Termination in Free-Radical Polymerizing Systems at High Conversion

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ABSTRACT: A theory for the termination rate coefficient in high-conversion free-radical polymerization systems, based on the concept of chain-end diffusion by propagational growth ("reaction diffusion" or "residual termination" mechanism), is proposed. This is used to formulate the appropriate diffusion coefficient of a macroradical, which yields in turn a diffusion-controlled termination rate coefficient. Expressions for an upper and lower bound of this rate parameter result, depending on whether the polymer chains are rigid or dynamically flexible. All parameters used in the model (such as entanglement spacing and unperturbed chain dimensions) can be readily determined. Comparison of theoretical predictions with experiment indicates that residual termination predominates throughout much of the conversion of monomer to polymer and, further, is well-described by the proposed equations. These comparisons also suggest new interpretations of several phenomena particular to high-conversion kinetics in many free-radical systems.

Introduction

Despite its fundamental importance, the process of termination in free-radical polymerization reactions is, at present, imperfectly understood. This is particularly so beyond the initial stages of conversion of monomer to polymer, the latter being the only régime for which classical low-conversion free-radical kinetics may be applied.[1,2] When it is recalled that, perforce, most polymers are generated in the presence of moderate-to-high weight fractions of polymer (certainly only a small fraction of polymer may be formed in the so-called dilute domain when the polymer coils are nonoverlapping), the current imperfect understanding of reaction mechanism is clearly undesirable. An additional incentive to a better understanding is the growing tendency by industry to produce polymers in continuous-feed reactors[3] which operate at high mass fractions of polymer. Such systems optimize the rate of polymer production by maintaining reaction conditions in the Trommsdorff–Norrish "gel" effect régime.[4] Although it is axiomatic that this phenomenon results at least partially from a decrease in the rate of chain termination, the exact reasons for this decrease are not known.

The dearth in understanding of termination mechanisms derives primarily from a lack of accurate experimental data, and, in turn, the reasons for this are 2-fold. On the one hand, there is generally a large degree of scatter in experimental results reported by different workers (see, for example, the range of values at a given temperature for the bimolecular termination rate coefficient, k_t, of a given monomer listed in ref 5). These discrepancies have arisen, in part, from the inherent uncertainties in the methods of measuring conversion as a function of time and the further exaggeration of these imprecisions as a result of the numerical differentiation of data to obtain rates of reaction. These problems are compounded in the middle stages of the reaction where the rates of polymerization are much higher and the experimental reproducibility is poorer. However, refinement of existing techniques and the advent of new techniques (e.g., electron spin resonance [ESR] spectroscopy coupled with rate measurements[6,7]) for determining rate coefficients has seen a considerable improvement in this state of affairs in recent years. Unfortunately this has not allayed the other source of uncertainty present in most rate coefficients deduced from raw experimental data: the use of model-based assumptions. Too often, for example, it is assumed that initiator decomposition efficiency is independent of conversion or that diffusion coefficients are identical in differing environments. This problem is particularly manifest in comparing values of k_t obtained via different forms of polymerization (although the situation is improving in this regard: for example, it is now possible to obtain unambiguously the rate parameters for emulsion polymerization[8-10]). In the absence of any critical comparison of theory with experiment, many models for the prediction of k_t have survived (see ref 11 for a recent review). Often these models are based on totally different and nonequivalent physical assumptions and, without exception, these theories incorporate at least one adjustable parameter.

It is generally accepted that in free-radical polymerization bimolecular termination can be regarded as a consecutive three-step reaction.[12] Firstly, the two radical coils must gain proximity to each other by translational diffusion. Then, the free-radical chain ends must make contact: this is achieved through conformational reorientations of the polymer molecules, the so-called process of segmental diffusion. Finally, the barriers to chemical reaction must be overcome. Given that both reactants are free-radical species, it is clear that the activation energy for this last step must be small. When this is coupled with the fact that macroradicals are large, cumbersome species for which diffusive processes are slow, it follows that termination is exclusively diffusion controlled. At low conversions, the translational mobility of the nonoverlapping polymer coils is sufficiently rapid for the subsequent free-radical encounter process to be rate determining. At the other extreme, corresponding to high conversions, the chains of the polymer matrix will be so entangled that center-of-mass diffusion will essentially cease. It has therefore been proposed that the active chain ends wander by "reaction diffusion"[13] (otherwise known as "residual termination"[14]): by the very nature of their propagational growth, the chains may diffuse, despite the translational immobility of the chains as a whole. The term "roving head diffusion" is also an apt description of this process. Although it is recognized that reaction diffusion was the phrase first coined to describe this process, subsequent workers have preferred the term residual termination, so we employ this latter expression throughout this work.

It is this concept of residual termination that is explored in this paper. In the sections that follow, existing theories are reviewed, and a new theory is presented. The predictions of this theory are then compared with reliable experimental values of k_t at high conversion and the im-

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plications of these comparisons discussed.

Review of Existing Theories of Residual Termination

Despite its elegant simplicity, many workers have not considered residual termination explicitly. For example, Tulig and Tirrell[15] discussed the kinetics of autoacceleration in terms of reptation[16] and included a term $k_{t,\min}$, a minimum value of k_t of unspecified origin below which k_t could not fall. However, at high conversions, residual termination is likely to be the rate-determining step for termination for the following reason. It is now well-established experimentally that free-radical polymerization can take place with nonnegligible rate beyond the glass transition point.[7,17] Of course, in the glassy rêgime polymer chains do not undergo center-of-mass diffusion, which would imply a vanishingly small value of k_t in the absence of residual termination. The fact that polymerization occurs in such media at slow, but nevertheless perceptible, rates makes a non-zero value of k_t (due to propagation events) highly likely. (This inference could be confirmed by showing that the free-radical population changes at a rate slower than that of free-radical creation. Unfortunately, a lack of experimental precision currently prohibits such measurements.)

One formulation of residual termination has been given by Gardon.[14] He derived the expression

$$(k_t/k_p)_{\min} = 0.185\phi_m/(1-\phi_m) \qquad (1)$$

where ϕ_m is the volume fraction monomer and k_p is the propagation rate coefficient. Equation 1 gives a hypothetical limiting ratio for k_t and k_p for which all free radicals would survive in emulsion polymerization. Since it stems from rate equations endemic to emulsion polymerization, it is clearly inappropriate as a universal expression. Additionally, and more importantly, eq 1 seems inadequate in that it contains no terms dependent on the nature of the system (i.e., which polymer is being considered). Recognizing this, Gardon developed a lattice model (denoted by subscript L) for termination, arriving at the equation

$$(k_t/k_p)_L = 2\mu(d_m/d_p)\phi_m \qquad (2)$$

where d_m and d_p are the monomer and polymer densities, respectively, and μ is a lattice parameter, the number of sites surrounding a given lattice site. Gardon suggests using $\mu = 8$ (for a closely packed, hexagonal lattice), but clearly this is an adjustable parameter as the underlying assumption of a lattice structure is only of limited value. Further, the specific system characteristics enter only through the density terms.

More recently, Soh and Sundberg[18] have proposed their theory of excess chain end mobility, which yields the expression

$$k_t = f_t\pi\delta^2 a k_p C_m/j_c^{1/2} \qquad (3)$$

where f_t is an efficiency factor, δ is a radius term associated with termination, a is the root-mean-square end-to-end distance per square root of the number of monomer units of the polymer, C_m is the monomer concentration, and j_c is the entanglement spacing of the polymer. (Note that k_t is expressed here in molecular units, as it is in all subsequent equations.) Several criticisms may however be leveled against this model. Firstly, it utilizes the kinetic expression of the "volume-swept-out" model[19] for reactions, a model which assumes a lattice structure of rigid spacing for the medium of reaction. Secondly, δ is calculated by equating the bulk macroradical concentration to a local macroradical concentration. This involves calculating the volume per free radical from the overall radical concentration and matching this with the length that a chain must possess to occupy such a volume. In other words, it is assumed that all parts of configurational space are accessible simultaneously to a single, but only one, macroradical. Not only does this ignore any consideration of the packing of the chains, but it does not permit any pockets of the polymerizing medium to be inaccessible to the macroradicals. Finally, although the need for its inclusion is clear, the efficiency factor f_t can only be estimated via a semiempirical scheme.

A Theory of Residual Termination

The foundations of our new model are similar to those previously set forth by Schulz.[13] Our starting point for predicting diffusion-controlled bimolecular rate coefficients is the Smoluchowski[20] expression

$$k_t = 4\pi D_{ab}(r_a + r_b) \qquad (4)$$

where r_a and r_b are the radii of interaction, respectively, of reactants A and B, whose mutual diffusion coefficient is D_{ab}. The only assumption involved in invoking this equation is that the reactants are spherical sinks; in the case of termination, which involves two free-radical chain ends, this supposition does not seem to be dangerously flawed. Further, in the case of residual homotermination, both reacting species are alike (although the chains may differ in degree of polymerization), so not only is the relation $D_{ab} = D_a + D_b$ justified, but it is also the case that $D_a = D_b$ and $r_a = r_b$; i.e.,

$$k_t = 16\pi D_a r_a \qquad (5)$$

In conditions such that residual termination prevails, it must not only be the case that macroradical mobility is the rate-determining termination step but also that center-of-mass diffusion of the polymer chains as a whole is negligible in comparison with the rate of so-called roving head diffusion. The central tenet underpinning any prediction of the residual termination rate coefficient, k_t(res), must therefore be that any translational diffusion of the polymer chains can be ignored. Given this, consider a rigid, but growing, chain that experiences no configurational changes between propagational steps (note that "rigid" here refers to dynamic flexibility on a time scale of propagation and termination, a point discussed in more detail at a later stage). From the Einstein relation,[21] one has

$$D_a = \langle r^2\rangle/6t \qquad (6)$$

where $\langle r^2\rangle$ is the mean square displacement of the active chain end in time t. In this time, suppose the chain has undergone j propagation steps. Since the frequency of propagation is $1/k_pC_m$, then

$$t = j/k_pC_m \qquad (7)$$

The specification of $\langle r^2\rangle$ relies on two generally accepted results of polymer physics. Firstly, in the melt or concentrated solution (certainly above 10% by mass), polymer chains adopt their unperturbed conformations.[22] In rêgimes where residual termination is dominant, this will indubitably be the case. Secondly, unperturbed chains are Gaussian and their mean-square end-to-end distance is linear in N, the number of monomer units.[23] It therefore follows that

$$\langle r^2\rangle = ja^2 \qquad (8)$$

Of course eq 8 is only exactly true in the limit of infinite j. However, if the polymer chains are not "stiff" (i.e., if they are not conformationally inflexible,[23] which the acrylates and methacrylates certainly are not), then the lengths of the chains for which $j \geqslant 100$ conform adequately to the ideal Gaussian distribution.[23] Since polymer chains are long (i.e., there are many propagation events before termination), eq 8 is certainly valid in the present application. Substitution of eq 7 and 8 into eq 6 yields the j-independent result,

$$D_a = k_p C_m a^2/6 \tag{9}$$

It should be noted at this juncture that the ideas expounded above are similar to (although derived in a different manner from) those in ref 13; the expression equivalent to eq 9 derived therein is couched in terms of Kuhn chain statistics and implicates, therefore, a term for the number of monomer units per chain segment. Our adoption of Flory chain statistics obviates the need for such a term.

Equation 9 describes the diffusivity of the growing end of a rigid chain. At the other extreme, consider a flexible macromolecule. In the concentrated régime such an entity will be constrained in its motion by nodes of entanglement (with surrounding chains) along its contour. It can therefore be envisaged[18] as having a dangling chain end which extends from the ultimate point of entanglment along the chain to the free-radical chain end itself. Since, as is assumed, this dangling chain end enjoys complete flexibility consistent with the chain geometry, and because short-time scale configurational rearrangements are much more rapid than propagation, the chain end will sample all the configurational phase space available to it between propagation events. It is clear then that the center of mass of the dangling chain end must, when averaged over time, be located exactly at the node of entanglement. Now, in j propagation steps, our dangling chain end has j monomer units added to it. Since j is not small (as already discussed) and since entanglement spacing does not vary with chain length, the terminal node of entanglement must also migrate j monomer units (on average) along the chain. So, the new center of mass of the dangling chain end must be j monomer units from its initial position. It therefore follows that eq 8 describes the mean-square displacement of the center of the mass of the dangling chain end and that eq 9 describes its diffusivity.

The above cases cover the two extremes of chain flexibility. Note that eq 9 is valid in all intermediate cases. This is because the fundamental tenet of residual termination is that center-of-mass chain diffusion resulting from segmental motions in negligible. Given this restriction, it is therefore apparent that the long time-scale displacement of a free-radical chain end is derived solely from its propagating nature and is independent of the extent of its short time-scale motions. Since polymer chains are long it is precisely this long time-scale diffusivity that determines the rate of residual termination. Combining eq 5 and 9 yields

$$k_t(\text{res}) = 8\pi k_p C_m a^2 r_a/3 \tag{10}$$

where only r_a remains unknown.

As already intimated, there are two limiting cases for r_a. The first of these is that of the rigid chain. In this case, the radius of interaction for termination is best approximated by a suitably defined radius of a monomer unit. One means of estimating this quantity is from monomer density.[24] However, this involves particle packing assumptions, so a procedure more in line with modern theories of chemical physics is adopted: the Lennard-Jones diameter of the monomer, σ, is used for estimating r_a. Since two free-radical entities maintained within a distance of σ should terminate on a time scale much faster than that for propagation (the only means for two rigid chain ends to migrate away from each other), σ seems an appropriate value for r_a. The resulting expression is the minimum possible value for k_t(res) and is

$$k_t(\text{res,min}) = 4\pi k_p C_m a^2 \sigma/3 \tag{11}$$

On the other hand, the maximum possible value for the residual termination coefficient will result in the case where the chain end is totally flexible. As already suggested, on average such a chain is characterized by having nodes of entanglement every j_c monomer units. Experimental measurements of j_c for pure polymer[25,26] indicate that j_c is commonly of the order of 100 monomer units, a value that will be even larger for polymer that is swollen by monomer (as is being considered). Hence, r_a may be estimated by the result[23]

$$r_a \simeq \langle r_a^2 \rangle^{1/2} = a j_c^{1/2} \tag{12}$$

Incorporation of eq 12 into eq 10 gives

$$k_t(\text{res,max}) = 8\pi k_p C_m a^3 j_c^{1/2}/3 \tag{13}$$

Equations 11 and 13 represent the two limits between which the residual termination coefficient must be encompassed.

Calculations

Calculations of residual termination rate coefficients for three monomers at 50 °C are presented, these being methyl methacrylate (MMA), butyl acrylate (BA), and butyl methacrylate (BMA). These were selected because recent experimental investigations[9,10,27,28] (at 50 °C) have determined unambiguously the value of k_t in these systems at high conversions of monomer to polymer, a condition for which reaction diffusion is a feasible rate-determining step. Since these k_t values were obtained via seeded emulsion polymerization experiments and matrix molecular weights are typically very high in latex particles,[29] the possibility of residual termination being rate determining is thus further enhanced.

The parameters common to eq 11 and 13 that require specification are C_m, k_p, and a. C_m is directly calculated from w_p, the weight fraction of polymer, by mass balance and by assuming ideal mixing of monomer and polymer. The propagation rate coefficient (k_p), being a quantitative measure of the germinal idea underlying residual termination, is the most crucial variable in eq 11 and 13. For BA and BMA its value at 50 °C was determined directly from kinetic experiments;[9,10] for MMA at 50 °C the following w_p dependence of k_p, as determined by ESR spectroscopy,[7] was used to generate the w_p dependence of k_t(res):

$$\begin{aligned} k_p &= k_p^0 & w_p &\leqslant 0.84 \\ &= k_p^0 \exp(-29.8[w_p - 0.84]) & w_p &> 0.84 \end{aligned} \tag{14}$$

where k_p^0 was set equal to 580 dm^3 mol^{-1} s^{-1}. The unperturbed chain dimension parameter, a, or equivalently the characteristic ratio of a chain of infinite length, C_∞, can be found tabulated in a number of commonly referenced sources;[5,25] the most recent reference for the value of a for poly-BMA (PBMA)[30] was utilized. There appears to be no information available at present on the unperturbed dimensions of poly-BA (PBA), so it was decided to assign, as an approximation, to this polymer the same a value as PBMA. Now, it is likley that the acrylates will not be as stiff as the corresponding methacrylates because the less substituted chain backbone associated with acrylates will facilitate easier bond rotations and so result in slightly smaller chain dimensions. Although stochastic simulations

Table I
Parameters for k_t(res) Calculation at 50 °C

quantity	symbol	monomer	value	ref
propagation rate coeff, $dm^3\ mol^{-1}\ s^{-1}$	k_p	BMA	600	9
		BA	450	10
		MMA	eq 14	7
root-mean-square end-to-end distance per square root of the no. of monomer units, nm	a	BMA	0.62	30
		BA	0.62	30
		MMA	0.69	25
Lennard-Jones diameter, Å	σ	BMA	6.81	32
		BA	6.54	32
		MMA	5.85	32
entanglement spacing of pure polymer, monomer units	j_{c0}	BMA	126	25
		BA	126	25
		MMA	47	25

for the simpler case of ethyl groups attached to a poly(methylene) backbone do not support this,[31] experimental C_∞ values for acrylate/methacrylate counterparts[5] do show this trend. Consequently it would seem that the above approximation probably slightly overestimates the dimensions of PBA polymers.

Particular to the rigid chain limit (eq 11) is the parameter σ. Since scattering or other gas-phase experiments to determine σ accurately for the foregoing monomers have not yet been performed, it was necessary to resort to an empirical scheme of proven accuracy due to Reid and Sherwood[32] to estimate this quantity

$$\sigma = 1.18 V_b^{1/3} \tag{15}$$

Here V_b is the Le Bas volume and is calculated from additive-volume increments of the substituent atoms of the molecule. For eq 13, it is necessary to specify j_c. According to Ferry[25] there are two types of experimentally measured pure polymer entanglement spacing: M_e, the average molecular weight between coupling loci from integration of loss compliance; and M_c, the critical molecular weight for influencing steady-flow viscosity by entanglement coupling. The relation between M_e and M_c is still unclear, although it is usually observed that M_c is about twice the value of M_e. Ferry concludes that M_e "should be considered as a measure of the spacing between topological restraints which may not have a clear physical definition but nevertheless can be assigned a numerical value". Consequently, it would seem consistent, in view of the envisaged picture of flexible chain residual termination, to use M_e values to define j_{c0}, the entanglement spacing (in monomer units) of pure polymer. To compute a w_p dependence of j_c, the relation (due to Bueche[26])

$$j_c = j_{c0}/\phi_p^{\,n} \tag{16}$$

was employed, where ϕ_p is the volume fraction of polymer and the exponent n was taken to be unity. Although the actual value of n in eq 16 is shrouded with uncertainty,[33] the physical reasoning behind this equation (with $n = 1$) appears sound, so it is employed here. Because no information on the entanglement spacing of PBA and PBMA appears available, it was decided to use the same j_{c0} value for these polymers as that observed for poly(2-ethylbutyl methacrylate).[25] Since j_{c0} values do not vary greatly from polymer to polymer,[25] and further since the dependence of k_t(res,max) on j_c is relatively weak (see eq 13), the error thus introduced into values of k_t(res,max) calculated for PBA and PBMA by making the above approximation is small.

Values of all parameters used in this work are listed in Table I.

Table II
Experimental Data and Theoretical Calculations for Butyl Acrylate (BA) and Butyl Methacrylate (BMA)[a]

quantity	symbol	eq	BA value	BMA value
wt fraction polymer	w_p		0.57	0.43
exptl termination rate coeff, $dm^3\ mol^{-1}\ s^{-1}$	k_t(exp)		8×10^2	7×10^3
rigid chain residual termination rate coeff, $dm^3\ mol^{-1}\ s^{-1}$	k_t(res,min)	11	9×10^2	1.5×10^3
flexible chain residual termination rate coeff, $dm^3\ mol^{-1}\ s^{-1}$	k_t (res,max)	13	3×10^4	5×10^4
ratio of termination rate coeff to propagation rate coeff:				
exptl	$k_t(\text{exp})/k_p$		1.7	12
rigid chain residual	$k_t(\text{res,min})/k_p$	11	2.3	2.5
lattice (Gardon)	$(k_t/k_p)_L$	2	6.4	8.2

[a] k_t values for BMA are from ref 9b, obtained by reanalysis of the original data of ref 9a.

Results and Discussion

Values of k_t(res,min) and k_t(res,max) have been calculated for BA and BMA (using eq 11 and 13, respectively) and are compared with experimental values of k_t for these monomers in Table II. It should be noted how small these values are: the experimental k_t values are more than 4 orders of magnitude lower than those typically observed[5] during the initial stages of bulk polymerizations. Nevertheless, the experimental value for PBA (at a w_p of 0.6) compares most favorably with the prediction of the rigid chain limit for residual termination (eq 11), especially given the uncertainties in the reported parameters, experimental and theoretical. Moreover, the value for PBMA (at a w_p of 0.4) lies between the predicted upper (flexible chain limit) and lower (rigid chain limit) bounds. This suggests that even at the moderate weight fractions under consideration here, the PBA chains are essentially rigid on the time scale of propagation; this is a point which will be discussed in more detail later. Referring to Table II, it is significant that, at higher w_p, the Gardon model (eq 2) appreciably overestimates the ratio k_t/k_p (the advantage of expressing results in the form of this ratio is that no recourse to experimental k_p values is required). This is presumably because the Gardon model employes the notion of the polymer solution having a lattice structure (and sets the lattice parameter, μ, at too high a value), an assumption which is not invoked in the model of this paper.

Values of both k_t(res,min) and k_t(res,max), and their w_p dependence, have been calculated for MMA and are presented graphically in Figure 1. Note that for MMA these values differ by between 1 and 2 orders of magnitude. Also plotted in Figure 1 are the experimentally observed[27] values of k_t for the emulsion polymerization of MMA. These experimental values are essentially free of any model-based assumptions. It is observed that for the entire range of w_p investigated, the experimental values of k_t are sandwiched between the theoretical maximum and minimum limits of the residual termination coefficient. At intermediate conversions, k_t is close to the totally flexible chain limit; this is quite reasonable, as the presence of the monomer diluent should allow the polymer chains conformational flexibility. That the k_t(res,max) value exceeds the experimental k_t values by a factor of about 2.5 (on average) merely indicates that the dangling chain end is not sufficiently mobile to explore its entire configurational space between propagation steps. As w_p increases (i.e.,

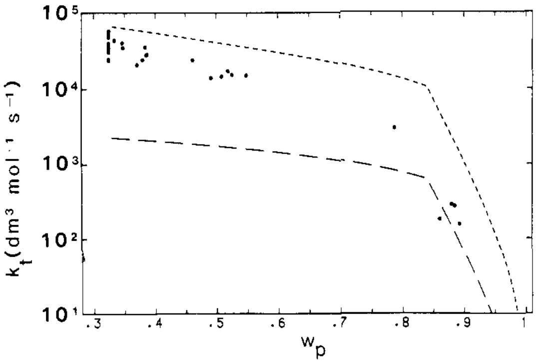

Figure 1. Experimental and theoretical values for the variation of the termination rate coefficient, k_t, with weight fraction polymer, w_p, for MMA at 50 °C; the points are experimental results, the upper line (- - -) represents predictions for k_t(res,max), and the lower line (– –) represents the predictions for k_t(res,min). Experimental data from Ballard et al.[27]

diminishing monomer concentrations cause polymer motions to become increasingly retarded), k_t is observed to approach the rigid chain limit. Since the chains would be expected to become less pliant as the polymer concentration increases, this seems to be a reasonable trend. It should be noted before proceeding further that because the value $j_{c0} = 47$ used in calculating k_t(res,max) is, it seems, a minimum value,[34] k_t(res,max) may in fact be somewhat larger than computed here. However, due to the weak dependence of this quantity on j_c (see eq 13), even if a value for j_{c0} of 200 were used,[34] k_t(res,max) would only be increased by a factor of 2; since orders of magnitude are under consideration here, this is not a large increase.

The sharp bend in the w_p profiles of k_t(res) values in Figure 1 is thought to be associated with the glass transition of the system. The glass transition temperature of poly-MMA (PMMA) is 105 °C;[5] hence for a PMMA–MMA solution at 50 °C there must exist a threshold monomer concentration below which there is no longer enough monomer (which acts as a plasticizer) present to render the polymer matrix nonglassy. This point is commonly referred to as the point of onset of diffusion-controlled propagation,[35] and once beyond it k_p is observed to decrease markedly with w_p.[7] This can be seen in eq 14 and imparts the characteristic shape to the k_t(res) curves. The implication of this physical behavior is important: once the polymer matrix becomes glassy (if not before), k_t must be specified by the rigid chain limit for k_t(res). According to Bueche,[26] the segmental jump frequency for polymer chains in a glass is of the order of 0.1 s^{-1}. Thus, it is clear that, even on the reduced time scale of propagational events beyond the glass transition point, the polymer chains are essentially frozen, so eq 11 should predict k_t with acceptable reliability. That this is not conclusively seen in Figure 1 is due to difficulties in implementing the experimental technique of ref 27 at very high conversions. Firstly, this has lead to a paucity of data in this rêgime, and secondly, k_t measurements become somewhat more inaccurate (compared to lower conversions) beyond the onset of diffusion-controlled propagation (due to a dramatic decrease in rate, the measurement of which is therefore prone to greater relative uncertainty). Another point worthy of mention is that, despite recent evidence that the glass transition point does not necessarily coincide with the point of onset of diffusion-controlled propagation,[36] the above conclusion should still hold. This is because the diffusion time scales implied by the measured k_p values are such that propagation occurs on the time scale of the most rapid chain motions, if not faster.[37]

A qualitative feature of the experimental variation of k_t with w_p, as illustrated in Figure 1, is that it is totally counterindicative of center-of-mass chain diffusion being the rate-determining step in termination. Modern theories of polymer diffusion and experimental measurements thereof, as reviewed in ref 38, show convincingly that, at the concentrations of polymer considered in the present paper, the variation of the center-of-mass diffusion coefficient of entangled polymer chains (as are under consideration here) is a far stronger function of polymer concentration than is seen for the experimental k_t of Figure 1. Further, by applying eq 9 to PMMA at 50 °C and $w_p = 0.33$ (the lowest w_p for the emulsion polymerization under consideration), it is calculated that $D_a = 3.0 \times 10^{-12}$ cm^2 s^{-1}, where D_a is the diffusion coefficient of a chain end moving by propagational growth. The most commonly espoused theory of entangled chain diffusion,[38] that of reptation, predicts that[39]

$$D_{\text{rept}} = D_s/N^2 \tag{17}$$

where D_{rept} is the center-of-mass diffusion coefficient of a reptating chain of degree of polymerization of N monomer units and D_s is the segmental diffusion coefficient of a monomer unit in the chain. In these MMA emulsion polymerizations, the number-average molecular weight is of the order of 10^6 amu or more,[27] so for PMMA one has $N = 10^4$. An upper bound for D_s is 10^{-6} cm^2 s^{-1}, and this value gives $D_{\text{rept}} = 10^{-14}$ cm^2 s^{-1}; this is 2 orders of magnitude less than the value for diffusion by propagational growth. When it is considered that, in view of free volume theories for segmental motions of polymer, the above value for D_s is possibly orders of magnitude too large,[38] and that D_{rept} will decrease much more with concentration than will D_a (as given by eq 9), it is clear that, throughout the range of w_p considered in this paper, growing chains can indeed diffuse faster by propagational growth than by center-of-mass diffusion. Not only does this conclusion indicate that termination is not controlled by center-of-mass diffusion in the experiments considered here, but it also supports the fundamental assumption of residual termination, which is that macroradicals be essentially immobile on the time scale of propagational growth.

Having established this conclusion for long chains, the possibility must be considered that small radicals (be they unentangled or slightly entangled) make a contribution to the rate of termination of a nonresidual nature. As Tulig and Tirrell have pointed out,[15] such species move around the matrix in a fashion more akin to that of free monomer than long chains. By virtue of this mobility, these small species may cause the rate of termination to be enhanced well above the value that would be observed if all radicals were long. However, for the experimental k_t values under consideration, this contingency may be discounted (as a major contributor to k_t) for several reasons. Firstly, and generally, small chains propagate and become entangled very rapidly. Secondly, these k_t values are for the emulsion polymerization of MMA. Under such conditions the dominant chain-stopping event is transfer to monomer.[27] The monomer free radicals so generated are then rapidly desorbed from the latex particles (which are the loci of polymerization) and, due to the relatively high aqueous-phase solubility of MMA, are not thought to undergo reentry into the particles until they add on additional monomer molecules. This being the case, a disproportionate contribution to the experimental k_t values of Figure 1 by small species is effectively ruled out. Finally, the nonexistence of such a contribution for BA (whose k_t value corresponds to the rigid chain limit even at intermediate w_p) makes such a phenomenon seem unlikely for MMA.

From the foregoing discussion, the following tentative conclusion may be reached: that at intermediate values of w_p PMMA chains are somewhat flexible, whereas PBA chains are relatively rigid. This is based on the observation that, at such w_p values, BA appears to conform to the rigid chain limit, whereas MMA systems appear to approach the flexible chain limit (and PBMA is intermediate). This conclusion would seem somewhat anomalous when it is considered that the glass transition temperature of PBA (−55 °C)[5] is much lower than that of PMMA; that of PBMA is 22 °C. However, this interpretation can be understood via the concept of "dynamic flexibility". This is a term employed by de Gennes[39] to describe how rapidly the backbone of a polymer chain undergoes local conformational changes (trans to gauche flips). If the energetic barrier to rotation is high (as it will be if the chain backbone carries bulky side groups), then the short time-scale motions of the chain (which are the ones of interest in terms of the flexibility of a dangling chain end) will be severly hindered. This notion is easily reconciled with the preceding conclusion, for PBA chains would be expected to be much more dynamically inflexible than PMMA chains, which have pendant methyl groups while PBA has pendant butyl groups. Involving PBMA in the comparison is difficult, since PBMA at lower w_p (ca. 0.4) lies between the two limits, whereas at somewhat higher w_p (ca. 0.6) PBA is already at the rigid chain limit. It is further anticipated that butyl groups would provide extensive steric hindrance to rotation by buttressing against neighboring chains at the relatively high polymer concentrations being examined. Finally, when it is considered that the lower glass transition temperature of PBA in relation to that of PMMA is thought to be due primarily to the butyl group acting as an intrachain plasticizer,[40] there is no reason to suppose that chains of this polymer should be any more flexible than those of PMMA at 50 °C. For these reasons, the above apparently counterintuitive conclusion regarding chain flexibility, unlikely as it at first seems, can be justified.

As a predictive tool, the model developed in this paper presents two major difficulties. To forecast the value of k_t for a polymer system at high conversion, one must first establish at what point rigid chain behavior begins to prevail and then determine what form the crossover from flexible chain behavior takes. The above discussion shows several instances in which these problems can be overcome. If, for example, the polymerizing system is glassy or close to the glass transition point, then k_t will be given by the rigid chain limit (eq 11). Also, one would predict that higher homologues of BA (such as octyl acrylate) and BMA would have k_t values given by eq 11 for intermediate values of w_p ($w_p \sim 0.5$) and beyond. Further, in the régime of residual termination, monomers such as ethyl methacrylate and propyl methacrylate should display k_t values between those of MMA and BMA. Another corollary of this theory for residual termination is that it is not confounded by any dependence on chain length (providing k_p is chain length independent) or chain shape: no matter whether the chains are branched, moderately cross-linked, or even starred, the values of k_t(res) are still the same.

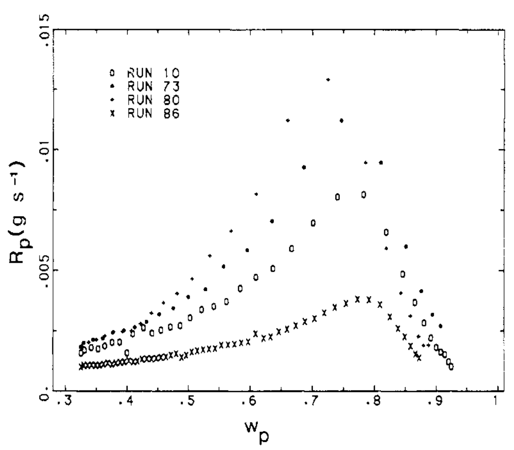

Figure 2. Values of rate of conversion of monomer to polymer (R_p, g s^{-1}) as a function of weight fraction polymer, w_p, for four different seeded emulsion polymerizations of MMA at 50 °C, showing the large acceleration in rate at very high conversions. Data from Ballard et al.[27]

The Trommsdorff–Norrish "Gel" Effect in Emulsion Polymerization

If it is accepted that the experimental k_t values of Figure 1 are indeed of a residual nature only, then a novel mechanism contributing to the Trommsdorff–Norrish ("gel") effect in emulsion polymerization may be afforded. The acceleration in rate associated with the Trommsdorff–Norrish régime in an emulsion polymerization may be of a different phenomenological nature from that in bulk polymerizations: the latter often occurs at lower w_p values (between 0.2 and 0.3 for MMA at 50 °C)[41] than for emulsion polymerization (w_p values somewhat beyond 0.5 for MMA at 50 °C).[27] This is illustrated in Figure 2: the rate of polymerization in an emulsion system is seen to increase steadily, and then spectacularly, as w_p increases, before finally subsiding during the terminal stages of polymerization. This gradual increase in rate differs quantitatively from that of the bulk Trommsdorff–Norrish effect, inasmuch as the latter manifests itself as a large increase in rate over a relatively narrow range of conversion. There is no a priori reason why the Trommsdorff–Norrish effects observed in different systems should have the same mechanistic basis: all that is required for such accelerations to be exhibited is for k_t to decrease sufficiently as polymerization proceeds. Such a decrease could arise from a variety of causes.

As stated, this acceleration in emulsion systems must arise from a decrease in k_t. Previously[4] it has been postulated that this phenomenon, in all systems, is due to a decrease in macroradical diffusivity and a concomitant decrease in the value of k_t. This explanation appears unlikely to be relevant to emulsion polymerization systems, for in such systems it appears that polymer chains are sufficiently entangled for center-of-mass diffusion to be unimportant in determining the value of k_t. An alternative explanation stems from the mechanism of residual termination expounded above: we suggest that the Trommsdorff–Norrish effect is at least partially associated with a transition from the flexible chain limit to the rigid chain limit. That is, we propose that on a molecular level there is a contribution to the Trommsdorff–Norrish effect from the disappearance of chain motions that accompany the approach to the glass transition point. Because the loss of chain motions is gradual, the observed acceleration is gradual. Of course, it is likely that other factors (for example, increasing entanglement and decreasing diffusivity of small free radicals) could also contribute to some extent to the decrease in k_t that gives rise to the Trommsdorff–Norrish effect, but a major contributor to this phenomenon appears to be the decreasing flexibility of the dangling chain ends. Note that, consistent with the above, an accleration is observed in emulsion polymerizations of MMA[27] and (to a lesser degree) styrene[42] (which shows qualitatively similar k_t behavior to MMA in emulsion systems) but not for BA[10] (which already conforms to the rigid chain limit for k_t even at intermediate

w_p). It should be further noted that these accelerations are not necessarily observed in bulk systems, and that, in emulsion systems, they may only be observed if termination is rate determining (e.g., no Trommsdorff–Norrish effect is observed when small seed particles are employed for the emulsion polymerization of styrene:[8] for such systems, free-radical desorption, not termination, is rate determining).

It is, of course, easy to reproduce the observed emulsion polymerization kinetics by simulation using assumed functional forms for the variation of k_t and other rate parameters with w_p. Such direct computer simulation of the kinetics of polymerization is a technique commonly used to deduce the variation of k_t with conversion.[15,18,24,33] However, it is inappropriate for *mechanistic* elucidation in the present case due to uncertainty in the other rate parameters involved (see below). Now, an alternative quantification aimed at shedding light on the above mechanistic interpretation of the Trommsdorff–Norrish effect is possible, as follows. We proceed by direct manipulation of the experimental data and make no reference to any presupposed termination mechanism.

The kinetics of emulsion polymerization for MMA[27] are given by the so-called pseudobulk equation,[43] which in the present case is

$$d\bar{n}/dt = \rho_a - 2k_t\bar{n}^2/(N_{av}V_s) \tag{18}$$

Here $\bar{n}$ is the average number of free radicals per latex particle (i.e., it is effectively a free-radical concentration), ρ_a is the coefficient for entry (per particle) of free radicals, which are generated in the aqueous phase, into the particles (i.e., it is a free-radical creation term), N_{av} is Avagadro's constant, and V_s is the swollen volume of a latex particle. This equation is devoid of an initiator efficiency term because initiation occurs in the aqueous phase; consequently, initiation events are encapsulated in the entry term. The rate of conversion of monomer to polymer, R_p, is then given by

$$R_p = k_pC_m\bar{n}M_0N_c/N_{av} \tag{19}$$

where M_0 is the molecular weight of the monomer and N_c is the concentration of latex particles. In the steady-state limit, eq 18 can be rearranged to give

$$1/\bar{n}^2 = 2k_t/(\rho_aN_{av}V_s) \tag{20}$$

This suggests that plots of experimental $1/\bar{n}^2$ values versus w_p should reflect the shape of the experimental k_t profile over that range of w_p (providing ρ_a and V_s do not change dramatically and the steady-state assumption is adequate). Some of the experimental data of Ballard et al.[27] for the emulsion polymerization of MMA have been reanalyzed according to this prescription. Figure 3 shows plots of $1/\bar{n}^2$ against w_p obtained by using the techniques and data of ref 27; the different experiments shown in this figure represent different concentrations of surfactant and initiator and the variation of seed latex and initial charge of monomer. The profiles are seen to have nearly identical shapes for the different sets of experimental conditions. Particularly noticeable is the presence of kinks at $w_p \simeq 0.75$ and 0.85. These kinks always occur around the same w_p values, despite the diversity of experimental conditions. This is a strong indication that these profiles are a semiquantitative representation of the variation of k_t with w_p, although because of possible changes in the value of ρ_a (V_s is approximately constant) and the uncertain validity of the steady-state hypothesis, these profiles may not reflect the exact variation of k_t with w_p. However, the kinks must reflect sharp changes in the experimental k_t profile, because neither ρ_a nor $d\bar{n}/dt$ should vary sharply at these points.

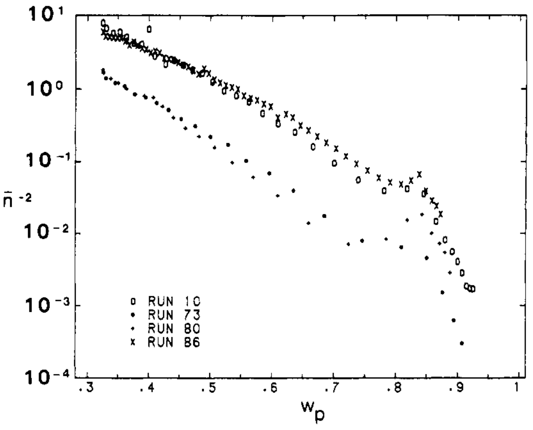

Figure 3. Variation of the average number of free radicals per particle, $\bar{n}$, plotted as $1/\bar{n}^2$ (see eq 20), with weight fraction polymer, w_p, for four different seeded emulsion polymerizations of MMA at 50 °C. Data from Ballard et al.[27]

These sharp changes must surely arise from some mechanistic transition, and these are therefore the features of interest in these profiles. The sharp change at $w_p \simeq 0.85$ may be associated with the onset of diffusion-controlled propagation (see eq 14): as k_p decreases beyond the onset of diffusion-controlled propagation, so too does k_t (see eq 11), and hence the free-radical concentration increases. The sharp change at $w_p \simeq 0.75$ must be of a different origin and must represent a leveling out in the value of k_t (i.e., a decline in the rate of decrease of k_t with w_p). We therefore speculate that, at this particular w_p, the dangling chain ends become completely rigid on the time scale of propagation. Up until this w_p, the chains are somewhat flexible and become increasingly inflexible as w_p increases; consequently, k_t decreases markedly as the rigid chain limit is approached. Once this limit is reached, k_t is essentially constant as w_p varies (provided k_p is constant; see eq 11), since C_m varies only slowly with w_p. This suggests that the increase in $\bar{n}$ with w_p should temporarily stop over the range $w_p \approx 0.75$–0.85. At the weight fraction at which the rigid chain limit is reached, it is expected that the Trommsdorff–Norrish effect should essentially cease, since k_t is no longer decreasing. Inspection of Figure 2 shows that this is the case, since the rate of polymerization stops increasing at around $w_p \sim 0.75$. Significantly, this plateau in the value of $\bar{n}$ is also seen at very high weight fractions of polymer in the emulsion polymerization of styrene,[42] a monomer which also may exhibit the Trommsdorff–Norrish effect at high conversions if the latex particles are sufficiently large.

The existence of the two sharp changes in the variation of k_t with w_p alluded to above is quite logical, for the onset of diffusion-controlled propagation should succeed the point at which the dangling chain ends become totally rigid. Recalling, from earlier discussion, that this rigidity is only on the time scale of propagation, it becomes clear that if the chain end has some flexibility on the time scale of propagation, then it can wander around between propagational events and thus encounter many monomer molecules. Under such circumstances, the diffusion of monomer will not be the rate-determining step in propagation; hence, the chain ends must become rigid before propagation can become diffusion controlled.

Conclusions and Outlook

The model developed in the present paper gives easily evaluated expressions for the upper and lower bounds to

k_t. These expressions, eq 11 and 13, contain no adjustable parameters and require only properties, such as the unperturbed chain dimensions, which are readily estimated. The model suggests that, at high conversions, the rate coefficient for termination is governed by the rate coefficient for propagation. This model should be wide ranging in its applicability, since all the monomers investigated in this work (MMA, BA, and BMA) were found to have k_t values in accord with residual termination being rate determining over more than half the entire range of conversion of monomer to polymer. (In saying this for BA and BMA, it is assumed, quite reasonably, that since k_t is dominated by roving head diffusion at intermediate w_p, it will continue to be so for higher w_p.) When it is considered that many industrial polymerizations are performed largely at high weight fractions polymer, this is by no means a trivial conclusion. Moreover, it is to be expected that the expressions given here should be applicable to cross-linked systems over a range of conversion that is even greater than that for the simple systems which are the subject of the present study, since cross-linking further reduces center-of-mass and segmental diffusion.

In a sense the model here presented marries the approaches of several previously published theories in the field of polymerization kinetics. The Martin–Hamielec idea of k_t being viscosity oriented[44] enters, albeit obliquely, through the possibility of k_p being diffusion-controlled, while the Cardenas–O'Driscoll concept of free-radical chains being entangled[33] is important in the notion of the dangling chain end; finally, the Tulig–Tirrell procedure of k_t being specified by the relevant diffusion coefficient[15] is utilized. However, there are two ways in which the theory of this paper breaks new ground with regard to all the above theories. Firstly, the theory is totally a priori in its predictions: no calibration with other values of k_t (zero conversion k_t for example) is required. Secondly, no adjustable parameters are introduced. Militating against these factors are several difficulties. One hitherto unmentioned uncertainty is the very applicability of the Smoluchowski equation to the problem of diffusion-controlled termination.[45] On a less abstract level, there is the real problem of what value of k_t(res) to use in predicting k_t— are the dangling chain ends rigid or flexible, and in the latter event, how flexible are they? As already evinced, the answer to these problems seems to lie with the concept of dynamic flexibility of chains, and this is therefore an obvious starting point for future work in this direction.

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Registry No. BMA, 97-88-1; BA, 141-32-2; MMA, 80-62-6.

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