Theoretical Aspects of Controlled Radical Polymerization in a Dispersed Medium

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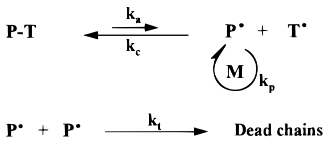
ABSTRACT: Kinetics of controlled radical polymerization (CRP) is examined in a dispersed medium, when the persistent radical effect operates. For that purpose, nitroxide-mediated CRP is considered in a miniemulsion system with oil-soluble alkoxyamine unimolecular initiator and in the absence of thermal self-initiation. An analytical expression of the rate of irreversible termination is proposed as a function of particle size, and it is compared with the rate of termination in bulk. From these expressions, the evolution with monomer conversion of the concentration of released nitroxide is calculated. For large particles, the polymerization kinetics was found to be similar in bulk and in the miniemulsion. In contrast for small particles, owing to slower terminations, the concentration of released nitroxide was shown to be smaller in the miniemulsion than in bulk, leading thus to a lower proportion of dead chains, a faster polymerization, and a broader molar mass distribution.

Introduction

Controlled radical polymerization (CRP) is a new, easy route to prepare well-defined (co)polymers with predictable molar mass and narrow molar mass distribution.[1] CRP is based either on a reversible termination process or on a reversible chain transfer process. In the first case, the now well-known nitroxide-mediated polymerization (NMP)[2] and atom transfer radical polymerization (ATRP)[3] are mainly applied. In the second case, control is provided by the transfer of the terminal group from a dormant chain to an active one. It can be the direct exchange of a terminal iodine atom[4] or an addition−fragmentation transfer process involving, for instance, dithioester end groups (RAFT).[5] In both cases, macromolecular chains are built up and grow simultaneously. They undergo successive activation/deactivation cycles, and a very small fraction of the chains are instantaneously active. Irreversible terminations are not precluded but the overall proportion of dead chains remains small. When a reversible chain transfer process is applied, a conventional radical initiator is needed and the polymerization kinetics follows a classical stationary state.[6,8] Thus, whatever the polymerization medium, i.e., homogeneous or heterogeneous, kinetics should not differ from that of a classical radical polymerization. In contrast, with a reversible termination process, the polymerization kinetics is strongly affected and is regulated by the persistent radical effect (PRE).[7,8] Analytical kinetic equations have been determined by Fischer[7] and Fukuda,[8] describing the time evolution of the various components of the system when PRE operates. This calculation was performed for instance in the case of nitroxide-mediated CRP under homogeneous conditions when the polymerization is governed by the reactions presented in Scheme 1.

Scheme 1



When initiation is performed by an alkoxyamine P−T in the absence of added free nitroxide, the initial concentrations are $[P{-}T]_0$ and $[P^\bullet]_0 = [T^\bullet]_0 = 0$, where $P^\bullet$ and $T^\bullet$ represent the propagating radicals and the free nitroxide, respectively. Upon heating, homolytic cleavage of the alkoxyamine occurs and leads to the formation of $P^\bullet$ and $T^\bullet$ in equal concentrations and with the same rate. Nevertheless, when $[P^\bullet]$ increases, the irreversible termination between transient radicals $P^\bullet$ cannot be neglected and results in a consumption of $P^\bullet$ together with an accumulation of $T^\bullet$. Fischer has demonstrated that $[P^\bullet]$ reaches a maximum value within a very short time scale (a few milliseconds). After this period, the time variations of $[P^\bullet]$ and $[T^\bullet]$ can be calculated and follow the power laws given below where k_a, k_c and k_t are the respective rate constants of activation, reversible recombination with the nitroxide, and irreversible termination (according to Scheme 1). K is the activation/recombination equilibrium constant ($K = k_a/k_c = [P^\bullet][T^\bullet]/[P{-}T]$).

$$[P^\bullet] = \left(\frac{K[P{-}T]_0}{3k_t}\right)^{1/3} t^{-1/3} \qquad (1)$$

$$[T^\bullet] = (3k_t K^2 [P{-}T]_0^{\,2})^{1/3} t^{1/3} \qquad (2)$$

$$k_c[P^\bullet][T^\bullet] = k_a[P{-}T]_0 \qquad (3)$$

Those equations were shown to apply when $K < [P{-}T]_0 k_c/4k_t$. Concentrations of $P^\bullet$ and $T^\bullet$ are self-regulated and polymerization kinetics reaches a pseudo-equilibrium state with $[P{-}T] \gg [T^\bullet] \gg [P^\bullet]$. Consequently, at this stage, the rate of irreversible termination between propagating radicals is much slower than the rate of recombination of the propagating radicals with the free nitroxide: $k_t[P^\bullet] \ll k_c[T^\bullet]$. The system is then essentially governed by both the activation and recombination reactions.

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Equations 1 and 2 have been established and solved for homogeneous polymerization conditions. It actually concerns the large majority of the published studies since CRP has been essentially applied to homogeneous systems such as bulk or solution. Besides, attempts to perform CRP in dispersed media have been recently reported using various techniques such as suspension,[9] dispersion,[10] seeded emulsion,[11] batch emulsion,[12−16] and miniemulsion polymerizations.[17−21] In a dispersed medium, when a reversible chain transfer process is used, the kinetics was shown not to be affected by the addition of the chain transfer agent[21] and thus does not require special investigation. In contrast, with a reversible termination, the situation is quite different. However, the previous equations, (1) and (2), should not apply anymore, and the system has to be reexamined according to the special features of heterogeneous conditions. For instance, it is often stated that the rate of irreversible termination should be much lower for CRP in dispersed media than in bulk, owing to compartmentalization of the propagating radicals. Does this assertion, which is generally true in conventional radical emulsion polymerization, remain correct when a controlled system is applied? What would be the consequences on kinetics of CRP in dispersed media? These are the main issues addressed here. In this paper, a complete description of CRP based on a reversible termination process in a dispersed medium is presented. To simplify the equations, nitroxide-mediated polymerization is studied in a miniemulsion system[22] with oil-soluble alkoxyamine unimolecular initiator. A polymerization temperature below 100 °C is considered, and consequently, thermal self-initiation is not taken into account. This situation is the heterogeneous counterpart of that studied by Fischer[7] and Fukuda[8] (Scheme 1). It corresponds well to our works concerning the application of the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) in miniemulsion, at temperatures below 100 °C.[20] Nevertheless, the conclusions would not be very different if ATRP was considered instead. A model able to simulate CRP in micro- and miniemulsion polymerizations has already been reported by Butté et al.[23] However, in their work, numerical rather than analytical determination of the equations was performed, and the purpose was quite different as the paper was essentially devoted to simulation. Moreover, they considered both the existence of thermal self-initiation and compartmentalization of the nitroxide which led to a different mathematical approach.

Expression of the Rate of Termination for Nitroxide-Mediated CRP in Model Miniemulsion

In the miniemulsion polymerization considered here, the organic phase composed of monomer and of dissolved alkoxyamine is initially divided into stabilized droplets with diameter D, and volume $v_p = \pi D^3/6$ in which polymerization takes place upon thermal activation. The water-solubility of the alkoxyamine initiator is supposed negligible. In such a system, the alkoxyamine dormant chains and the active macroradicals are compartmentalized, i.e., they cannot exit from the particles. In contrast, the free nitroxide molecules are not compartmentalized and can exchange between the particles, via diffusion through the aqueous phase. Unlike classical emulsion or miniemulsion polymerizations, no radicals are supplied from decomposition of a water-soluble radical initiator; the propagating radicals are only generated in the polymerization loci by activation of the alkoxyamines. To simplify, the concentration of nitroxide in the aqueous phase will be first considered as negligible (partition is neglected). All the concentrations are expressed per volume unit of the organic phase; $[P^\bullet]$, $[T^\bullet]$, and $[P{-}T]$ are the overall concentrations calculated for the total organic volume.

Considering N_i, the fraction of particles containing i active macroradicals, $\sum N_i = 1$ and $\tilde{n} = \sum iN_i = N_A v_p [P^\bullet]$ is the average number of radicals per particle (with N_A, Avogadro's number). According to Smith and Ewart's model of kinetics in a dispersed medium[24]

$$\frac{dN_i}{dt} = N_A v_p k_a [P{-}T](N_{i-1} - N_i) + k_c[T^\bullet]((i+1)N_{i+1} - iN_i) + \frac{k_t}{N_A v_p}((i+2)(i+1)N_{i+2} - i(i-1)N_i) \quad (4)$$

$$\frac{d[P^\bullet]}{dt} = \frac{1}{N_A v_p}\frac{d\sum(iN_i)}{dt} \quad (5)$$

$$\frac{d[P^\bullet]}{dt} = k_a[P{-}T]\sum N_i - \frac{k_c[T^\bullet]}{N_A v_p}\sum iN_i - \frac{2k_t}{(N_A v_p)^2}\left(\sum i^2 N_i - \sum iN_i\right) \quad (6)$$

$$\frac{d[P^\bullet]}{dt} = k_a[P{-}T] - k_c[T^\bullet][P^\bullet] - \frac{2k_t}{(N_A v_p)^2}\left(\sum i^2 N_i - \sum iN_i\right) \quad (7)$$

Interestingly, both the rate of activation and the rate of recombination with the nitroxide are written the same way as in the bulk, considering the overall concentrations in the organic phase.

The rate of irreversible termination R_t, i.e., the rate of formation of dead chains, P^{dead}, is given by

$$R_t = \frac{d[P^{\text{dead}}]}{dt}$$

(termination by disproportionation only)

$$R_t = \frac{2k_t}{(N_A v_p)^2}\left(\sum i^2 N_i - \sum iN_i\right) \quad (8)$$

To simplify the equations, the value of k_t will be considered as constant throughout the polymerization although it is likely that a chain-length dependence exists.

Two main situations can be considered, depending on the level of segregation of the system.

First Case: $\tilde{n} = \sum iN_i = N_A v_p [P^\bullet] > 1$. This case applies essentially when the particles are large enough to all contain at least one propagating radical ($N_0 \approx 0$). When $\tilde{n}$ is far above 1, the concentration of $P^\bullet$ in a given particle is the same as in the bulk (pseudo-bulk system). If the N_i values obey a Poisson distribution (which is expected when $\tilde{n}$ is large), the time evolution of $[P^\bullet]$ simplifies according to[25]

$$\frac{d[P^\bullet]}{dt} = k_a[P{-}T] - k_c[T^\bullet][P^\bullet] - \frac{2k_t}{(N_A v_p)^2}\left(\sum iN_i\right)^2 \quad (9)$$

$$\frac{d[P^\bullet]}{dt} = k_a[P-T] - k_c[T^\bullet][P^\bullet] - 2k_t[P^\bullet]^2 \quad (10)$$

The system behaves similarly as in a homogeneous medium (i.e., eq 10 is the same as it would be in bulk or solution). Thus, in the pseudo-equilibrium regime, the concentrations of $T^\bullet$ and $P^\bullet$ can be calculated according to eqs 1 and 2.

Second Case: $\tilde{n} = \sum iN_i = N_A v_p[P^\bullet] < 1$. Only a fraction of the particles contain propagating radicals. If $\tilde{n}$ is far below 1, the system can be simplified if one considers that only particles with 0 (N_0) or 1 radical (N_1) exist. In relation with the terminology which is used in conventional emulsion polymerization, this situation will be referred to as a zero/one system. It has been shown to be the case for the SG1-mediated miniemulsion polymerizations of styrene at 90 °C for which $\tilde{n}$ was always found lower than 0.2.[26] This means that the activation of an alkoxyamine in a particle which already contains one propagating radical is immediately followed by a termination reaction which can be either a reversible one with $T^\bullet$ or an irreversible one with $P^\bullet$. For this reason, the fraction N_2 of particles containing 2 radicals remains negligible and follows a steady state with $dN_2/dt = 0$.

$$N_0 + N_1 = 1$$

$$N_2 \approx 0 \text{ and more generally } N_i = 0 \quad \text{for } i > 2$$

$$\tilde{n} = N_1 = N_A v_p[P^\bullet]$$

$$\frac{dN_2}{dt} = N_A v_p k_a[P-T](N_1 - N_2) - 2k_c[T^\bullet]N_2 - \frac{2k_t}{N_A v_p}N_2 \quad (11)$$

Since, in this case, N_2 is considered to be small with respect to N_1, then dN_2/dt can be written more simply:

$$\frac{dN_2}{dt} = N_A v_p k_a[P-T]N_1 - 2k_c[T^\bullet]N_2 - \frac{2k_t}{N_A v_p}N_2 \quad (12)$$

This situation, which is specific for our considered second case, is only true when

$$N_A v_p k_a[P-T] < 2k_c[T^\bullet] + \frac{2k_t}{N_A v_p} \quad (13)$$

which corresponds actually to

$$(N_A v_p)^2 k_a[P-T]_0 < 2k_t \quad (14)$$

at the initial stage of the polymerization, in the absence of added free nitroxide. For a given initial concentration of alkoxyamine $[P-T]_0$, this relationship applies when the particle volume is small enough. Indeed, it should be smaller than

$$v_p = 1/N_A\sqrt{2k_t/k_a[P-T]_0}$$

$$\frac{dN_2}{dt} = 0$$

leads to

$$N_2 = \frac{k_a[P-T]N_1}{2k_t/(N_A v_p) + 2k_c[T^\bullet]} N_A v_p \quad (15)$$

In this case, eq 7 becomes

$$\frac{d[P^\bullet]}{dt} = k_a[P-T] - k_c[T^\bullet][P^\bullet] - \frac{4k_t}{(N_A v_p)^2} N_2 \quad (16)$$

and the rate of termination is then given by the modified eq 8

$$R_t = \frac{4k_t}{(N_A v_p)^2} N_2 \quad (17)$$

$$R_t = 2k_a[P-T]N_1 \frac{k_t/(N_A v_p)}{k_t/(N_A v_p) + k_c[T^\bullet]} \quad (18)$$

$$R_t = 2k_a[P-T]N_1 p_t \quad (19)$$

where $k_a[P-T]N_1$ is the rate of activation of the alkoxyamines in the particles which already contain a radical $P^\bullet$ and p_t represents the probability that the newly formed radical undergoes an irreversible termination with the existing radical $P^\bullet$ rather than a reversible recombination with a free nitroxide molecule ($1/(N_A v_p)$ represents the concentration of one radical in a particle of volume v_p).

The term p_t is the probability of irreversible termination in a given particle which contains two propagating radicals. It does not properly describe the overall termination kinetics. Actually, a large value of p_t (larger than $1/2$) does not mean that the overall rate of termination in the system is larger than the overall rate of recombination with $T^\bullet$. The overall rate of termination is given by eq 19 while the overall rate of recombination is given by $R_c = k_c[T^\bullet][P^\bullet] = k_c[T^\bullet]N_1/(N_A v_p)$. The polymerization can be considered as properly controlled and the activation–deactivation equilibrium is established when $R_c \gg R_t$, i.e., when $[T^\bullet]$ is larger than $2K[P-T]N_A v_p p_t$. This relationship can also be written: $k_c[T^\bullet][P^\bullet] = k_a[P-T] \gg 2k_a[P-T]N_1 p_t$, which means that the average number of radical per particle should be smaller than $1/(2p_t)$. In that case, the overall rate of termination R_t can be written differently, from eq 18.

$$R_t = 2k_a[P-T][P^\bullet]N_A v_p \frac{k_t/(N_A v_p)}{k_t/(N_A v_p) + k_c[T^\bullet]} \quad (20)$$

$$R_t = 2k_t[P^\bullet]^2 \frac{k_c[T^\bullet]}{k_t/(N_A v_p) + k_c[T^\bullet]} \quad (21)$$

$$R_t = 2k_t[P^\bullet]^2(1 - p_t) \quad (22)$$

Thus, for a given concentration of $P^\bullet$ and $T^\bullet$, the rate of termination in a zero/one miniemulsion is smaller than it would be in bulk under similar conditions.

When p_t is very small, i.e., when the following condition is satisfied

$$\frac{k_t}{k_c[T^\bullet]N_A v_p} \ll 1$$

$$[T^\bullet]N_A v_p \gg k_t/k_c \quad (23)$$

in other words, when the average number of free $T^{\bullet}$ per particle is larger than k_t/k_c, then the rate of termination can be written $R_t = 2k_t[P^{\bullet}]^2$, in a similar way as in a bulk polymerization.

If, in contrast, the condition is not satisfied and

$$\frac{k_t}{k_c[T^{\bullet}]N_A v_p} \gg 1 \tag{24}$$

then the probability p_t that two propagating radicals in the same particle undergo an irreversible termination event equals 1 and the overall rate of termination is given by

$$R_t = 2k_a[P-T]N_1 \tag{25}$$

In that case, the rate-determining step for the irreversible termination is the activation of an alkoxyamine in an already active particle. This situation occurs at the very beginning of the polymerization when the concentration of free nitroxide is not large enough and lasts as long as $[T^{\bullet}]N_A v_p$ is small with respect to k_t/k_c.

Analytical Equations for the Evolution of $[T^{\bullet}]$ with Monomer Conversion

Each irreversible termination step leads to the formation of two free nitroxide molecules. Thus, the rate of formation of free nitroxide equals R_t, which gives

$$\frac{d[T^{\bullet}]}{dt} = 2k_a[P-T]N_1 p_t$$

$$\frac{d[T^{\bullet}]}{dt} = 2k_a[P-T][P^{\bullet}]N_A v_p p_t$$

This equation can be written as a function of monomer conversion (x):

$$\frac{d[T^{\bullet}]}{dx} = \frac{2k_a[P-T]N_A v_p p_t}{k_p(1-x)}$$

$$\frac{d[T^{\bullet}]}{dx} = \frac{2k_a[P-T]N_A v_p}{k_p(1-x)} \frac{\dfrac{k_t}{N_A v_p}}{\dfrac{k_t}{N_A v_p} + k_c[T^{\bullet}]} \tag{26}$$

$$\left(\frac{k_t}{N_A v_p} + k_c[T^{\bullet}]\right)d[T^{\bullet}] = \frac{2k_a[P-T]k_t}{k_p}\frac{dx}{(1-x)} \tag{27}$$

If one considers that the concentration of alkoxyamine does not change significantly and remains equal to $[P-T]_0$, this equation can be easily integrated to give the concentration of free nitroxide as a function of monomer conversion

$$[T^{\bullet}]_{(ME)} = -A + \sqrt{(A + [T^{\bullet}]_0)^2 - B\ln(1-x)} \tag{28}$$

with $[T]_0$, the initial concentration of nitroxide in the system, and

$$A = \frac{k_t}{N_A v_p k_c}$$

$$B = \frac{4K[P-T]_0 k_t}{k_p}$$

If now, one considers the evolution of $[T^{\bullet}]$ in a bulk polymerization, when the pseudo-equilibrium regime is established:

$$\frac{d[T^{\bullet}]}{dt} = 2k_t[P^{\bullet}]^2 \tag{29}$$

$$\frac{d[T^{\bullet}]}{dx} = \frac{2k_t[P^{\bullet}]}{k_p(1-x)} = \frac{2k_t K[P-T]}{[T^{\bullet}]k_p(1-x)}$$

$$[T^{\bullet}]_{(BULK)} = \sqrt{[T^{\bullet}]_0^{\,2} - B\ln(1-x)} \tag{30}$$

This equation is the same as the equation (eq 2) derived by Fischer[7] and Fukuda[8] except that $[T^{\bullet}]$ is expressed as a function of monomer conversion instead of polymerization time.

The relationship between $[T^{\bullet}]_{(ME)}$ and $[T^{\bullet}]_{(BULK)}$ can be written

$$[T^{\bullet}]^2_{(BULK)} = [T^{\bullet}]^2_{(ME)} + 2A([T^{\bullet}]_{(ME)} - [T^{\bullet}]_0) \tag{31}$$

Therefore, the concentration of free nitroxide which is released at a given conversion owing to the PRE is always larger in bulk than in miniemulsion. However, when A is very small either because k_t/k_c is small or because particle volume is large, then the concentration of released nitroxide is the same in both cases. As a consequence, and specially for small particles, the polymerization will be faster in miniemulsion than in bulk but the molar mass distribution will be broader; however, the proportion of dead chains will be smaller.

All these calculations are based on the insolubility of the nitroxide in the water phase. This is obviously wrong for most of the nitroxides which can be used. Therefore, the partition of the nitroxide between the two phases should be considered and will result in a decrease of $[T^{\bullet}]$ in the organic phase, leading simultaneously to an increase of $[P^{\bullet}]$ and thus to an increase of both the rate of propagation and the overall rate of termination.

Actually, one can consider that only a fraction α of the nitroxide remains in the organic phase:

$$[T^{\bullet}]_{particles} = \alpha[T^{\bullet}]_{tot.}$$

α is a function of the partition coefficient ($[T^{\bullet}]_{H_2O}/[T^{\bullet}]_{particles}$) and of the respective volumes of the monomer and the water phases. To simplify, one will suppose that α remains constant throughout the polymerization.

The concentration of nitroxide in the particles becomes

$$[T^{\bullet}]_{particles} = \alpha[T^{\bullet}]_{tot.} = -A + \sqrt{(A + \alpha[T^{\bullet}]_0)^2 - B\alpha\ln(1-x)} \tag{32}$$

where $[T^{\bullet}]_0$ and $[T^{\bullet}]_{tot.}$ represent the overall concentrations of nitroxide respectively at conversion = 0 and conversion = x (calculated per volume unit of organic phase) and $[T^\bullet]_{particles}$ represents the actual concentration inside the particles.

Molar Mass Distribution as a Function of Monomer Conversion

The zeroth, first and second moments of the species containing polymerized monomer units (respectively m_0, m_1, and m_2) can be defined and calculated in the same way as that presented by Fischer.[7] $[P_i - T]$, $[P_i^\bullet]$, and $[P_i^{dead}]$ represent the concentrations of dormant, active, and dead chains respectively, containing i monomer units.

$$m_0 = \sum([P_i - T] + [P_i^\bullet] + [P_i^{dead}]) = [P-T]_0 \quad (33)$$

$$m_1 = \sum i([P_i - T] + [P_i^\bullet] + [P_i^{dead}]) = x[M]_0 \quad (34)$$

with $[M]_0$, the initial concentration of monomer in the organic phase.

$$m_2 = \sum i^2([P_i - T] + [P_i^\bullet] + [P_i^{dead}]) \quad (35)$$

$$m_2 = x[M]_0 + \frac{x^2[M]_0^{\,2}}{[P-T]_0} + \frac{2k_p[M]_0^{\,2}}{k_a[P-T]_0}\int[P^\bullet](1-x)\,dx \quad (36)$$

$$m_2 = x[M]_0 + \frac{x^2[M]_0^{\,2}}{[P-T]_0} + \frac{2k_p[M]_0^{\,2}}{k_c}\int\frac{(1-x)}{[T^\bullet]}\,dx \quad (37)$$

The number-average degree of polymerization is given by

$$DP_n = m_1/m_0 = \frac{x[M]_0}{[P-T]_0} \quad (38)$$

while the weight-average degree of polymerization is

$$DP_w = m_2/m_1 = 1 + \frac{x[M]_0}{[P-T]_0} + \frac{2k_p[M]_0}{xk_c}\int\frac{(1-x)}{[T^\bullet]}\,dx \quad (39)$$

Then, the polydispersity index can be calculated as

$$PDI = DP_w/DP_n = 1 + \frac{[P-T]_0}{x[M]_0} + \frac{2k_p[P-T]_0}{x^2k_c}\int\frac{(1-x)}{[T^\bullet]}\,dx \quad (40)$$

which can be numerically integrated when the evolution of $[T^\bullet]$ as a function of monomer conversion x is known. In the calculation of the polydispersity index, the initiator ($i = 0$) was considered as a polymer chain, which explains the high PDI values obtained at low conversions.

The main interesting result is that the value of PDI is larger when the concentration of the nitroxide is smaller. Therefore, it should be larger in miniemulsion than in bulk as it will be illustrated in the following part.

Comparison of the Kinetics for Bulk and Miniemulsion CRP

On the basis of the previous equations, (28) and (30), the evolution of $[T^\bullet]$ with conversion can be calculated, respectively, for miniemulsion and bulk polymerizations. The equilibrium relationship (3) gives the simultaneous evolution of $[P^\bullet]$ and consequently ñ with conversion. The evolution with time of monomer conversion can be numerically calculated on the basis of the propagation rate: $dx/dt = k_p[P^\bullet](1 - x)$ and knowing the evolution of $[P^\bullet]$ with conversion. The polydispersity index value (PDI) can be numerically calculated according to eq 40. The rate constants used are those of the reactions involved in the SG1-mediated CRP of styrene at 90 °C (Table 1).

Table 1. Rate Constants of the Reactions Involved in the SG1-Mediated CRP of Styrene at 90 °C

dissociation of the alkoxyamine P-SG1[27]	k_a	$4 \times 10^{-4}\ s^{-1}$
recombination of $P^\bullet$ with SG1[27]	k_c	$8 \times 10^{5}\ L{\cdot}mol^{-1}{\cdot}s^{-1}$
constant of the activation/deactivation equilibrium[27]	K	$5 \times 10^{-10}\ mol{\cdot}L^{-1}$
propagation of styrene[28]	k_p	$900\ L{\cdot}mol^{-1}{\cdot}s^{-1}$
irreversible termination[29]	k_t	$10^{8}\ L{\cdot}mol^{-1}{\cdot}s^{-1}$

Figures 1 and 2 illustrate the effect of particle size on the polymerization kinetics considering two different initiator concentrations and neglecting the partition of the nitroxide between the two phases. It is clearly seen that the rate of miniemulsion polymerization decreases when the diameter is increased and, for large particles, the rate is the same as in bulk. The decrease of D is accompanied by a strong decrease of ñ, the value of which is usually far below 1. The large polymerization rates for small particles are the consequence of slow terminations which result in the formation of a low proportion of dead chains and of released nitroxide as conversion progresses. Another consequence of fast propagation is the broadening of the molar mass distribution as the diameter decreases. In Figure 3 the effect of the nitroxide partition coefficient is displayed. For given initial concentrations and particle size, it can be seen that the polymerization rate increases as α decreases (increased water-solubility of $T^\bullet$). The trend is the same for ñ. In contrast to the previous results with $\alpha = 1$ (i.e., negligible water-solubility of $T^\bullet$), the faster polymerization is accompanied by a larger proportion of dead chains and of released nitroxide together with an increase of the PDI.

Conclusions

Kinetics of nitroxide-mediated CRP in miniemulsion has been examined. The evolution with monomer conversion of the concentration of released free nitroxide is calculated and compared with that in bulk polymerization. Compartmentalization of the alkoxyamine dormant chains and of the active macroradicals is considered. In contrast, the free nitroxide molecules are supposed to exchange very rapidly between the particles, via diffusion through the aqueous phase. For a given nitroxide and a given temperature (i.e., given activation and deactivation rate constants), the kinetics was shown to strongly depend on both particle size and partition coefficient of the nitroxide between the monomer and the water phases. When water-solubility of the nitroxide is negligible, especially for large particles the kinetics was found to be similar in bulk and in miniemulsion. However, when particle size becomes smaller, the situation changes depending on the concentration of free nitroxide within the particles. At high concentration of $T^\bullet$ (when $[T^\bullet]N_Av_p \gg k_t/k_c$; i.e., when the average number of free $T^\bullet$ per particle is larger than k_t/k_c) the rate of termination is also the same as in a bulk polymerization. In contrast, when the concentration of

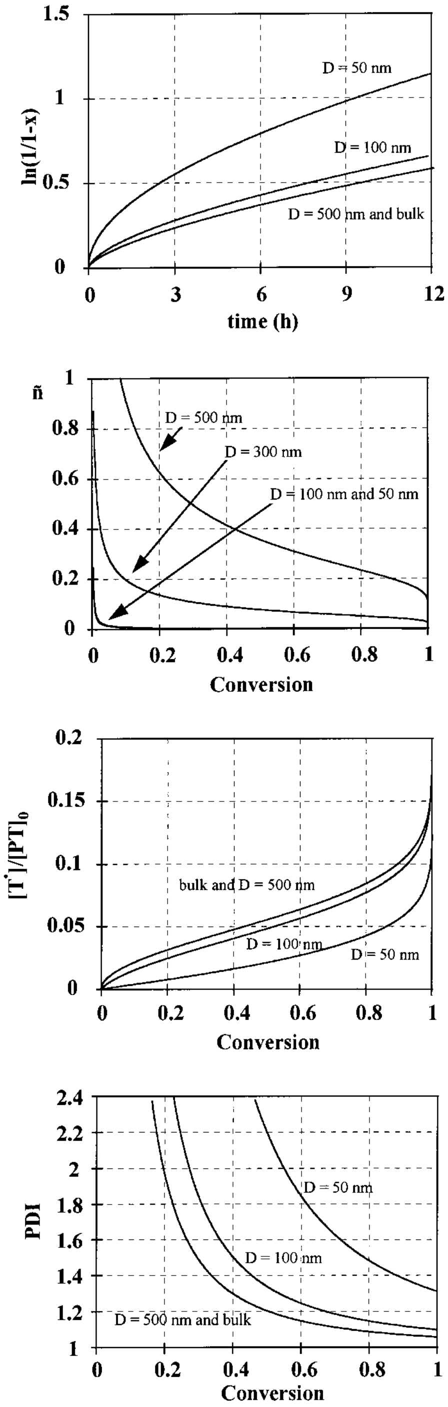

Figure 1. SG1-mediated CRP of styrene at 90 °C. Effect of the diameter when $[P-T]_0 = 0.05$ mol·L^{-1}, $[T^\bullet]_0 = 0$, and $\alpha = 1$.

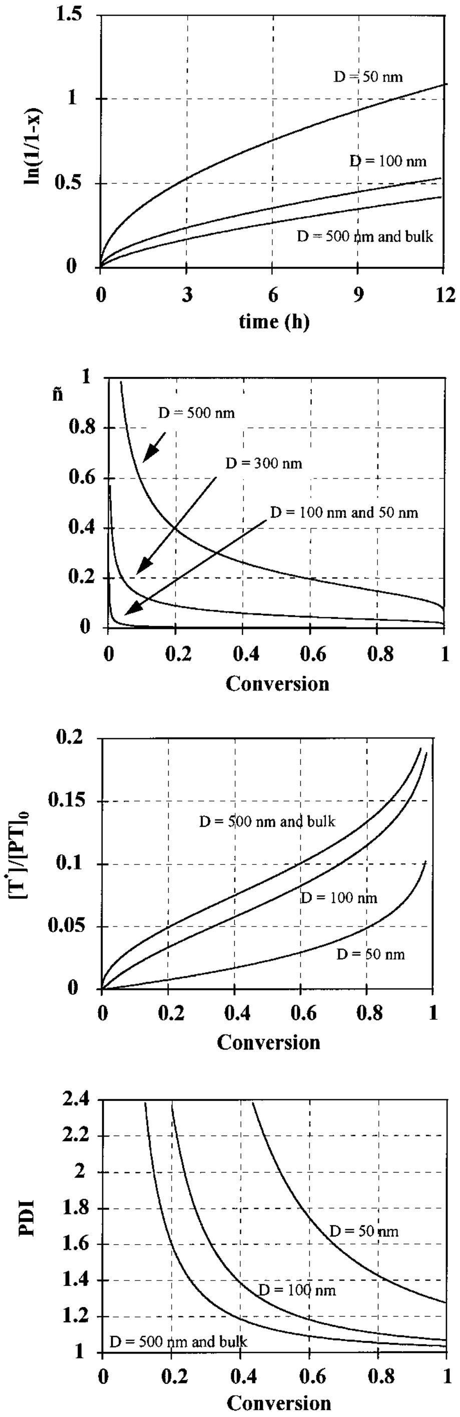

Figure 2. SG1-mediated CRP of styrene at 90 °C. Effect of the diameter when $[P-T]_0 = 0.02$ mol·L^{-1}, $[T^\bullet]_0 = 0$, and $\alpha = 1$.

free nitroxide within the particles is too small (for instance at the beginning of the polymerization when no free nitroxide is added), the irreversible termination is slower in a dispersed medium than in bulk. The consequence is that both the overall proportion of dead chains and the concentration of released nitroxide are lower, the polymerization is then faster and the molar mass distribution is broader. When the nitroxide is partitioned between the two phases, for a given particle size, the polymerization is faster when the water solubility is larger and the molar mass distribution is broader; in addition, the overall proportion of released nitroxide and consequently the proportion of dead chains is also larger. In all cases, like it is also in bulk, the possible thermal self-initiation and/or slow decomposition of an added radical initiator would contribute to the consumption of the excess of free nitroxide and would lead therefore to an increased rate of polymerization together with a broadening of the molar mass distribution. The equations derived in this paper would not apply anymore.

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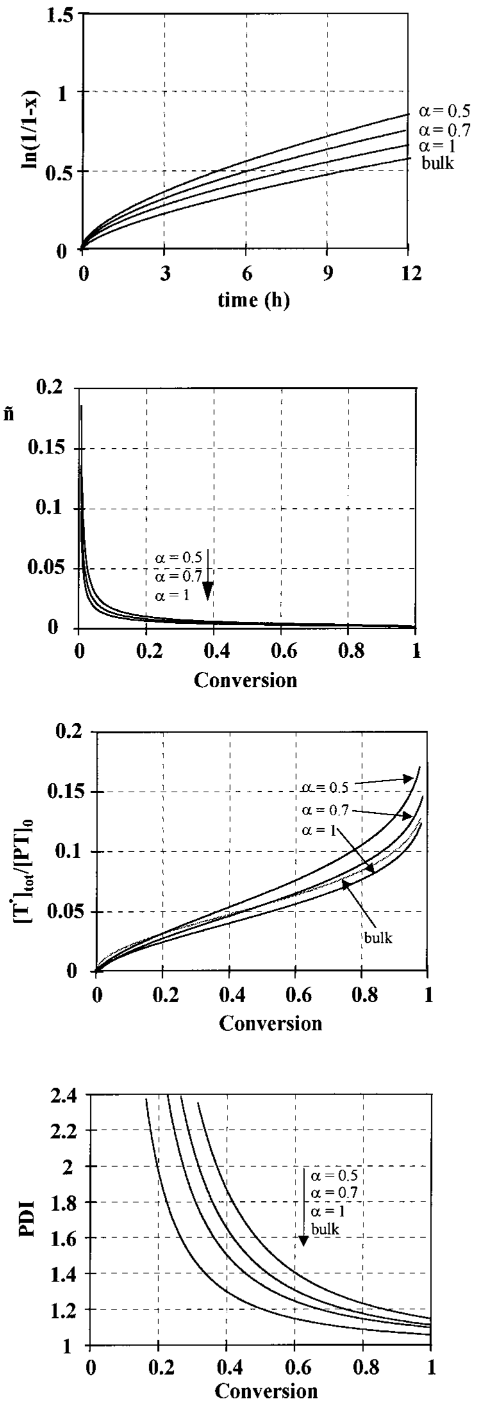

Figure 3. SG1-mediated CRP of styrene at 90 °C. Effect of α when $[P-T]_0 = 0.05$ mol·L^{-1}, $[T^\bullet]_0 = 0$, and $D = 100$ nm.

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