Initiator Efficiencies in High-Conversion Bulk Polymerizations

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Received September 15, 1987

ABSTRACT: By consideration of relative rates of diffusion and of propagation, it is shown that, in some bulk polymerizations, there exists a certain weight fraction of polymer (w_p) beyond which initiator efficiency (f) must rapidly decrease. At this critical w_p, the two free radicals formed from initiator decomposition are immobilized by propagation faster than they can diffuse apart; consequently, their likely fate is to become trapped in close proximity to each other and undergo geminate recombination. A quantitative theory for the onset of this phenomenon is derived. This effect explains why some bulk polymerizations are extremely slow at high conversions while the corresponding emulsion polymerizations are not; further, it removes apparent discrepancies between k_p values directly measured from ESR in emulsion polymerizations and those estimated from bulk kinetics. Bulk kinetic data are employed to give the variation of f with w_p for a range of initiator types and concentrations; these $f(w_p)$ are shown to be consistent with the proposed theory. This suggests that the common assumption that f is independent of conversion, while k_p drops rapidly at the glass transition, is seriously in error. Instead, it appears that k_p changes slowly beyond the onset of diffusion-controlled propagation while f drops dramatically beyond a conversion that depends on a number of chemical and physical properties of the system.

Introduction

At high conversions there often seems to be two apparently irreconcilable discrepancies between bulk and emulsion polymerizations: (i) bulk systems may virtually stop polymerizing well short of complete conversion, whereas emulsion systems continue polymerizing at a reduced (compared to lower conversions) but appreciable rate to complete conversion; and (ii) the high-conversion values of the propagation rate coefficient, k_p, deduced from bulk kinetics are reported to be many orders of magnitude less than those obtained by direct measurement with emulsion systems.[1] The purpose of this paper is to show how these discrepancies can be easily resolved from an understanding of initiator efficiencies.

It has long been recognized that some bulk polymerizations virtually stop at high conversions of monomer to polymer well before complete conversion.[2] Since the growing chains are likely to be entangled with the matrix polymer at such high polymer concentrations and are therefore capable of undergoing only extremely slow center-of-mass diffusion, it is axiomatic that the origin of this vanishing rate cannot be an increasing termination rate coefficient, k_t. It has therefore been proposed that k_p must diminish markedly in this high-conversion régime.[2] Such an explanation appeared plausible because model monomers such as methyl methacrylate (MMA) and styrene are commonly polymerized below their glass transition temperatures; under such conditions it appeared physically reasonable that, as the monomer concentration diminishes with increasing conversion and the polymer matrix becomes glassy, propagation should become diffusion controlled. Thus, at the glass transition point, monomer molecules would become essentially immobilized in the polymer network, and consequently propagation would virtually cease.[2] Support for this mechanism came from the observation that bulk polymerizations cease at weight fractions of polymer, w_p, which are in the vicinity of where the glass transition point is thought to occur.[2] The foregoing mechanism implies that to model the kinetics of polymerization at high w_p requires only a functional form for k_p that is independent of conversion until a critical conversion, beyond which k_p drops rapidly to a negligible value. From these notions many theories for the prediction of k_p at high conversions,[3-5] all based on the concept of free volume, have been developed. Because rates of polymerization in bulk media are so minuscule at these high conversions, it has been impossible to compare critically the predicted rate coefficients with the actual experimental values.

Several recent experimental investigations have cast considerable doubt on the rectitude of the above mechanistic proposal. (i) The first of these are studies of the variation of k_p with w_p in emulsion polymerizations.[1,6] By coupling direct measurements of rate with free-radical concentrations as determined by electron spin resonance (ESR) spectroscopy, it was found that k_p for MMA at 50 °C[1] at very high conversions ($w_p \sim 0.85$ and higher) is many orders of magnitude greater than predicted by free volume models (see Appendix). Importantly, these measurements of k_p are essentially free of any model-based assumptions. Since latex particles are simply small compartments that should be similar in composition to the corresponding bulk systems, the k_p values from emulsion systems should be very similar to those in bulk polymerizations under comparable conditions. Any environmental differences between bulk and emulsion systems (for example, small quantities of water penetrating the latex particles) could not account for the above discrepancy, since an appreciable increase in free volume is necessary to redress the many orders of magnitude difference between the emulsion data and the bulk models. While it is indeed observed, in emulsion, that the value of k_p decreases significantly at high weight fractions of polymer, it is found experimentally that, even close to 100% conversion, k_p has decreased by only 2 orders of magnitude from its low conversion (régime of chemically controlled propagation) value. Such a relatively small decline not only contradicts the predictions of current free volume theories but also appears to conflict with the observed cessation of bulk polymerizations at high conversions if one adopts the hitherto-accepted mechanistic descriptions. (ii) With moderate initiator concentrations it is possible to attain almost complete conversion of MMA to poly-MMA (PMMA) at 50 °C in less than 1 day in emulsion systems.[1] Complete conversion of the same monomer at the same temperature is also possible on the same time scale via suspension polymerization.[7] Further experimental evidence militating against the usual models for propagation at high conversions has come from the refinement of gravimetric techniques for the measurement of conversion. This has enabled tracking of the rate of polymerization of MMA at high conversions and has revealed

0024-9297/88/2221-2141$01.50/0

that, given sufficient time (e.g., more than 10 days for MMA at 80 °C), complete conversion can be achieved in bulk systems.[5,8] This effectively refutes the notion that bulk polymerizations stop at the glass transition point. However, it does not resolve the apparent discrepancy between bulk and emulsion rates at high conversions. (iii) A third experimental refutation of traditional models of diffusion-controlled propagation has come from direct investigation of diffusion coefficients. If propagation is diffusion controlled, then k_p should be directly proportional to the diffusion coefficient of the monomer, D_m. Hence, if k_p falls by orders of magnitude at high conversions (as free volume theories suggest), then D_m would also be expected to exhibit parallel behavior. However, recent measurements by forced Rayleigh scattering of probe organic penetrant diffusion in polymer solutions of high polymer concentration[9] have revealed these diffusion coefficients to be relatively insensitive to the glassy or nonglassy nature of the system. In other words, there is no cataclysmic decrease in the rate of solvent diffusion upon the onset of glassy behavior. Additionally, the diffusion coefficients reported by Tirrell and co-workers[9] are in semiquantitative agreement with those implied by the k_p values as measured by ESR for emulsion systems[1] (an exact comparison cannot be made because of the different operative conditions and species present in the two experiments). These results taken together constitute compelling evidence that the halting of bulk polymerizations at high conversions cannot be due to a drastic decrease in the value of k_p.

We propose here that this experimental phenomenon is due to a large decrease in the initiator efficiency, f, at high conversions in these bulk systems, i.e., the cataclysmic fall is in f rather than k_p. This conclusion is suggested by the fact that in emulsion systems initiation occurs in the aqueous phase (which is distinct from the latex particles, the loci of polymerization), whereas in bulk systems initiation takes place in the organic phase, which becomes very viscous at high conversions. In a bulk system, this may lead to a marked decrease in f at high w_p for the following reason. In such bulk systems at high conversions, the time for two free radicals formed from an initiator molecule to diffuse apart is found to be comparable to that for propagation. Once propagation has commenced, the free radicals will be even less mobile. At a critical conversion, the two free radicals are thus highly likely to be trapped in close proximity to each other and so to undergo geminate recombination. Hence, once diffusion and propagation times become comparable, the initiator efficiency is expected to decrease dramatically.

In the following section, evidence for the conclusion that initiator efficiencies are low at high conversions in some bulk systems is presented; subsequently, it is shown that low initiator efficiencies are inherent in experimental conversion–time data for certain bulk polymerizations at high conversions. A discussion of the variation of initiator efficiency throughout the course of these bulk polymerizations follows.

Calculation of Diffusion Distances of Initiator Moieties

There are sound reasons for suggesting that initiator efficiencies are low at high w_p values in some bulk systems, and these are now presented in detail. These arguments are based on consideration of diffusion distances and propagation time scales at high conversions.

We first use available experimental data to deduce the diffusion coefficients of small species in the types of system under consideration. The directly measured ESR values of k_p for MMA at 50 °C are reported as being fitted by[1]

$$k_p = k_p^0, \qquad w_p < 0.84$$
$$= k_p^0 \exp(-29.8[w_p - 0.84]), \qquad w_p \geq 0.84$$

where k_p^0 may be taken as being 580 dm^3 mol^{-1} s^{-1}.[1,10] The mechanistic interpretation of this result is that propagation becomes diffusion controlled above $w_p \simeq 0.84$ for the polymerization of MMA at 50 °C. At conversions well above this w_p, the time scale of reactant diffusion will be very much slower than that for surmounting the chemical barriers to propagation. Hence, at these w_p values, the value of k_p will correspond to that in the absence of chemical control (i.e., absolute diffusion control), which we denote by $k_{p,d}$. It therefore follows that

$$k_{p,d} = k_p^0 \exp(-29.8[w_p - 0.84]) \tag{1}$$

Although deduced for $w_p \gg 0.84$, we assume eq 1 to hold over the high-conversion range of interest. One may estimate $k_{p,d}$ from the Smoluchowski[11] expression:

$$k_{p,d} = 4\pi D_{ab}\sigma N_A \tag{2}$$

where D_{ab} is the mutual diffusion coefficient of the reacting species (in this case the monomer/polymer-chain-end cross-diffusion coefficient), N_A is Avogadro's constant, and σ is the radius of interaction of the reactants. For diffusion-controlled propagation, an appropriate value for σ is the Lennard-Jones diameter of MMA. From the above definition, it follows that $D_{ab} = D_m + D_p$, where D_p is the diffusion coefficient of a macroradical chain end. Because the major contribution to the motion of the chain end at high w_p comes from propagation ("reaction diffusion"[12]), it follows[13] that

$$D_p = k_p C_m a^2/6 \tag{3}$$

Here C_m is the monomer concentration and a is the root-mean-square end-to-end distance per square root of the number of monomer units of the polymer. In eq 3 k_p is the overall rate coefficient for propagation and is calculated via the expression[4]

$$1/k_p = 1/k_p^0 + 1/k_{p,d}$$

Combining eq 2 and 3 gives

$$D_m = k_{p,d}/(4\pi\sigma N_A) - k_p C_m a^2/6 \tag{4}$$

Although not used in the present context, we note that the above equations yield

$$k_{p,d}^2 + k_{p,d}(k_p^0 - 4\pi\sigma N_A D_m - 2\pi\sigma N_A k_p^0 C_m a^2/3) - 4\pi\sigma N_A D_m k_p^0 = 0$$

This expression enables $k_{p,d}$, and hence k_p, to be calculated from D_m.

By use of values of σ = 5.85 Å,[14] a = 0.69 nm,[15] and the relevant value of C_m,[13] it is calculated that, at the point of onset of diffusion-controlled propagation for MMA at 50 °C (which we take to be at w_p = 0.84), $D_m = 9.0 \times 10^{-13}$ cm^2 s^{-1}. Now, initiators used in bulk polymerizations are oil-soluble organic compounds that are often similar in size to MMA; hence, the diffusion coefficient, D_I, of such an initiator moiety in a bulk system of MMA at w_p = 0.84 should not be too different from the above value of D_m (certainly a difference of more than an order of magnitude for a commonly used initiator such as 2,2′-azoisobutyronitrile [AIBN] would be highly unlikely).

We now use the foregoing estimate of the diffusion coefficient to estimate the distance that initiator moieties

diffuse on the time scale of propagation. From the Einstein[16] relation, the mean-square displacement of an initiator free radical, $\langle r^2 \rangle_I$, in time t is

$$\langle r^2 \rangle_I = 6D_I t \tag{5}$$

We define δ as the root-mean-square displacement of an initiator free radical before a monomer molecule is added to it. As an approximation, it is assumed that $D_I = D_m$. The average time between propagation events for a growing chain is simply the inverse of the frequency of propagation, $k_p C_m$. Thus, from eq 5 one has

$$\delta \simeq \langle r^2 \rangle_I^{1/2} = [6D_m/(k_p C_m)]^{1/2} \tag{6}$$

For an MMA–PMMA system at $w_p = 0.84$, it is thus calculated that $\delta = 10$ Å. Of course, given the assumptions above (and, further, recalling that the polymer environments of emulsion and bulk systems at similar w_p values may differ slightly in composition), this value of δ is far from precise; however, for the reasons already expounded, it is highly unlikely that δ is more than half an order of magnitude different (due to the square root dependence of δ on D_m in eq 6) from that given above. In fact, given that propagation appears to be more rapid for monomeric free radicals than for long-chain free radicals,[17] it is most likely that the above value is an overestimation of δ. This is discussed further in a later section.

The implications of the above result are 2-fold. Firstly, and most obviously, it is evident from the calculated value of $\delta \sim 10$ Å that at high conversions of MMA an initiator moiety diffuses a distance of the order of a monomer molecular diameter prior to propagation. Now, the chemical barriers to recombination of two free radicals are very small, whereas the activation energy for propagation (which involves only one free-radical species) will be much higher. Thus, the recombination of two contiguous initiator fragments will occur on a much faster time scale than propagation between adjacent monomer and initiator species. Hence, the above value of δ shows that, on the time scale of propagation, initiator moieties will be virtually trapped next to each other at high conversions in bulk polymerizations akin to that of MMA, for on this time scale an initiator species can barely, if at all, diffuse out of the restraining cage of its environment. Thus, it seems highly likely that, at high conversions, initiator moieties will undergo "primary recombination",[18] by which phrase is meant the geminate recombination of initiator fragments that have not escaped the cage in which they were formed. (This is distinct from "secondary recombination",[18] which is the process whereby free radicals that have separated from an encounter subsequently, in the course of diffusion, reencounter each other and undergo geminate recombination.) Furthermore, it is clear that, as w_p increases and D_I decreases, the fraction of initiator radicals escaping primary recombination will decrease, and hence the overall initiator efficiency, f, will decrease.

Secondly, a more subtle consequence of δ being of the order of a monomer diameter at high conversions is as follows. Consider an initiator radical that successfully escapes the cage in which it is formed. From the calculations presented above, the fate of such a species must be to undergo propagation with a monomer molecule after diffusing a distance of the order of one monomer diameter. This addition process generates a dimeric free radical which diffuses (by virtue of its increased mass) more slowly than the original monomeric free radical. The distance such a species diffuses before again undergoing propagation is thus smaller than δ, and this distance is in turn even less for the trimeric free radical next generated. This process will continue until the oligomeric free radical is of sufficient length to become entangled in the surrounding polymer matrix, at which point the propagating chain is effectively immobilized on the time scale of propagation. At the high conversions under consideration, this entanglement length will be only marginally greater than the entanglement spacing of pure polymer, which is of the order of 100 monomer units.[13] It is thus clear that, at appropriately high conversions, two separating initiator moieties will, by virtue of their propagating nature, very quickly become trapped in the neighborhood of each other. The probability of a separating pair of initiating free radicals undergoing several propagation steps and then recombining will therefore be greatly enhanced compared with that at lower conversions. We therefore predict that in bulk systems at high conversions a disproportionately large population of polymer chains of relatively small degrees of polymerization should be formed. Indeed, this is also a prediction of the model of bulk polymerization of Stickler et al.,[19] although these authors suggest this effect for different reasons from those above. Unfortunately, direct experimental evidence for or against such a phenomenon currently appears to be lacking.

An interesting corollary of the above calculations is as follows. Hitherto, models of bulk polymerization (of which ref 3–5 are typical) have postulated that f is essentially independent of conversion and that at high conversions k_p decreases by many orders of magnitude from its low-conversion value. Since propagation is thought to be diffusion controlled in this high-conversion régime, the implication of such a mechanism would be that D_m should decrease by many orders of magnitude at high w_p. However this postulated decrease in D_m is many orders of magnitude in excess of that observed experimentally (see Appendix). When it is considered that the foregoing calculations use values of D_m inherent in the experimental values of k_p, it is clear that, at high conversions, the diffusion length scales implied by the various free volume theories for D_m are certainly orders of magnitude smaller than those computed above. Initiator efficiencies predicted using these values of D_m would therefore be even lower than those suggested above; this contradicts the initial assumption in these models that f is essentially independent of conversion. This suggests that the traditional explanation of the observed high-conversion retardation of bulk polymerization rates (in terms of constant f and decreasing k_p) is internally inconsistent.

Calculation of Initiator Efficiencies from Bulk Polymerization Data

The fundamental proposal of this paper is that initiator efficiencies are very much lower at high conversions than at low conversions in many bulk polymerizations. This can be verified from an analysis of relevant bulk polymerization data as follows. Given the fractional conversion of monomer to polymer, x, as a function of time, t, it is possible to calculate the free-radical concentration, [R•], via the rate equation

$$dx/dt = k_p(1 - x)[R^\bullet] \tag{7}$$

Given the rate equation $d[R^\bullet]/dt = 2fk_d[I] - 2k_t[R^\bullet]^2$, where k_d denotes the initiator decomposition rate coefficient for initiator of concentration [I], and invoking the steady-state assumption for [R•], it follows that

$$2fk_d[I] = 2k_t[R^\bullet]^2 \tag{8}$$

Rearrangement of eq 7 and 8 yields

$$f = \{(dx/dt)/[k_p(1 - x)]\}^2 k_t/(k_d[I]) \tag{9}$$

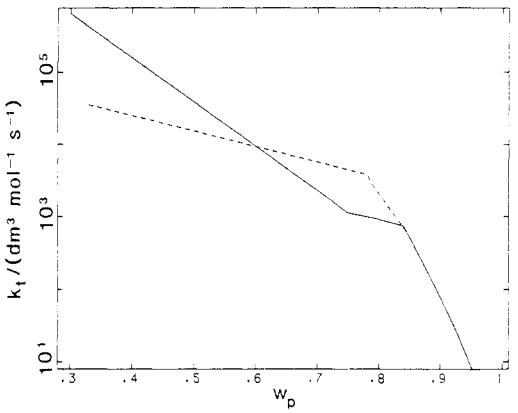

Figure 1. Variations of the termination rate coefficient, k_t, with weight fraction polymer, w_p, for MMA at 50 °C; these values were used to calculate initiator efficiency, f, from experimental conversion–time data; (—) values given by eq 10; (- - -) values given by eq 11.

It is therefore possible to evaluate f from experimental x versus t data provided values of k_p, k_d, and k_t are known.

Following this method, f has been calculated as a function of w_p using published conversion–time data from bulk polymerizations of MMA at 50 °C with three different initiators: AIBN,[20] 2,2′,4,4′-tetramethyl-2,2′-azovaleronitrile (AVN),[19] and dilauroyl peroxide (LPO).[19] In order to do this, the relevant values of k_d were utilized,[21] [I] as a function of t was calculated according to the method and data of Stickler,[5] and the experimental $k_p(w_p)$ values[1] were used. The derivative, dx/dt, was computed from experimental x versus t values by successive piecewise polynomial fitting of the data. Although k_t as a function of w_p is not known with certainty, there are extremely sound reasons for k_t being given by the so-called rigid chain residual termination limit[13] for $w_p \approx 0.75$ and greater; consequently the values given by this theory of termination were employed for $w_p \geq 0.75$. For $w_p \leq 0.75$, the variation of k_t with w_p was obtained from plots of the free-radical concentration as a function of w_p in emulsion polymerizations, as theoretical considerations indicate that such plots should reflect the variation of k_t with w_p.[13] The values for k_t that follow are

$$\ln [k_t \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})] = 17.7 - 14.2w_p, \quad w_p \leq 0.75$$

$$k_t = 4\pi k_p C_m a^2 \sigma/3, \quad w_p > 0.75 \qquad (10)$$

The k_t profile given by eq 10 (along with a second profile, discussed below) is plotted in Figure 1. It is noted that portions of this profile stem from emulsion polymerization data. Now, because of possible differences in the lengths of both the growing chains and matrix polymer, there is in general no a priori reason why bulk and emulsion systems should have identical k_t values for a particular w_p. Notwithstanding this, at the high conversions that are of particular interest here, termination is expected to be predominantly residual in character in both emulsion and bulk systems.[13] Since the rate of residual termination depends only on w_p,[12,13] the difference between bulk and emulsion k_t values should not be large (certainly no more than an order of magnitude) at high w_p (say $w_p \approx 0.7$ and greater). Hence, it seems justifiable to use the above expressions for the variation of k_t with w_p in order to calculate experimental high-conversion f values in bulk polymerizations.

Values of f calculated using the values of k_t given by eq 10 are presented in Figures 2 and 3. Several important results are evident from these figures. (i) Firstly, and most importantly, it is clear that values of f are indeed very small

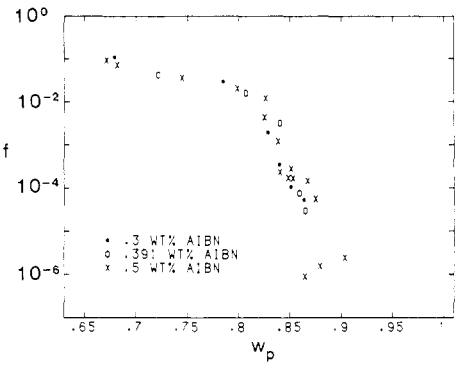

Figure 2. Variation of initiator efficiency, f, with weight fraction polymer, w_p, for three different bulk polymerizations of MMA at 50 °C with AIBN (at the indicated concentrations) as initiator. These values were calculated using k_t given by eq 10. Experimental data are from Balke and Hamielec.[20]

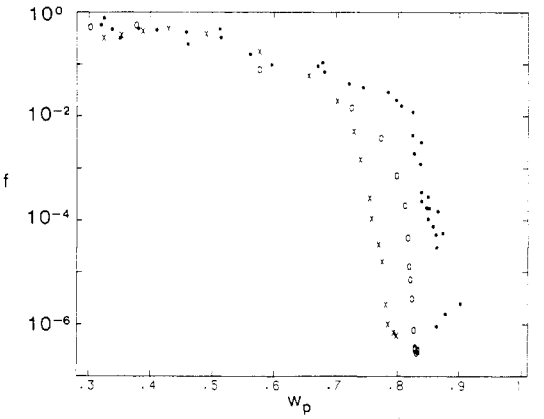

Figure 3. Variation of initiator efficiency, f, with weight fraction polymer, w_p, for the bulk polymerization of MMA at 50 °C; (×) LPO, at a concentration of 2.31×10^{-2} mol dm^{-3}, as initiator; (○) AVN, at a concentration of 3.66×10^{-3} mol dm^{-3}, as initiator; (*) AIBN, at the concentrations indicated in Figure 2, as initiator. These values were calculated using k_t given by eq 10. Experimental data are from Balke and Hamielec[20] (AIBN) and from Stickler et al.[19] (AVN and LPO).

at high conversions for the bulk polymerizations analyzed. For example, in polymerizations with AIBN values of f at $w_p = 0.88$ appear to be 6 orders of magnitude less than the low-conversion values; f values of this order of magnitude were also calculated for AVN and LPO, although for these initiators they were attained at even lower conversions than for the AIBN polymerizations. Although, as already discussed, the k_p and k_t values employed in calculating these high-conversion f values are uncertain to some extent, it is extremely unlikely that either is in error by even an order of magnitude. Since the other quantities in eq 9 are known with relative accuracy, it is clear that these low f values have not been introduced by errors in parameter estimation but are a real feature of the polymerizations considered. (ii) Secondly, the qualitative trend revealed by Figures 2 and 3 is that f declines relatively slowly with w_p for w_p of less than approximately 0.7–0.8 and that beyond this w_p range f falls spectacularly with w_p (from Figure 3 it is clear that the point at which this fall begins depends on initiator type). The scatter in the values of f at the highest w_p for each initiator (see Figure 3) probably does not reflect a leveling out in the value of f; rather, this is probably just noise that arises from poor polynomial fitting of these isolated tail points of the x versus t curve.

In order to check that these results are not simply artifacts of the chosen w_p dependence of k_t, as given by eq 10, the above calculations were repeated using a different variation of k_t with w_p. In this second instance, the ex-

perimental fit of Ballard et al.[22] for the variation of k_t with w_p as measured in emulsion polymerization systems was employed in conjunction with the rigid chain residual termination limit as used above. The resulting k_t profile is given by:

$$\ln [k_t \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})] = 12.1 - 4.94w_p, \quad 0.33 < w_p \leq 0.78$$

$$\ln [k_t \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})] = 28.9 - 26.6w_p, \quad 0.78 < w_p \leq 0.84$$

$$k_t = 4\pi k_p C_m a^2 \sigma/3, \quad w_p \geq 0.84 \qquad (11)$$

The variation of k_t with w_p given by eq 11 is also plotted in Figure 1. The use of these k_t values had no effect on the qualitative aspects of the variation of f with w_p observed in Figures 2 and 3 for $w_p \geq 0.65$; the quantitative variation of f values never exceeded an order of magnitude for the two sets of k_t values studied. Although this by no means proves that the variation of f with w_p in these bulk polymerizations is exactly as presented in Figures 2 and 3, it does indicate strongly that the qualitative nature of the variation of f with w_p at high conversions is as depicted in these figures and that the actual values of f are unlikely to be in error by more than an order of magnitude, if that.

A further result that suggests the rectitude of eq 10 is as follows. Inspection of Figure 3 indicates that values of f seem to approach a low-conversion limit that is somewhere between $f \approx 0.1$ and 1.0, which is exactly the range in which low-conversion f values for common initiators such as AIBN, AVO, and LPO typically fall. Given that the calculated values are derived without the use of any adjustable parameters or scaling factors, this agreement between the experimental measurements of f at low conversions and the f values calculated here purely from high-conversion x versus t data is quite remarkable. Not only does this agreement suggest that eq 10 provides an accurate description of the variation of k_t over intermediate ranges of conversion, but also that this analysis furnishes a meaningful lower bound for the value of f at $w_p = 0$, denoted by f^0. It is evident from Figure 3 that over the range $w_p \approx 0.3$–0.5 the variation of f with w_p is only very slight. Since the diffusion arguments of the preceding section illustrate that f certainly does not increase with w_p, the value of f^0 must be higher, but probably only slightly so, than the value of f at $w_p \approx 0.3$. The following lower bounds for f^0 for the bulk polymerization of MMA at 50 °C are thus estimated by averaging all calculated f values between $w_p = 0.3$ and 0.5: $f^0 \geq 0.47$ for AIBN, 0.55 for AVN, and 0.40 for LPO. These values are indeed marginally smaller than the experimental values reported for f^0: 0.72 for AIBN,[5] 0.60 for AVN,[21] and 0.64 for LPO.[21]

Dependence of f on Initiator Concentration. Figure 2 shows the values of f calculated from the data of Balke and Hamielec[20] for three bulk polymerizations of MMA at 50 °C, each with a different concentration of AIBN as initiator. From Figure 2 it is evident that f is seemingly independent of initiator concentration over the range studied, for no distinction among the three sets of f values can be discerned. Such a result is physically reasonable because geminate recombination of initiator moieties will only involve the two separating initiator fragments and will occur independently of other initiator molecules; the value of f is thus expected to be independent of initiator concentration. Another point to emerge from these calculations is as follows. Since [I]-independent values of k_p were used to calculate the values of f in Figure 2, it is clear from Figure 2 that the quantity $k_p f^{1/2}$ is independent of initiator concentration over the concentration range studied. This is important because it illustrates that any effect that the initiator concentration or the polymer chain length (different values of [I] give rise to different chain lengths) has on the total free volume of the polymerizing medium is negligible in determining the value of $k_p f^{1/2}$. In other words, the contribution of initiator or polymer chain ends (with which there is associated a slightly higher free volume than that of mid-chain segments[23]) to the total free volume of the system is unimportant in determining the value of $k_p f^{1/2}$. This follows because the differing amounts of initiator, and the differing chain lengths so induced, in the three AIBN polymerizations studied had no effect on the experimentally observed value of $k_p f^{1/2}$. The importance of this result will become obvious below.

Dependence of f on Initiator Type. The three sets of AIBN results for f have been combined and are presented along with those for bulk polymerizations of MMA at 50 °C with AVN and LPO in Figure 3. Scrutiny of Figure 3 reveals that, at conversions beyond $w_p \approx 0.7$, the value of f is strongly dependent on initiator type. Again, since the values of k_p used are independent of initiator type, it follows that $k_p f^{1/2}$ depends markedly on initiator type at high conversions in bulk polymerizations. On the basis of free volume theories, it may be argued that this is possible because the free volume of the medium depends on the nature of the initiator and on polymer chain length (which may vary with the value of k_d[I]). Such a suggestion is unlikely to be correct because initiator is present in very small concentrations relative to that of monomer and polymer and because not only will the differences in chain length be relatively small for the polymerizations being considered, but the variation of free volume with chain length is also very weak for chains of the length typically produced in bulk polymerizations.[23] Further confirmation that this suggestion is spurious follows from the discussion set forth in the previous paragraph. Therefore, the observed dependence of $k_p f^{1/2}$ on initiator type cannot be explained by the hitherto-accepted free volume theories of polymerization. These theories assign f a value that does not vary with w_p and allow k_p to vary according to the free volume of the reacting medium. Since, in the polymerizations being considered at present, free volume depends only negligibly on initiator type and chain length, these theories predict that k_p, and hence $k_p f^{1/2}$, must depend only on w_p and not on initiator type. This contradicts the results in Figure 3 and thus constitutes further evidence that f varies significantly with w_p. In addition, since k_p will certainly be effectively independent of initiator type (only for very small oligomers will k_p depend on the nature of the initiator), the observation that $k_p f^{1/2}$ depends strongly on initiator type at high conversions indicates that f depends markedly on initiator type at such conversions.

A final point worth mentioning in light of the above analysis is the following. Rearrangement of eq 9 gives

$$k_p f^{1/2} = \{k_t/(k_d[\text{I}])\}^{1/2}(dx/dt)/(1 - x) \qquad (12)$$

It is thus clear that previously advanced theories of bulk polymerization,[3-5] which have sought to explain the observed decline in dx/dt solely in terms of a changing k_p, have in reality been modeling the variation of $k_p f^{1/2}$ with conversion. Of course, values of k_p (including its dependence on w_p) should be essentially independent of such factors as initiator type and mode of polymerization (e.g., bulk versus emulsion). However, when possible variation with w_p of the $f^{1/2}$ term in eq 12 is ignored, all these models have needed to resort to the use of adjustable parameters (see Appendix) to give agreement with particular experimentally observed conversion–time profiles. A proper theoretical description of the variation of f with w_p should,

were it available, render such practices unnecessary.

Critical Conversion for Onset of Fall-Off in Initiator Efficiency

We next consider the variation of f with w_p. It is known that values of f at low conversion are typically of the order of, though slightly less than, 10^0. Given that f is of the order of 10^{-6} at the highest conversions achieved in the polymerizations analyzed in this work (the actual w_p that this corresponds to seems to vary with initiator type, but seems to be between $w_p \approx 0.8$ and 0.9 for MMA at 50 °C), the problem arises as to how f varies qualitatively with w_p. It can be inferred from Figure 3 that f declines slowly with w_p through the middle ranges of convesion and then falls drastically with w_p beyond some critical high conversion that appears to depend on initiator type. This interpretation is supported by the experimental observation that some bulk polymerizations slow down drastically over a small range of conversion at high conversions, a phenomenon indicative of a rapidly changing rate parameter (the possibility of two independent rate parameters simultaneously changing sharply is remote, though by no means precluded). Having said this, it must be admitted that, due to the uncertainty in the exact variation of k_t over the middle stages of conversion (a variation that may well depend, through chain length, on initiator type), the precise variation of f with w_p depicted in Figures 2 and 3 is by no means certain: it is possible, for example, that f may vary smoothly with w_p. However, the fact that use of a significantly different (see Figure 1) variation of k_t with w_p in no way altered the qualitative trends of Figures 2 and 3 is highly suggestive that f does in fact vary with w_p in the fashion discussed.

If it is accepted that there is a sharp decline in the value of f at a critical high conversion in bulk systems, the problem as to what triggers this fall-off must be addressed. A first suggestion might be to attribute the onset of this decrease to some physical change in the polymerizing medium; one possibility would be a glass transition (which must occur at some high conversion in bulk polymerizations of MMA at 50 °C). However, the observed dependence of this critical conversion on initiator type implies that this supposition cannot be correct, for initiator is present in such small proportions in bulk systems that the physical properties of the reacting medium will depend only trivially, if at all, on initiator type. Rather, what this result indicates is that this critical conversion depends highly on the nature of the initiator.

What will determine the ability of two initiator moieties to avoid primary geminate recombination and propagate beyond the initial stages of their existence is their ability to escape from their cage of formation. Obviously the slower the rate of diffusion of the initiator moieties, the longer the two decomposition fragments take to escape from their cage of formation, so the higher the likelihood of primary geminate recombination. To do this, two initiator moieties must diffuse a distance of the order of a monomer molecular diameter. If an initiator fragment can diffuse such a distance before propagating, then once addition of monomer does occur the chances of immediate recombination with the other free-radical species formed from initiator decomposition will be reduced, for successive oligomeric adducts diffuse slower and slower. However, if the initiator does not diffuse out of its cage environment before undergoing monomer addition, then once propagation does occur the likelihood of cage escape is further reduced due to the lower mobility of the oligomer so formed. Since such an oligomer should be capable of undergoing considerable orientational rearrangement inside its cage of formation on the slow time scale of propagational events, the chances of initiator (or short oligomeric) recombination must be enhanced under these circumstances. The sharp decline in f with w_p at high conversions is thus explicable in terms of this autocatalytic effect: due to slower and slower diffusion times, the chances of primary geminate recombination are increased. This effect is augmented by propagation reducing the possibility of subsequent cage escape even further. An additional factor is that the frequency of propagation, which is given by k_pC_m, also decreases with conversion. In fact, if propagation is diffusion controlled, this decrease becomes even stronger. Consequently the time scale of propagation increases with w_p, so the time over which geminate recombination of initiator moieties may occur is prolonged. This is expected to be an important consideration if diffusion and propagation time scales are comparable.

If the above is in fact the mechanism behind the high-conversion strong decline of f with w_p, then the onset of this decline should correspond approximately with the point at which an initiator moiety can only diffuse a monomer molecular diameter before undergoing propagation. At this point a crossover to primary geminate recombination as the dominant mode of initiator recombination is anticipated. The distance diffused by an initiator decomposition fragment prior to addition of monomer is δ; f should begin to decline strongly with w_p when $\delta = \sigma$. From eq 5 and 6 it follows that this critical conversion will be the value of w_p at which

$$\delta = [6D_I(w_p)/(k_{p1}C_m)]^{1/2} = \sigma \qquad (13)$$

where k_{p1} is the rate coefficient for addition of a monomer unit to an initiator free radical. Now, the monomer concentration in the immediate environment of a newly generated initiating free radical will be identical with the equilibrium (overall) monomer concentration. For this reason, k_{p1} is independent of the rate of reactant transport, and consequently $k_{p1} = k_{p1}^0$, where k_{p1}^0 is the value of k_{p1} in the absence of diffusion control.

By setting $D_I = D_m$ and $k_{p1}^0 = k_p^0$ it is found for MMA at 50 °C that eq 13 is satisfied at $w_p \approx 0.86$. Due to the assignments $D_I = D_m$ and $k_{p1} = k_p^0$, the value of δ obtained by using eq 13 is of course only applicable to an initiator of similar size and reactivity (i.e., propensity to propagate) as an MMA free radical. Of the three initiators studied in this work, AIBN decomposition yields moieties that are closest in size to MMA. These moieties will in reality propagate much more rapidly than poly(MMA) macroradicals,[17] the k_p^0 value of which is used above as k_{p1}^0. In fact, k_{p1}^0 may be up to an order of magnitude greater than k_p^0.[17] If one uses $k_{p1} = 2k_p^0$, then eq 13 is satisfied at $w_p \approx 0.83$, while $k_{p1} = 5k_p^0$ results in eq 13 being obeyed at $w_p \approx 0.80$. Referring to Figure 2, it is evident that f begins declining rapidly in bulk polymerizations of MMA at 50 °C with AIBN at $w_p \approx 0.82$, a value which is exactly within the range of uncertainty of the onset predicted according to eq 13. This suggests that the onset of efficiency decline is at that value of w_p where $\delta = \sigma$.

Since, amongst the initiators used in polymerizations studied in this work, AIBN is smaller than AVN which is in turn smaller than LPO, the values of D_I should decrease in the same order for these initiators. Hence, polymerizations with LPO should show declines in f at a lower w_p than those with AVN, which should in turn precede those in polymerizations with AIBN. This prediction is confirmed in Figure 3. This provides a possible explanation for the hitherto-unexplained dependence of the so-called "limiting conversion"[3,5] (which, as earlier discussed, is a misnomer) on initiator type in bulk polymerizations.

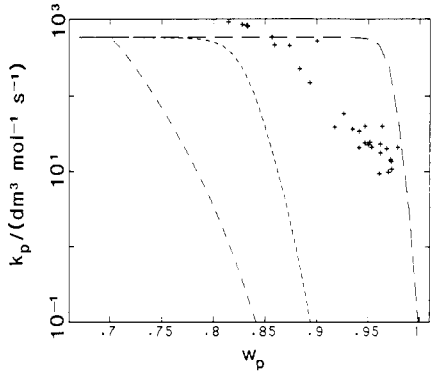

Figure 4. Experimental and theoretical values for the variation of the propagation rate coefficient, k_p, with weight fraction polymer, w_p, for MMA at 50 °C; (points) experimental results of Ballard et al.;[1] (- -) predictions of Marten and Hamielec;[3] (- · -) predictions of Soh and Sundberg;[4] (— —) predictions of Stickler.[5]

Conclusions and Outlook

The severe retardation of some bulk polymerizations at high conversions is a well-documented phenomenon[2-5,19,20] that has hitherto been explained solely in terms of a rapidly diminishing value of k_p, the onset of which is postulated to coincide with the glass transition of the polymerizing medium. However, there exists a growing corpus of experimental data[1,6-8,11] that challenges, both directly and indirectly, this explanation. Although some workers have suggested that f may decline slightly with w_p,[24,25] these decreases have not been nearly extensive enough to account for the minuscule rates of polymerization observed in some bulk systems at high conversions. It has therefore been proposed in this paper that initiator efficiencies may decline dramatically at high conversions in bulk polymerizations and that this is the primary reason for polymerization in these systems virtually ceasing at high w_p values. Analysis of conversion–time data confirms that in certain bulk systems f is very low at high conversions and indicates that in these systems the decrease of f with w_p is slight prior to a critical conversion and is sharp beyond it. This variation can be explained in terms of the ability of separating initiator fragments to diffuse apart before propagation can occur. Prior to this critical conversion, the dominant mode of initiator recombination seems to be secondary geminate recombination; subsequent to it, primary geminate recombination seems to prevail. From this idea a model has been developed that adequately predicts the onset of this rapid decrease in f and explains qualitatively its variation with initiator type. The point of onset of the possible fall-off in f is given by eq 13; the $D_I(w_p)$ therein can either be found from diffusion studies or approximated by using eq 4. This expression for the critical w_p is easily evaluated given various physical and chemical properties of the polymerizing system. Since such systems virtually cease polymerizing beyond the onset of this decline, a knowledge of this critical conversion, as may be furnished by eq 13, is largely sufficient for modeling of these high-conversion bulk polymerizations.

Although the prediction of this possible crossover in the variation of f with w_p is pivotal in the modeling of high-conversion bulk kinetics, a full theoretical quantification of the variation of f with w_p is clearly desirable. The discussions of this paper indicate that an essential aspect of such a theory would be accounting for the role of propagation in determining initiator efficiency. For this reason, a greater knowledge of the intricacies of propagation would be desirable for a better understanding of initiator efficiency. In particular, the entire variation of k_p with w_p for systems other than MMA at 50 °C and further knowledge of the propagation time scales of differing initiator moieties would enable refinement of the ideas contained in this paper.

Acknowledgment. We acknowledge the Australian Research Grants Scheme for their financial support of these studies. G.T.R. was supported by a Commonwealth Postgraduate Research Award. Dr. Manfred Stickler is thanked for supplying raw experimental data.

Appendix: Calculation of the Propagation Rate Coefficient by Free Volume Theories

We here give details of the calculation of k_p (the results of which are presented in Figure 4) using various versions of free volume theory. All yield k_p values at very high conversions that are much less than those observed experimentally.[1]

Soh and Sundberg[4] use

$$1/k_p = 1/k_p^0 + 1/k_{pvf} \tag{A.1}$$

where k_p^0 is the value of k_p in the absence of diffusion control (i.e., the low-conversion value of k_p) and k_{pvf} is the value of k_p in the absence of chemical control (i.e., absolute diffusion control). According to the version of free volume theory of these authors,

$$k_{pvf} = 4\pi R_{ab} D_{m0} \exp(-[1/v_f - 1/v_{fm}]) \tag{A.2}$$

Here R_{ab} is the radius of interaction between a monomer molecule and a growing free-radical chain end, D_{m0} is the self-diffusion coefficient of pure monomer, v_f denotes the fractional free volume of the polymerizing medium, and v_{fm} is the fractional free volume of pure monomer (k_{pvf} is expressed in molecular units in eq A.2, as it is in subsequent equations). To calculate v_f, additivity of free volume is assumed:

$$v_f = v_{fm}\phi_m + v_{fp}\phi_p \tag{A.3}$$

Here v_{fp} is the fractional free volume of pure polymer and ϕ_m and ϕ_p are the volume fractions of monomer and polymer, respectively. For MMA at 50 °C, k_p^0 was chosen[1,10] to be 580 dm^3 mol^{-1} s^{-1}, R_{ab} was estimated from monomer density according to the method of Arai and Saito[24] to be 0.704 nm, and D_{m0} was set equal to 1×10^{-5} cm^2 s^{-1}, a value consistent with measurements of monomer viscosity. The quantities ϕ_m and ϕ_p were calculated simply from w_p and monomer and polymer densities. Finally, the free volume expressions of Soh and Sundberg[4] for MMA (monomer) and poly-MMA (polymer) were adopted:

$$v_{fm} = 0.149 + 2.9 \times 10^{-4}(T + 126)$$

$$v_{fp} = 0.0194 + 0.428 \times 3.0 \times 10^{-4}(T - 105) \tag{A.4}$$

Here $T = 50$, the temperature in °C.

Stickler[5] has suggested calculating k_p via a method essentially identical with that of Soh and Sundberg, except that a modified Smoluchowski expression for k_{pvf} is used:

$$k_{pvf} = 4\pi R_{ab} D_{m0} \exp(-V^*[1/v_f - 1/v_{fm}]) \tag{A.5}$$

Although V^* is nominally a critical free volume fraction for diffusional jumping, Stickler treated it as an adjustable parameter, and its average value for bulk polymerizations of MMA over a range of temperatures and with a variety of initiators was determined as 0.335; this value was adopted in these calculations.

The propagation model of Marten and Hamielec[3] is

$$k_p = k_p^0, \qquad v_f \geq v_{f,cr2}$$

$$k_p = k_p^0 \exp(-B[1/v_f - 1/v_{f,cr2}]), \qquad v_f < v_{f,cr2} \tag{A.6}$$

For MMA bulk polymerizations, the adjustable parameters

in eq A.6 are reported[3] as being $B = 1.0$ and $v_{f,cr2} = 0.066$.

The variations of k_p with w_p for MMA at 50 °C predicted by the above three models are compared with the experimentally observed variation[1] in Figure 4. It is seen that none of the above variants of free volume theory gives an adequate description of diffusion-controlled propagation. This is further illustrated by the fact that a value of $k_p = 4.9$ dm^3 mol^{-1} s^{-1} is extrapolated for $w_p = 1.0$ (pure polymer) from the experimental measurements[1] (see eq 1), whereas the Soh–Sundberg model (eq A.1 and A.2) gives $k_p = 1.5 \times 10^{-23}$ dm^3 mol^{-1} s^{-1} for this w_p, the Marten and Hamielec model (eq A.6) 1.4×10^{-26} dm^3 mol^{-1} s^{-1}, and the Stickler model (eq A.1 and A.5) 6.7×10^{-2} dm^3 mol^{-1} s^{-1} (the relatively good agreement in this case between the Stickler prediction and experiment is redressed by the inability of this model to predict the point of onset of diffusion control [see Figure 4]). This level of agreement is extremely poor, especially when it is considered that these models (with the exception of that of Soh and Sundberg) contain adjustable parameters.

While many variations of the three models for k_p exist, all of these appear to concentrate on the variation of the adjustable parameters with experimental conditions (e.g., temperature and initiator type). The equations that result are therefore comparable to, if not identical with, one of the above types. Another common practice[3,5] is to use the "universal" free volume expressions of Kelley and Bueche[26] in lieu of those used above (eq A.4). This practice could not be adopted for the present calculations because the Kelley–Bueche equations yield a negative value for ν_{fp} for poly-MMA at 50 °C, which is physically impossible.

Registry No. MMA, 80-62-6; AVN, 4419-11-8; AIBN, 78-67-1; LPO, 105-74-8.

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Influence of the Tacticity of Poly(methyl methacrylate) on Its Miscibility with Chlorinated Polymers

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Received September 11, 1987

ABSTRACT: Differential scanning calorimetry was used to determine the miscibility behavior of poly(methyl methacrylate) (PMMA)/chlorinated polymer blends. Nine PMMA's differing in tacticity were blended with three chlorinated polymers: poly(vinyl chloride) (PVC), a chlorinated PVC having a chlorine content of 68% (CPVC), and Saran, which is a random copolymer of vinyl chloride (12%) and vinylidene chloride (88%). The results show that all these PMMA's are miscible with PVC, CPVC, and Saran under proper thermal treatments and especially at 298 K. They all exhibit a lower critical solution temperature (LCST) which varies as a function of the microstructure of PMMA and the chlorine content of the chlorinated polymer. This LCST increases with the syndiotactic content for PMMA's blended with PVC or CPVC but decreases with the syndiotactic content of PMMA for Saran/PMMA blends. An increase in the chlorine content of the chlorinated polymer results in a decrease of the temperature of phase separation except for highly isotactic PMMA where the temperature of phase separation increases with the chlorine content. When the sample is annealed between its LCST and its T_g, miscibility is obtained. When the sample is annealed above its LCST, phase separation occurs. Correlations are made between the phase behavior of these polymer blends and the specific interactions occurring between them.

Introduction

A large number of aliphatic and aromatic polyesters are miscible with chlorinated polymers, including poly(vinyl chloride) (PVC), chlorinated PVC (CPVC), and Saran (a statistical copolymer containing at least 80% of vinylidene chloride co-units).[1-8] The miscibility of these blends is due

0024-9297/88/2221-2148$01.50/0