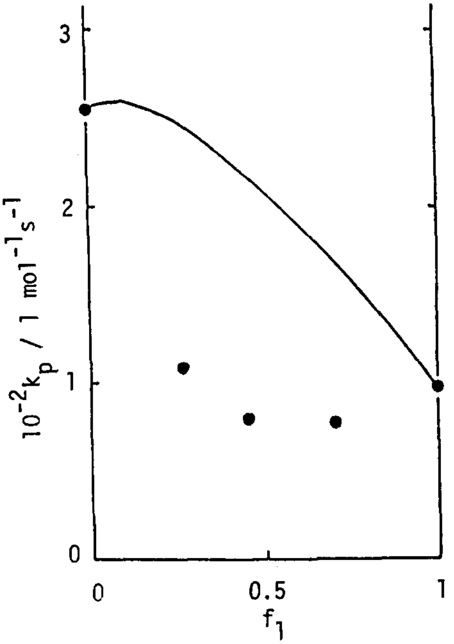

Fig. 1. Plot of k_p vs. f_1: the filled circles were measured, and the solid curve was calculated with the terminal model.

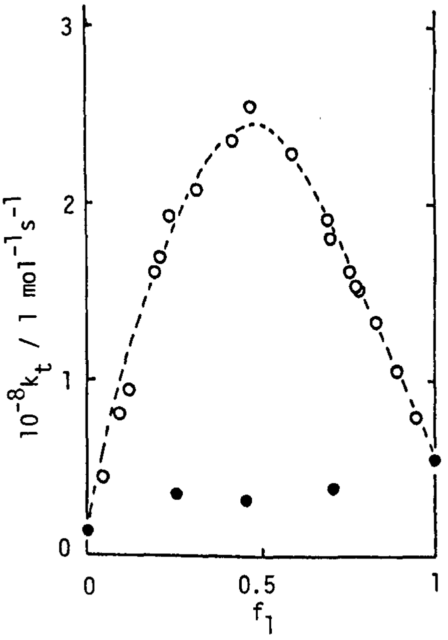

Fig. 2. Plot of k_t vs. f_1: the filled circles were measured, and the open circles were calculated with the terminal model.

where $[P^\bullet]$ is the total radical concentration, [M] is the total monomer concentration, and R_t is the termination rate, which is equal to the initiation rate R_i in a stationary state. Ellimination of $[P^\bullet]$ from eq.(1) and (2) gives the familiar relation

$$R_p = (k_p/k_t^{1/2})R_i^{1/2}[M] \tag{3}$$

The radical lifetime τ is related to the rate constants by (4,8)

$$\tau R_{ps} = (k_p/k_t)[M] \tag{4}$$

where R_{ps} is the rate of polymerization under steady illumination.

In Figures 1 and 2, we plot measured values of k_p and k_t against the monomer concentration f_1. The solid curve in Figure 1 represents the k_p predicted by the terminal model, and the open circles in Figure 2 represent the k_t computed from eq.(3) by using the terminal-model k_p. The differences between the measured and calculated results are far beyond experimental uncertainty, and this unequivocally leads to the conclusion that terminal-model kinetics entirely fails to describe the rate equations of this system.

Figure 2 reveals that k_t is close to the composition average of those of the homopolymerizations, or in terms of Walling's cross-termination parameter (10), ϕ is close to one. The present system has been believed to have relatively large, composition-dependent ϕ. In accordance with previous results (11), the open circles in Figure 2 give values of ϕ ranging from about 10 to about 30 (from left to right). Our experiments have shown that the large ϕ is a direct consequence of applying the erroneous model for the propagation step. Systems which are characterized by large ϕ are rather numerous, and much controversy exists regarding the mechanism of the termination step (11). Clearly, reexamination of the propagation step is needed. In this connection, the results reported by Ito and O'Driscoll (3) on the copolymerizations of methacrylates may be suggestive in the following three respects: their systems are characterized by reactivity ratios close to one and by a rather "normal" mechanism of the termination reaction (i.e., $\phi \sim 1$), and the measured k_p is close to that calculated with the terminal model.

At present, the mechanism of the propagation step of the S-MMA system is not necessarily clear. However, the fact that addition of various solvents to the system does not change the essential features of the R_p vs. f_1 curve (12,13) implies penultimate effects. In fact, the penultimate model (5,14) is able to describe the behavior of k_p exhibited in Figure 1, if the ratios k_{jii}/k_{iii} (i, j = 1 or 2) are regarded as adjustable parameters (6), where k_{pmn} (p, m, n = 1 or 2) is the rate constant for the terminal radical m with a penultimate unit p to add monomer n. Clearly, more work is needed to disclose the mechnisms of the propagation as well as termination reactions. A more complete report on the S-MMA system will be shortly published (9).

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