Method of Determination of Initiator Efficiency: Application to UV Polymerizations Using 2,2-Dimethoxy-2-phenylacetophenone

Devdatt L. Kurdikar and Nikolaos A. Peppas*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-1283

Received October 6, 1993®

ABSTRACT: Initiator efficiency is usually between 0.3 and 0.8 at the start of the polymerization reaction and decreases as the reaction proceeds until it reaches a limiting value of zero. Using 2,2-dimethoxy-2-phenylacetophenone as a model initiator, a theoretical investigation of the initiator efficiency was undertaken. Taking into consideration all the significant reactions that the radicals undergo, expressions were developed that allow for the prediction of the initiator efficiency at the onset and during the course of the polymerization. All the parameters involved in these expressions have physical and fundamental significance. A comparison of the predicted value for the initiator efficiency with an available experimental value showed excellent agreement. The effect of various model parameters on the efficiency prediction is discussed. Comparisons were also made with previous models in an effort to explain some experimental observations that could not be explained by them.

Introduction

Light-sensitive compounds such as 2,2-dimethoxy-2-phenylacetophenone (DMPA) are required to initiate photopolymerizations.[1,2] These compounds absorb light in the ultraviolet–visible wavelength range and undergo fragmentation to lead to the formation of radicals which subsequently initiate polymerizations. Extensive use of photoinitiated polymerizations is made in a variety of applications including the production of highly cross-linked materials for use in information technology systems,[3] printings and coatings,[4] curing of dental materials,[5] and photoimaging.[6]

One of the earlier studies on the photolysis of DMPA was by Sandner and Osborn,[7] who reported that DMPA underwent α-cleavage to form benzoyl and benzoyl ketal radicals. These results were supported by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) studies by Borer *et al.*[8] They reported on the subsequent β-cleavage of the product of the α-cleavage reaction. Electron spin resonance (ESR) spectroscopy was used to gain further insight into the photolysis and photoinitiation reactions of DMPA.[9] 1,1-Diphenylethylene was used as a model for unsaturated vinyl monomers. A complete reaction scheme was reported accounting for the α- and β-cleavage reactions, the initiator disappearance reactions, e.g., radical recombination reactions to form inactive initiator molecules, and polymerization initiation reactions. Borer *et al.*[8] also reported on the initiation efficiency of DMPA. Recently, Fouassier *et al.*[4] have also investigated the practical aspects of excited-state interactions between light stabilizers and DMPA using time-resolved laser spectroscopy.

Initiator efficiency, f, is defined as the fraction of the radicals produced upon decomposition of the initiator that actually initiate propagating chains. For most systems, it assumes a value between 0.3 and 0.8 at the start of the polymerization reactions. This is because some of the radicals recombine to form compounds that cannot decompose into radicals further, while some primary radicals are responsible for the reaction with and termination of active polymer chains.

The efficiency is not constant through the course of the polymerization because, as the viscosity of the reaction medium increases, the diffusive displacement of the radicals away from each other becomes difficult and radical recombination reactions become preferred until the term f reaches a limiting value of zero. This behavior has been observed experimentally[10–13] for the thermal decomposition of 2,2′-azobis(isobutyronitrile) using ESR spectroscopy. However, accurate values of the term f are difficult to obtain without making any assumptions for the polymerization rate equations. For example, Russell *et al.*[10] used the steady-state approximation for radical concentration to calculate f. While such an approximation may be reasonable at the onset of linear polymerizations, as was their case, it is not valid for the case of multifunctional polymerizations.[14]

Even though it is known that there is a large variation in the term f throughout the polymerization process, most models for bulk polymerizations assume it to be constant.[14–19] Some of the earlier models concentrated on the calculation of the fraction of radicals that underwent recombination reactions.[20–28] These models were concerned with the investigation of the viscosity dependence of the efficiency. Arai and Saito[29] were among the first to include the change in the initiator efficiency with conversion in their model for bulk linear polymerizations though it was done semiempirically by estimating the frequency at which radicals initiated chains as compared to the frequency of their recombination.

Ito[30] presented a model for the initiator efficiency using the Smoluchowski theory at first and later[31] using the theory of recombination reactions. This model did take into account the β-scission reaction that some initiators undergo but did not take into account the consumption of radicals by monomer molecules and active polymer chains in the model development. A subsequent model[11,12] included this but was developed only for those initiators that decomposed into two equivalent radicals, both of which could initiate chains. Recent models[32–34] have accounted for the changing efficiency but have done so either by treating the term f as an adjustable parameter or by expressing it with empirical relations. None of the models developed so far have been able to predict *a priori* the initiator efficiency or continuously calculate the term f through the course of the polymerization.

In this contribution we attempt to bridge the gap between the experimental observations of the initiator efficiency and the available predictive models. Results of

---

* Corresponding author.

® Abstract published in *Advance ACS Abstracts,* January 1, 1994.

0024-9297/94/2227-0733$04.50/0

$$\mathrm{I} \xrightarrow{k_{d,i}} [\mathrm{A}^\bullet + \mathrm{A}^{1\bullet}]$$
$$\mathrm{A}^{1\bullet} \xrightarrow{k_{d,r,1}} [\mathrm{PhCOOCH_3} + \mathrm{B}^\bullet]$$
$$[\mathrm{A}^\bullet + \mathrm{A}^{1\bullet}] \xrightarrow{k_{i,1}} \mathrm{I}_1$$
$$[\mathrm{A}^\bullet + \mathrm{B}^\bullet] \xrightarrow{k_{i,2}} \mathrm{I}_2$$
$$[\mathrm{A}^\bullet + \mathrm{A}^{1\bullet}] \xrightarrow{k_{D,1}} \mathrm{A}^\bullet + \mathrm{A}^{1\bullet}$$
$$[\mathrm{A}^\bullet + \mathrm{B}^\bullet] \xrightarrow{k_{D,2}} \mathrm{A}^\bullet + \mathrm{B}^\bullet$$
$$[\mathrm{A}^\bullet + \mathrm{M}] \xrightarrow{k_{p,1}} \mathrm{M}_1^\bullet$$
$$[\mathrm{B}^\bullet + \mathrm{M}] \xrightarrow{k_{p,2}} \mathrm{M}_2^\bullet$$
$$[\mathrm{A}^\bullet + \mathrm{M}_p^\bullet] \xrightarrow{k_{t,1}} \mathrm{M}_p$$
$$[\mathrm{B}^\bullet + \mathrm{M}_q^\bullet] \xrightarrow{k_{t,2}} \mathrm{M}_q$$

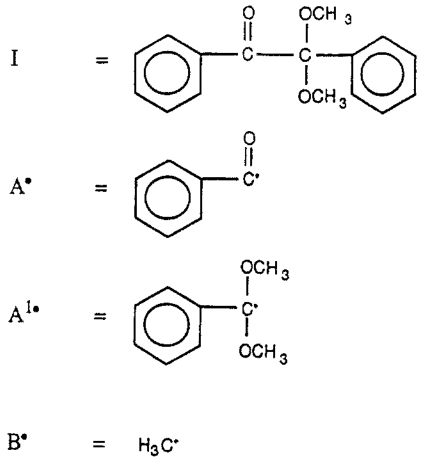

Figure 1. Reaction scheme for 2,2-dimethoxy-2-phenylacetophenone (DMPA) showing cage recombination and chain initiation reactions. Square brackets around the radicals indicate the presence of a solvent cage.

our theoretical investigation on the initiation efficiency of DMPA are presented. This study take into account the secondary decomposition of the initiator and the scavenging of the radicals by unreacted monomer molecules and growing polymer chains. Typical values for each of the parameters involved in the model are used to calculate the initiation efficiency of DMPA and compared with the available literature value. Some of the parameter values change during polymerizations, causing significant changes in the initiator efficiency. Such effects are discussed. Finally, some comparisons are made with some of the previous models to explain the viscosity dependence of the term *f*.

Model Development

Figure 1 shows the possible reactions that occur on the decomposition of an initiator such as DMPA.[2,6-9] The initiator, I, can decompose into two unequal primary radicals, benzoyl, A•, and the benzoyl ketal radical, A1•. These radicals can recombine to form I which can decompose again. This recombination does not lead to a decrease in initiator efficiency. Radicals A1• may decompose in the solvent cage to form another primary radical, the methyl radical, B•, and methyl benzoate. The solvent cage defines the region around a radical within which a recombination reaction may occur if another radical is found.

The recombinations of A• with A1• and A• with B• to form inactive molecules, I_1 and I_2, are the primary reactions that cause the decrease in initiator efficiency. Usually only A• and B• are effective in initiating chains, thus attacking a monomer molecule, M, to form an active monomer molecule which can undergo propagation reactions. On the other hand, A• and B• can undergo primary termination with growing chains to form dead polymer chains. In the above scheme, delineated in Figure 1, $k_{d,i}$ is the rate constant for decomposition of I to form A• and A1•, $k_{d,r,1}$ is the rate constant for decomposition of A1• to form methyl benzoate and B•, $k_{i,1}$ and $k_{i,2}$ are the rate constants for the primary recombination of the radicals in the solvent cage, $k_{D,1}$ and $k_{D,2}$ are the rate constants for diffusion of the radicals out of their solvent cages, $k_{p,1}$ and $k_{p,2}$ are the rate constants for the primary radical–monomer reactions, and $k_{t,1}$ and $k_{t,2}$ are the rate constants for the primary termination reactions.

For the radicals to be able to initiate chains, the radicals must escape recombination within the solvent cage; once they have escaped recombination, the primary radicals must initiate chains as opposed to terminate growing chains. Thus, the initiator efficiency, *f*, can be written as

$$f = F_0 F_i \tag{1}$$

where F_0 is the probability that the primary radicals initiate chains rather than terminate growing chains once they escape the solvent cage, and F_i is the probability that the radicals escape recombination within the solvent cage.

Since F_0 is defined as the probability that the primary radicals initiate as opposed to terminate growing chains, it may be written as

$$F_0 = \frac{k_{p,1}[\mathrm{M}]}{k_{p,1}[\mathrm{M}] + k_{t,1}[\mathrm{M}^\bullet]} \tag{2}$$

where [M] is the monomer concentration, [M•] is the total concentration of all the radicals in the reacting system, and $k_{p,1}$ and $k_{t,1}$ are the rate constants for the chain initiation and primary termination reactions which are equivalent to $k_{p,2}$ and $k_{t,2}$.

The term F_i can be further written as

$$F_i = F_{i_A} F_{i_B} \tag{3}$$

where F_{i_A} is the probability that A• and A1• will escape primary recombination, and F_{i_B} is the probability that A• and B• will escape primary recombination. Thus the product of F_{i_A} and F_{i_B} gives the total probability that the radicals will escape primary recombination.

Let $\rho_A(r,t)$ be the probability per unit volume of finding a A1• radical at distance *r* from a A• radical at time *t*. Fixing the frame of reference on the A• radical allows us to write a mass balance for A1• in the region outside the solvent cage as

$$\partial\rho_A/\partial t = D_A(\nabla^2\rho_A) - k_{d,r,1}\rho_A \tag{4}$$

where D_A is the relative diffusional constant given by the sum of the diffusional constants of radicals A• and A1•, and $k_{d,r,1}$ is the rate constant for the decomposition reaction of A1•. Using spherical coordinates for a situation in which the distribution of A1• around A• is uniform, an axissymmetric situation exists which allows us to write the Laplacian as

$$\frac{\partial\rho_A}{\partial t} = D_A\left[\frac{\partial^2\rho_A}{\partial r^2} + \frac{2}{r}\frac{\partial\rho_A}{\partial r}\right] - k_{d,r,1}\rho_A \tag{5}$$

In the above scenario, let the initial distance of separation between the A• and A1• radicals be *r′*.

The initial condition for this differential equation can be written as

$$\rho_A(r,0) = 0 \qquad \text{and} \qquad \rho_A(r',0) = 1 \tag{6}$$

and the boundary conditions can be written as

$$t > 0 \qquad r = a \qquad D_A(\partial\rho_A/\partial r)_{r=a} = k_{i,1}\rho_A(a,t) \tag{7}$$

and

$$t > 0 \qquad r = \infty \qquad \rho_A(r,t) = 0 \tag{8}$$

Here, $k_{i,1}$ is the specific intrinsic reaction rate constant for the recombination of $A^{\bullet}$ and $A^{1\bullet}$, and a is the radius of the solvent cage. The first boundary condition of eq 7 is called the radiation boundary condition[35] and recognizes the fact that not all collisions may lead to reaction.

A similar expression is obtained for $\rho_B(r,t)$, the probability per unit volume of locating a $B^{\bullet}$ radical at a distance r from an $A^{\bullet}$ radical at time t. Again, writing a mass balance for the probability of locating a $B^{\bullet}$ radical in the region outside the solvent cage of radius b, we obtain

$$\frac{\partial\rho_B}{\partial t} = D_B\left[\frac{\partial^2\rho_B}{\partial r^2} + \frac{2}{r}\frac{\partial\rho_B}{\partial r}\right] + k_{d,r,1}\rho_A - K\rho_B \tag{9}$$

Here, D_B is the relative diffusional coefficient of $A^{\bullet}$ and $B^{\bullet}$ and

$$K = k_{p,1}[M] + k_{t,1}[M^{\bullet}] \tag{10}$$

The initial and boundary conditions used for the solution of the above differential equations are

$$\rho_B(r,0) = 0 \tag{11}$$

$$t > 0 \qquad r = b \qquad D_B(\partial\rho_B/\partial r)_{r=b} = k_{i,2}\rho_B(b,t) \tag{12}$$

and

$$t > 0 \qquad r = \infty \qquad \rho_B(r,t) = 0 \tag{13}$$

Here, $k_{i,2}$ is the specific intrinsic reaction rate constant for the recombination of $A^{\bullet}$ and $B^{\bullet}$.

The above differential equations were solved to obtain the following results. An outline of the method of solution used is presented in Appendix A.

$$\int_0^\infty \rho_A(a,t)\,dt = \frac{1}{4\pi[D_A + ak_{i,1} + a(k_{d,r1}D_A)^{1/2}]a} \tag{14}$$

and

$$\int_0^\infty \rho_B(b,t)\,dt = \frac{k_{d,r,1}\exp[(k_{d,r,1}/D_A)^{1/2}(a-b)]}{4\pi[(K/D_B)^{1/2} + (k_{d,r,1}/D_A)^{1/2}][D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}]}\,\frac{1}{[D_B + bk_{i,2} + b(KD_B)^{1/2}]} \tag{15}$$

The total probability for the recombination of $A^{\bullet}$ and $A^{1\bullet}$ radicals, p_A, is given as[36]

$$p_A = 4\pi a^2k_{i,1}\int_0^\infty \rho_A(a,t)\,dt \tag{16}$$

Thus, from eq 14 the following result is obtained:

$$p_A = \frac{ak_{i,1}}{D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}} \tag{17}$$

Hence, the probability that $A^{\bullet}$ and $A^{1\bullet}$ radicals do not recombine is obtained from p_A by writing

$$F_{i_A} = 1 - p_A \tag{18}$$

Therefore,

$$F_{i_A} = 1 - \frac{ak_{i,1}}{D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}} \tag{19}$$

Similarly, the total probability for the recombination of $A^{\bullet}$ and $B^{\bullet}$ radicals, p_B, is given by

$$p_B = 4\pi b^2k_{i,2}\int_0^\infty \rho_B(b,t)\,dt \tag{20}$$

Therefore, from eq 15 we get

$$p_B = \frac{b^2k_{i,2}k_{d,r1}\exp[(k_{d,r1}/D_A)^{1/2}(a-b)]}{[(K/D_B)^{1/2} + (k_{d,r,1}/D_A)^{1/2}][D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}]}\,\frac{1}{[D_B + bk_{i,2} + b(KD_B)^{1/2}]} \tag{21}$$

Therefore, the probability of $A^{\bullet}$ and $B^{\bullet}$ not recombining is given by

$$F_{i_B} = 1 - p_B \tag{22}$$

and hence,

$$F_{i_B} = 1 - \frac{b^2k_{i,2}k_{d,r,1}\exp[(k_{d,r,1}/D_A)^{1/2}(a-b)]}{[(K/D_B)^{1/2} + (k_{d,r,1}/D_A)^{1/2}][D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}]}\,\frac{1}{[D_B + bk_{i,2} + b(KD_B)^{1/2}]} \tag{23}$$

Equations 1–3, 19, and 23 complete the mathematical expression required for the prediction of the initiator efficiency of DMPA.

Results and Discussion

Model Predictions. The initiator efficiency can be calculated from

$$f = F_0F_{i_A}F_{i_B} \tag{24}$$

where F_0, F_{i_A}, and F_{i_B} are given by eqs 2, 19, and 23, respectively. If all the individual rate constants and diffusional parameters required in each of the equations for F_0, F_{i_A}, and F_{i_B} are available, eq 24 can be used to calculate the value of the initiator efficiency throughout the polymerization reaction. Since all the parameters are often unavailable, certain assumptions are made to decrease the number of parameters involved in the calculation of f.

During a polymerization reaction, $[M^{\bullet}]$ is usually less than 10^{-5} M and hence $[M] \gg [M^{\bullet}]$. Additionally, $k_{p,1}$ describes the rate constant for the reaction of a primary radical with a monomer while $k_{t,1}$ is the rate constant for the reaction of a primary radical at a cross-link point in a polymer network. Also for diffusion-controlled reactions, $k_{p,1} > k_{t,1}$. Therefore, one could write $k_{p,1}[M] \gg k_{t,1}[M^{\bullet}]$ and thus $F_0 \approx 1$. The size of the solvent cages can be taken to be approximately equal, i.e., $a \approx b$ and the relative diffusional constants can also be taken to be nearly equal so that $D_A \approx D_B$.

The specific intrinsic reaction rate constants for the recombination reactions of $A^{\bullet}$ and $A^{1\bullet}$, $k_{i,1}$, and $A^{\bullet}$ and $B^{\bullet}$, $k_{i,2}$, are also taken as being approximately equal and are calculated as

$$k_{i,1} = \frac{1000k_{i,1}^{*}}{4\pi a^2N_A} \tag{25}$$

where $k_{i,1}^{*}$ is the intrinsic rate constant. Radical–radical

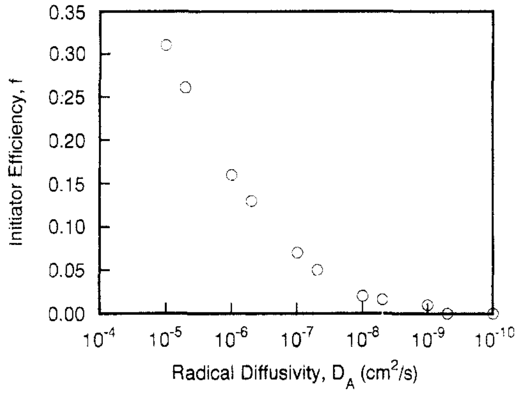

Figure 2. Effect of changes in the diffusivity of the radicals on the initiator efficiency. The efficiency approaches the limiting value of zero as the diffusion coefficient changes over 4 orders of magnitude as is common in bulk polymerizations. The values of the parameters used in these calculations were $k_{d,r,1} = 10^{11}$ s^{-1}, $K = 10^9$ s^{-1}, and, $k_{i,1} = 1.32 \times 10^3$ cm/s.

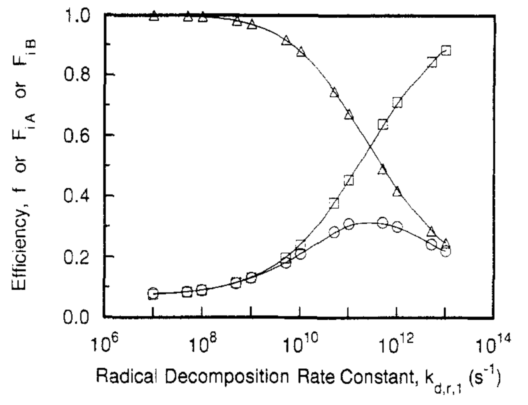

Figure 3. Effect of changes in the β-scission rate constant, $k_{d,r,1}$, on the initiator efficiency f (○) and the radical recombination probabilities F_{i_A} (□) and F_{i_B} (△). The values of the parameters used in these calculations were $D_A = 10^{-5}$ cm^2/s, $K = 10^9$ s^{-1}, and, $k_{i,1} = 1.32 \times 10^3$ cm/s.

reactions often have a rate constant on the order of 10^{11} L/mol·s.[5,20] Using a value of 10 Å for the radius of the solvent cage a, $k_{i,1}$ is calculated to be 1.32×10^3 cm/s.

At low conversions, the relative diffusivities of the radicals can be approximated to be around 10^{-5} cm^2/s. The β-scission reaction of $A^{1\bullet}$ to lead to the formation of $B^\bullet$ is extremely rapid,[9] and the rate constant for typical β-scission reactions[20] is on the order of 10^{10} s^{-1}. DMPA is known to exhibit large photocleavage rates,[37] and hence we approximate $k_{d,r,1} \approx 10^{11}$ s^{-1}. Finally, the term K accounts for the primary chain initiation and chain termination reactions. Thus, $k_{p,1}[M] \gg k_{t,1}[M^\bullet]$ and $k_{p,1}$ typically has a value of 10^8 L/mol·s at low conversions[38,39] and $[M] \approx 10$ M; hence, the value of K is taken to be 10^9 s^{-1}. Calculations show f to be quite insensitive to variations of the term K by 3 orders of magnitude from 10^6 to 10^9 s^{-1}; hence, the approximation made above for K is sufficient.

Using the above values, the term f was calculated to be 0.31. The value agrees very well with that measured experimentally using ^{1}H NMR spectroscopy by Groenenboom *et al.*,[9] who reported a value of 0.3 for the initiating efficiency of an equimolar mixture of DMPA and 1,1-diphenylethylene. The excellent agreement of the model prediction with the experimental result makes the model of considerable value for the estimation of initiator efficiency in the simulation of polymerization kinetics.

Most polymerization simulations assume f to be constant throughout the polymerization process. Experimental evidence has indicated that this is not a valid assumption.[10-13] In fact it is now well-known that, as the reaction medium becomes increasingly viscous, the initiator efficiency approaches a value of zero. The model presented predicts this trend as is shown in Figure 2. This figure shows the variation in the efficiency as the relative diffusional constant decreases by 5 orders of magnitude from an initial value of 10^{-5} cm^2/s. Such decreases in the diffusion coefficient are known to occur during bulk polymerizations. The initiator efficiency shows a rapid decrease initially as the diffusion coefficient decreases and then decreases slowly as it approaches the limiting value of zero. In the simulations of polymerization reactions, the diffusion coefficient of the radicals in the reaction medium can be calculated using the Vrentas–Duda theory[40-45] and thus the initiator efficiency can be predicted at each instant of time during the reaction.

The existence of the fast β-scission reaction helps to keep the initiation efficiency to a value higher than what would be available had the β-scission reaction been extremely slow or absent. The effect of the β-cleavage reaction rate constant on f, F_{i_A}, and F_{i_B} is shown in Figure 3. In the event of an extremely slow β-cleavage reaction, the term f has a very low value. This is because the ability of the $A^{1\bullet}$ radical to escape recombination is hampered by the fact that it can no longer easily decompose to the $B^\bullet$ radical. This leads to a very low value of F_{i_A} as is seen from the plot. As the value of $k_{d,r,1}$ increases, the ease with which the $A^{1\bullet}$ radical can escape recombination increases; however, the possibility of the $B^\bullet$ radical recombining with the $A^\bullet$ radical increases since the number of $B^\bullet$ radicals in the solution increases. As $k_{d,r,1}$ increases to a very high value, the initiator efficiency decreases due to the fact that, though F_{i_A} continues to increase, F_{i_B} decreases to a low value. This is because, at high values of $k_{d,r,1}$, essentially only $A^\bullet$ and $B^\bullet$ radicals are present on initiator decomposition and can thus have higher recombination rates.

The radical recombination reaction rate constant, $k_{i,1}$, has a significant effect on the initiator efficiency. At higher radical recombination rates, the cage recombination reactions become more favorable and hence the initiator efficiency decreases. This effect is shown in Figure 4 which shows the variation in the term f with changes in the values of $k_{i,1}$. For very low values of $k_{i,1}$, the recombination reactions are unfavorable as compared to the diffusive displacement of radicals away from each other, and f approaches unity. As $k_{i,1}$ increases, the term f decreases since the cage recombination reactions can now compete with the diffusive displacement of radicals away from the solvent cage.

Comparison with Other Models. Pryor *et al.*[20,21] presented an equation for the efficiency of an initiator that decomposes into two radicals which do not undergo any subsequent decomposition.

$$\frac{1}{1-f} - 1 = \frac{1}{\left(\frac{k_{-1}}{A_D}\right)\left(\frac{\eta}{A_V}\right)^{\alpha}} \tag{26}$$

Here, k_{-1} is the rate constant for the recombination reaction of the radicals to reform the initiator, η is the solvent viscosity, and A_V and A_D are constants. They reported that $\alpha = 0.5$ satisfies a wide variety of experimental data.[21]

Koenig and collaborators[22-24] have presented theoretical arguments to justify the value of α of 0.5. They developed the following equation for the term f.

$$\frac{1}{1-f} - 1 = \left(\frac{D}{k_c \rho^2}\right)^{1/2} \beta \tag{27}$$

Here, D is the relative diffusion coefficient of the radical

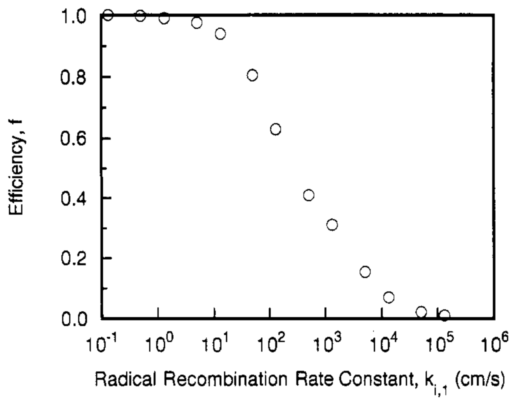

Figure 4. Effect of the radical recombination rate constant, $k_{i,1}$, on the initiator efficiency, f. A high value of $k_{i,1}$ causes the efficiency to decrease drastically. The values of the parameters used in these calculations were $D_A = 10^{-5}$ cm²/s, $k_{d,r,1} = 10^{11}$ s^{-1}, and, $K = 10^9$ s^{-1}.

pair, k_c is the rate constant for the recombination reaction, ρ is the combination diameter, and β is a constant. The diffusion coefficient can be written in terms of viscosity by using the Stokes–Einstein equation as

$$D = k_BT/6\pi\eta R \qquad (28)$$

where k_B is the Boltzmann constant, T is temperature, and R is the effective radius of the diffusing particle. Using the Stokes–Einstein expression in eq 27 gives a theoretical value of 0.5 for the exponent α in eq 26.

However, Pryor and co-workers[20] showed that α could have a value different from 0.5. They obtained α values of 0.72 when benzene was used as a model of caged radical fragments, 0.74 when toluene was used, and 0.76 when iodine was used. Hence, experimental evidence suggests that the value of α could be considerably different for different initiators.

The model presented in this publication may explain why the exponent of the solvent viscosity should be 0.5 for some initiators and not for some others. Since the above equations did not consider the subsequent decomposition of one of the radicals, the present model can be easily reduced to such a case by setting $k_{d,r,1}$ to zero and hence $f = F_{i_A}$.

Equation 19 can then be rearranged using eq 28 to give

$$\frac{1}{1-f} - 1 = \frac{k_BT}{6\pi\eta Rak_{i,1}} + \frac{k_{d,r,1}{}^{1/2}}{k_{i,1}}\left(\frac{k_BT}{6\pi\eta R}\right)^{1/2} \qquad (29)$$

For situations where the second term on the right-hand side of eq 29 is much larger than the first, the value of the exponent of the solvent viscosity would be 0.5, and for converse situations, the value of the exponent would be unity. Hence, depending on the specific initiator being investigated, the value of the exponent would be different than 0.5 as has been experimentally observed.[20] Koenig[23] has also reported that $1/(1-f) - 1$ could be correlated to η^{-1} over a finite viscosity range and extrapolation to infinite viscosity leads to a zero intercept if plotted against $\eta^{-1/2}$. Equation 29 also shows this behavior.

Finally, the Noyes equation[25-28] gives the following expression for the case where the initial separation is equal to the molecular diameter of the radicals:

$$\frac{1}{1-f} - 1 = \frac{(mk_BT/24)^{1/2}}{\pi\eta b^2} \qquad (30)$$

where m is the mass and b is the radius of the diffusing radical. If $D_A \gg a^2k_{d,r,1}$, eq 29 reduces to

$$\frac{1}{1-f} - 1 = \frac{k_BT}{6\pi\eta Rak_{i,1}} \qquad (31)$$

and gives the same dependence on η as the Noyes model. This implies that the Noyes model is a specific case of the model derived in this report.

Conclusions

In this work, a theoretical expression for the prediction of the initiator efficiency was developed. The model takes into account all the significant reactions that the radicals can undergo which lead to a change in the initiator efficiency and hence is of a general nature. Such a model can be used to predict the initiator efficiency through the course of a polymerization reaction instead of assuming a constant value as is done in most simulations. This is a significant step toward the development of a model for the prediction of the kinetic behavior of polymerization reactions. The model predictions compare well with available experimental data on the initiation efficiency of DMPA. A qualitative analysis of the model helps in understanding the dependence of the initiator efficiency on various parameters.

Acknowledgment. This work was presented in part at the National American Chemical Society Meeting in Chicago, IL, in August 1993. This work was supported by a grant from the National Science Foundation (Grant No. CTS-93-11563) and a Purdue Research Foundation Fellowship.

Appendix

To solve the coupled differential equations (5) and (9), the following substitutions are necessary.

$$\rho_A = \alpha(r,t)\exp[-(k_{d,r,1} + K)t] \qquad (A\text{-}1)$$

$$\rho_B = \beta(t,t)\exp[-(k_{d,r,1} + K)t] \qquad (A\text{-}2)$$

Equation 5 can then be written as

$$\frac{\partial\alpha}{\partial t} = D_A\left[\frac{\partial^2\alpha}{\partial r^2} + \frac{2}{r}\frac{\partial\alpha}{\partial r}\right] + K\alpha \qquad (A\text{-}3)$$

with initial conditions of

$$\alpha(r,0) = 0 \quad \text{and} \quad \alpha(r',0) = 1 \qquad (A\text{-}4)$$

and boundary conditions of

$$t > 0 \quad r = a \quad D_A(\partial\alpha/\partial r)_{r=a} = k_{i,1}\alpha(a,t) \qquad (A\text{-}5)$$

and

$$t > 0 \quad r = \infty \quad \alpha(r,t) = 0 \qquad (A\text{-}6)$$

Let

$$\alpha = \alpha'\exp(Kt) \qquad (A\text{-}7)$$

With this substitution, eq A-3 becomes

$$\frac{\partial\alpha'}{\partial t} = D_A\left[\frac{\partial^2\alpha'}{\partial r^2} + \frac{2}{r}\frac{\partial\alpha'}{\partial r}\right] \qquad (A\text{-}8)$$

with initial conditions of

$$\alpha'(r,0) = 0 \quad \text{and} \quad \alpha'(r',0) = 1 \qquad (A\text{-}9)$$

and boundary conditions of

$$t > 0 \quad r = a \quad D_A\left(\frac{\partial\alpha'}{\partial r}\right)_{r=a} = k_{i,1}\alpha'(a,t) \qquad (A\text{-}10)$$

and

$$t > 0 \quad r = \infty \quad \alpha'(r,t) = 0 \qquad (A\text{-}11)$$

By defining a Laplace transform, eq A-8 has been solved by Monchick[36] for the case in which the initial separation is $r' = a$.

$$\overline{\alpha'} = \int_0^\infty \alpha' e^{-k_{d,r,1}t}\,dt \tag{A-12}$$

The solution is

$$\overline{\alpha'} = \frac{\exp[(k_{d,r,1}/D_A)^{1/2}(a-r)]}{4\pi[D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}]r} \tag{A-13}$$

Since

$$\alpha = \alpha' \exp(Kt) \tag{A-14}$$

we have

$$\alpha' = \alpha \exp(-Kt) \tag{A-15}$$

Equation A-12 becomes

$$\overline{\alpha'} = \int_0^\infty \rho_A(r,t)\,dt \tag{A-16}$$

From eqs A-13 and A-16, eq 14 of the main text is easily obtained.

Using the substitutions (A-1) and (A-2) in eq 9, we obtain

$$\frac{\partial \beta}{\partial t} = D_B\left[\frac{\partial^2 \beta}{\partial r^2} + \frac{2}{r}\frac{\partial \beta}{\partial r}\right] + k_{d,r,1}(\alpha + \beta) \tag{A-17}$$

with initial conditions of

$$\beta(r,0) = 0 \tag{A-18}$$

and boundary conditions of

$$t > 0 \qquad r = b \qquad D_B(\partial\beta/\partial r)_{r=b} = k_{i,2}\beta(b,t) \tag{A-19}$$

and

$$t > 0 \qquad r = b \qquad \beta(r,t) = 0 \tag{A-20}$$

To solve eq A-17, it is necessary to transform the partial differential equation into an ordinary differential equation with the help of Laplace transforms. We define two transforms as

$$\hat{\alpha} = \int_0^\infty \alpha e^{-(k_{d,r,1}+K)t}\,dt \qquad \text{and} \qquad \hat{\beta} = \int_0^\infty \beta e^{-(k_{d,r,1}+K)t}\,dt \tag{A-21}$$

so that

$$\hat{\alpha} = \int_0^\infty \rho_A(r,t)\,dt \qquad \text{and} \qquad \hat{\beta} = \int_0^\infty \rho_B(r,t)\,dt \tag{A-22}$$

Laplace transforming the partial differential equation (A-17) into an ordinary differential equation, we get

$$\frac{d^2\hat{\beta}}{dr^2} + \frac{2}{r}\frac{d\hat{\beta}}{dr} + \frac{k_{d,r,1}}{D_B}\hat{\alpha} - \frac{K}{D_B}\hat{\beta} = 0 \tag{A-23}$$

with boundary conditions

$$t > 0 \qquad r = b \qquad D_B(d\hat{\beta}/dr)_{r=b} = k_{i,2}\hat{\beta}(b,t) \tag{A-24}$$

and

$$t > 0 \qquad r = \infty \qquad \hat{\beta}(r,t) = 0 \tag{A-25}$$

On solving eq A-23 and applying the boundary conditions, one can obtain the following result at $r = b$.

$$\hat{\beta}(b) = \frac{k_{d,r,1}\exp[(k_{d,r,1}/D_A)^{1/2}(a-b)]}{4\pi[(K/D_B)^{1/2} + (k_{d,r,1}/D_A)^{1/2}][D_A + ak_{i,1} + a(k_{d,r,1}D_A)^{1/2}]} \frac{1}{[D_B + bk_{i,2} + b(KD_B)^{1/2}]} \tag{A-26}$$

Using eqs A-22 and A-26, eq 15 of the main text is easily obtained.

References and Notes

(1) Hageman, H. J. In *Radiation Curing of Polymers II*; Randell, D. R., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1991; p 46.

(2) Bassi, G. L. *J. Radiat. Curing* **1987**, *14*, 18.

(3) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.

(4) Fouassier, J. P.; Ruhlmann, D.; Erddalane, A. *Macromolecules* **1993**, *26*, 721.

(5) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1992; p 234.

(6) Pappas, S. P. *J. Radiat. Curing* **1987**, *14*, 6.

(7) Sandner, M. R.; Osborn, C. L. *Tetrahedron Lett.* **1974**, *5*, 415.

(8) Borer, A.; Kirchmayer, R.; Rist, G. *Helv. Chim. Acta* **1978**, *61*, 305.

(9) Groenenboom, C. J.; Hageman, H. J.; Overeem, T.; Weber, A. J. M. *Makromol. Chem.* **1982**, *183*, 281.

(10) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2141.

(11) Shen, J. C.; Tian, Y.; Wang, G. B.; Yang, M. L. *Sci. China, Ser. B* **1990**, *33*, 1046.

(12) Shen, J. C.; Tian, Y.; Wang, G. B.; Yang, M. L. *Makromol. Chem.* **1991**, *192*, 2669.

(13) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Polymer* **1990**, *31*, 154.

(14) Bowman, C. N.; Peppas, N. A. *Macromolecules* **1991**, *21*, 1914.

(15) Marten, F. L.; Hamielec, A. E. In *Polymerization Reactors and Processes*; Henderson, J. N., Bouton, T. C., Eds.; ACS Symposium Series 104; American Chemical Society: Washington, DC, 1979; p 43.

(16) Konstadinidis, K.; Achilias, D. S.; Kiparissides, C. *Polymer* **1992**, *33*, 5019.

(17) Dube, M. A.; Rilling, K.; Pendilis, A. *J. Appl. Polym. Sci.* **1991**, *43*, 2137.

(18) Coyle, D. J.; Tulig, T. J.; Tirrell, M. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 343.

(19) Mikos, A. G.; Takoudis, C. G.; Peppas, N. A. *Macromolecules* **1986**, *19*, 2174.

(20) Pryor, W. A.; Morkved, E. H.; Bickley, H. T. *J. Org. Chem.* **1972**, *37*, 1999.

(21) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 5403.

(22) Koenig, T.; Deinzer, M. *J. Am. Chem. Soc.* **1968**, *90*, 7014.

(23) Koenig, T. *J. Am. Chem. Soc.* **1969**, *91*, 2558.

(24) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; p 157.

(25) Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042.

(26) Noyes, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 551.

(27) Noyes, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 566.

(28) Noyes, R. M. In *Progress in Reaction Kinetics*; Porter, G., Ed.; Pergamon Press: New York, 1961; Vol. 1, p 129.

(29) Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* **1976**, *9*, 302.

(30) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 57.

(31) Ito, K. *Polym. J.* **1985**, *17*, 421.

(32) Kim, K. J.; Liang, W.; Choi, K. Y. *Ind. Chem. Eng. Res.* **1989**, *28*, 131.

(33) Batch, G. L.; Macosko, C. W. *J. Appl. Polym. Sci.* **1992**, *44*, 1711.

(34) Achilias, D. S.; Kiparissides, C. *Macromolecules* **1992**, *25*, 3739.

(35) Collins, F. C.; Kimball, G. E. *J. Colloid Sci.* **1949**, *4*, 425.

(36) Monchick, L. *J. Chem. Phys.* **1956**, *24*, 381.

(37) Wang, X.; Li, M.; Chang, Z.; Wang, E. *Chin. J. Polym. Sci.* **1993**, *11*, 26.

(38) Kuhlmann, R.; Schnabel, W. *Polymer* **1977**, *18*, 1163.

(39) Kuhlmann, R.; Schnabel, W. *Angew. Makromol. Chem.* **1978**, *70*, 145.

(40) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403.

(41) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 417.

(42) Vrentas, J. S.; Duda, J. L. *J. Appl. Polym. Sci.* **1991**, *42*, 1931.

(43) Vrentas, J. S.; Vrentas, C. M. *J. Polym. Sci., Polym. Lett.* **1990**, *28*, 379.

(44) Vrentas, J. S.; Duda, J. L.; Ling, H. C.; Hou, H. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 289.

(45) Duda, J. L.; Vrentas, J. S.; Ju, S. T.; Liu, H. T. *AIChE J.* **1982**, *28*, 279.