

Effects of Diffusion Control on the Propagation and Transfer Rate Coefficients in Free Radical Polymerization

Brendan S. Casey,* Martin F. Mills,
David F. Sangster, Robert G. Gilbert, and
Donald H. Napper

School of Chemistry, University of Sydney, Sydney,
NSW 2006, Australia

Received July 13, 1992

Introduction

This note indicates the correct mathematical analysis, within the framework of the encounter-pair model, for the competing kinetic processes of propagation and transfer in a polymerization reaction. While our treatment is very simple, it has apparently not been carried out hitherto, and the present paper corrects some errors in the literature. The encounter-pair model is of particular applicability to polymerizations as the change in viscosity is often so large near the glass transition that translational diffusion may become rate determining.

The theory of diffusion-controlled reactions, with regard to the encounter-pair model, has been discussed and reviewed in detail by Noyes¹ and North.² The fundamental assumption in this model is that a bimolecular reaction in the liquid state can be considered as a two-stage process: first diffusion together of the reactants to form an encounter pair, which has a fixed encounter radius, and then chemical reaction. This model (while open to question in ordinary solvents where more modern theories are probably more physically correct³) is expected to be especially apt for polymerization in glassy systems due to the long-lived nature of the encounter pair.

The encounter-pair model yields the following equation for bimolecular reactions:

$$\frac{1}{k} = \frac{1}{k_{\text{diff}}} + \frac{1}{k^{\circ}} \quad (1)$$

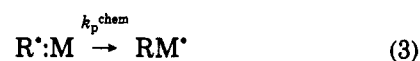
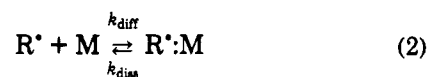
where k is the overall second-order rate coefficient for the process under all conditions, k_{diff} is the diffusion-controlled rate coefficient, which is usually calculated via the application of the Smoluchowski equation,⁴ and k° is the rate coefficient for the reaction in the limit of very rapid diffusion (i.e. "chemical" control). In polymer kinetics this has been widely applied to bimolecular termination⁵⁻¹⁰ and, less commonly, to initiator decomposition^{11,12} and free radical propagation.^{9,12-19} However, the possibility that the transfer reaction will also become diffusion controlled at high conversion has apparently not been properly appreciated. Even when the equation above has been applied for propagation, which requires the same diffusive step as transfer, it is common to employ an invariant rate coefficient for the transfer reaction.^{9,12-19} Indeed, this paper serves as a correction of earlier work, from this research group, in which the rate coefficient of transfer was held constant at high conversion.¹⁹

The importance of transfer to monomer with regard to molecular weight distributions, and hence the physical properties of the resulting polymer, has long been known. However, in the classic free radical kinetics texts (for example, see ref 20) only generic free radicals were considered and thus transfer, which has no effect on the overall radical population, played no part in the kinetic

scheme. Over the last 20 years the polymer literature has increasingly considered chain-length-dependent kinetics^{8,9,12-14,16,17,19,21-29} and thus the rate coefficient of the transfer reaction, which transforms a long chain into a short radical species, has become of significance in kinetic studies as well as molecular weight analysis. Further, the kinetics of polymerization at high conversion has also increased in importance in recent times for both economic and environmental reasons. It is thus critical that proper account of the influence of increasing viscosity on the transfer rate coefficient be taken.

Derivation of Diffusion-Controlled Competitive Reaction Kinetics

The following derivation is a general one for any two competing bimolecular reactions for which the fundamental assumption of physical and chemical separability, inherent in the encounter-pair model, is valid. To minimize repetition, however, the derivation is carried out for the two competing reactions of immediate concern—free radical propagation and transfer to monomer. The appropriate kinetic equations are



where R^{\bullet} is a growing polymeric free radical of arbitrary length, M is a monomer molecule, $R^{\bullet}:M$ represents the "encounter pair", i.e. the reactants being within the chosen encounter radius, RM^{\bullet} is the propagated free radical, R is the terminated polymer chain, M^{\bullet} is a monomeric free radical, k_{diff} is the second-order rate coefficient for diffusion together of the reactants, k_{diss} is the first-order rate coefficient for dissociation of the encounter pair, $k_{\text{p}}^{\text{chem}}$ is the first-order rate coefficient for the propagation step within the encounter pair, and $k_{\text{tr}}^{\text{chem}}$ is the first-order rate coefficient for the transfer of free radical activity within the encounter pair. Upon application of the steady-state assumption to the encounter pair, the reaction rates are given by

$$\frac{d[RM^{\bullet}]}{dt} = k_{\text{p}}^{\text{chem}} \left(\frac{k_{\text{diff}}}{k_{\text{p}}^{\text{chem}} + k_{\text{tr}}^{\text{chem}} + k_{\text{diss}}} \right) [R^{\bullet}][M] \quad (5)$$

$$\frac{d[M^{\bullet}]}{dt} = k_{\text{tr}}^{\text{chem}} \left(\frac{k_{\text{diff}}}{k_{\text{p}}^{\text{chem}} + k_{\text{tr}}^{\text{chem}} + k_{\text{diss}}} \right) [R^{\bullet}][M] \quad (6)$$

and thus we can consider the rate coefficients for the overall reactions, k_{p} and k_{tr} , to be given by

$$k_{\text{p}} = \frac{k_{\text{p}}^{\text{chem}} k_{\text{diff}}}{k_{\text{p}}^{\text{chem}} + k_{\text{tr}}^{\text{chem}} + k_{\text{diss}}} \quad (7)$$

$$k_{\text{tr}} = \frac{k_{\text{tr}}^{\text{chem}} k_{\text{diff}}}{k_{\text{p}}^{\text{chem}} + k_{\text{tr}}^{\text{chem}} + k_{\text{diss}}} \quad (8)$$

Clearly, the experimentally determined overall rate coefficients will, in general, be functions of both the chemical and the diffusive process.

* Author for correspondence.

If we define $K = k_{\text{diff}}/k_{\text{diss}}$ (the equilibrium constant for the encounter process when no reaction is occurring), then

$$k_p = \frac{k_p^{\text{chem}} K k_{\text{diff}}}{K(k_p^{\text{chem}} + k_{\text{tr}}^{\text{chem}}) + k_{\text{diff}}} \quad (9)$$

$$k_{\text{tr}} = \frac{k_{\text{tr}}^{\text{chem}} K k_{\text{diff}}}{K(k_p^{\text{chem}} + k_{\text{tr}}^{\text{chem}}) + k_{\text{diff}}} \quad (10)$$

If we now note that invariably $k_p^{\text{chem}} \gg k_{\text{tr}}^{\text{chem}}$ in any polymerization and we put $k_p^\circ = k_p^{\text{chem}} K$ and $k_{\text{tr}}^\circ = k_{\text{tr}}^{\text{chem}} K$, then we have

$$k_p = \frac{k_p^\circ k_{\text{diff}}}{k_p^\circ + k_{\text{diff}}} \quad (11)$$

$$k_{\text{tr}} = \frac{k_{\text{tr}}^\circ k_{\text{diff}}}{k_{\text{tr}}^\circ + k_{\text{diff}}} \quad (12)$$

or alternatively, in the form that kinetic equations derived from the encounter-pair model are more commonly expressed:

$$\frac{1}{k_p} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_p^\circ} \quad (13)$$

$$\frac{1}{k_{\text{tr}}} = \frac{k_p^\circ}{k_{\text{tr}}^\circ k_{\text{diff}}} + \frac{1}{k_{\text{tr}}^\circ} \quad (14)$$

Thus we see that the application of the encounter-pair model to the competing reactions of propagation and transfer to monomer yields the expression for diffusion-controlled propagation that is commonly found in the literature, but a *different* form of the equation for transfer. This equation for the dependence of the transfer rate coefficient on the rate of diffusion, and thus the viscosity of the polymerizing medium, is the primary result in this paper. Note that the changeover from chemical to diffusion control will occur at exactly the same conversion for both transfer and propagation; a result which has not apparently been realized hitherto.

A consideration of the two limits of these reactions provides a useful test of the appropriateness of the assumptions made in the encounter-pair model. It also illustrates the important point that a reaction becomes diffusion controlled when the dissociation step (reverse of eq 2), rather than the diffusion step (eq 2), becomes slower than the chemical step (eqs 3 or 4). When $k_{\text{diss}} \ll k_p^{\text{chem}}$ or, equivalently, $k_{\text{diff}} \ll k_p^\circ$, then both chemical reactions are diffusion controlled and thus

$$k_p = k_{\text{diff}} \quad k_{\text{tr}} = \frac{k_{\text{tr}}^\circ k_{\text{diff}}}{k_p^\circ} \quad (15)$$

Note that the value of k_{tr}° does not play a role in determining the onset of diffusion control, as the competing rates are chemical reaction, with rate coefficient ($k_p^{\text{chem}} + k_{\text{tr}}^{\text{chem}}$), and dissociation, with rate coefficient k_{diss} . Since $k_p^{\text{chem}} \gg k_{\text{tr}}^{\text{chem}}$, only the magnitude of k_p^{chem} (relative to k_{diss}) determines whether chemical reaction or dissociation is the rate-determining step. When $k_{\text{diss}} \gg k_p^{\text{chem}}$ or, equivalently, $k_{\text{diff}} \gg k_p^\circ$, then the chemical reaction is considered to be rate determining and

$$k_p = k_p^\circ \quad k_{\text{tr}} = k_{\text{tr}}^\circ \quad (16)$$

Thus the previously defined k_p° and k_{tr}° prove to be

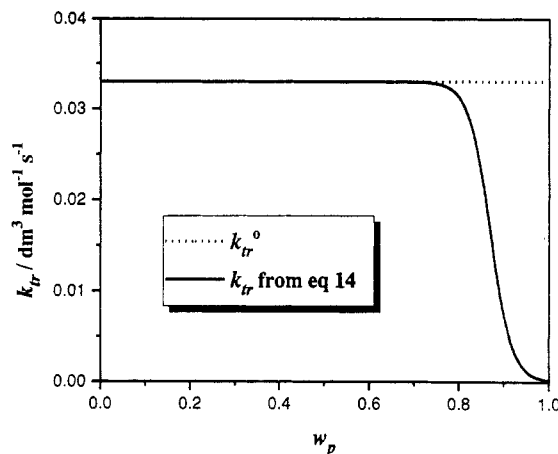


Figure 1. Difference, for the polymerization of methyl methacrylate (MMA), between the constant, low conversion value of the transfer rate coefficient (k_{tr}°) of MMA at 50 °C and the corrected value given by eq 12 or, equivalently, eq 14 (using k_p as given by Ballard et al.¹⁶). w_p is the weight fraction of polymer in the polymerizing medium.

equivalent to the overall rate coefficients obtained in the limit of very rapid diffusion. Note that, if the encounter-pair model is applicable throughout a polymerization, then these low viscosity values of the rate coefficients of propagation and transfer to monomer would be expected to be equivalent to those measured at low conversions. However, the fact that a rate coefficient does not vary with viscosity does not, of course, prove that this model is appropriate.

It is noted here, for reasons of completeness, that the appropriate kinetic equation for transfer to a molecule other than the monomer is given by eq 1, since there are usually no competing reactions. Diffusion control is, however, still only likely to become important in a glassy system.

Effect of Diffusion-Controlled Transfer Rate Coefficient on Earlier Work

As previously indicated, most literature kinetic studies simply quote a fixed value of k_{tr} , it not being generally recognized that this value may vary with conversion. This is seen, for example, in a recent paper by the IUPAC Working Party on "Modeling of Free Radical Polymerization Kinetics and Processing"¹⁸ which discusses the effects of diffusion control on propagation but not transfer. Some authors, for example Russell et al.,¹⁷ have stated that transfer is chemically controlled whereas propagation will become diffusion controlled at high conversion. However, as dictated by the kinetic analysis above, transfer actually becomes diffusion controlled at the same stage of the polymerization as propagation. For this reason, errors in the values of k_{tr} do not cause problems for work carried out at low to intermediate conversions, which are the regions most studied, but large errors in k_{tr} , and hence errors in simulated results, might be expected at high conversion. Figure 1 illustrates the difference, for the polymerization of methyl methacrylate (MMA), between the constant, low conversion value of the transfer rate coefficient (k_{tr}°) of MMA at 50 °C and the corrected value given by eq 12 or, equivalently, eq 14 (using k_p as given by Ballard et al.¹⁵).

An example of where the constant value of k_{tr} was used at high conversion is the work of Mills et al.¹⁹ who modeled high conversion reaction/diffusion processes, in the emulsion homopolymerizations of MMA and styrene, in order to determine conditions likely to cause nonuniform

polymerization within latex particles. This work implicitly utilized eq 1 for k_{tr} , which results in no effect of vitrification on the value of k_{tr} . However, the effect of a diffusion-controlled k_{tr} on the predicted morphologies, resulting from the effects of chain-length-dependent termination, would be slight due to growth by propagation becoming the dominant diffusion mechanism.⁸ Nevertheless, when the exit of free radicals is considered, the effect of the decreasing k_{tr} at high conversion may be large due to the resultant reduction in the production of short free radicals which are capable of desorbing. That work¹⁹ was aimed at obtaining a qualitative understanding of factors giving rise to inhomogeneities within latex particles. Errors in k_{tr} will have a more serious effect on detailed studies that attempt to quantitatively model high conversion kinetics using chain-length-dependent rate coefficients, or which attempt to predict molecular weight distributions.

Conclusion

The correct mathematical analysis of the competing kinetic processes of propagation and transfer to monomer, in terms of the encounter-pair model, has been detailed. The appropriate equations for the rate coefficients, in terms of the diffusion and chemical processes, were presented. This note serves as a correction of both earlier misconceptions concerning the influence of viscosity on the transfer rate coefficient and the implicit assumption that k_{tr} remains constant at high conversions. However, it appears at this stage that the effects of this error on the qualitative conclusions made in earlier works were, fortuitously, minimal.

Acknowledgment. The Australian Research Grants Committee and the Australian Institute for Nuclear Science and Engineering are thanked for support of this work. B.S.C. would like to acknowledge the financial support of a Gritton Postgraduate Research Scholarship and an AINSE Postgraduate Supplementary Award. We would like to thank Mr. Bradley R. Morrison for helpful discussion.

References and Notes

- (1) Noyes, R. M. In *Effects of Diffusion Rates on Chemical Kinetics*; Porter, G., Ed.; Pergamon Press, London, 1961; pp 129-160.
- (2) North, A. M. *Quart. Rev.* **1966**, *20*, 421.
- (3) Hynes, J. T. *Ann. Rev. Phys. Chem.* **1985**, *36*, 573.
- (4) Smoluchowski, M. v. *Z. Phys. Chem.* **1917**, *92*, 129.
- (5) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1959**, *81*, 1339.
- (6) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935.
- (7) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
- (8) Adams, M. E.; Russell, G. T.; Casey, B. S.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624.
- (9) Buback, M. *Makromol. Chem.* **1990**, *191*, 1575.
- (10) Dionisio, J.; Mahabadi, H. K.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1891.
- (11) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2141.
- (12) Zhu, S.; Hamielec, A. E. *Macromolecules* **1989**, *22*, 3093.
- (13) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1331.
- (14) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1345.
- (15) Ballard, M. J.; Gilbert, R. G.; Napper, D. H.; Pomery, P. J.; O'Sullivan, P. W.; O'Donnell, J. H. *Macromolecules* **1986**, *19*, 1303.
- (16) Mita, I.; Horie, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1987**, *C27*, 91.
- (17) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 2459.
- (18) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 851.
- (19) Mills, M. F.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1990**, *23*, 4247.
- (20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- (21) Cardenas, J. N.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 883.
- (22) Cardenas, J. N.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1883.
- (23) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1759.
- (24) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
- (25) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1299.
- (26) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1315.
- (27) Buback, M.; Schweer, J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 145.
- (28) Buback, M.; Schweer, J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 699.
- (29) Zifferer, G.; Olaj, O. F. *Makromol. Chem.* **1990**, *191*, 1699.