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Spontaneous Polymerization in the Emulsion Polymerization of Styrene and Chlorobutadiene

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ABSTRACT: Spontaneous initiation in emulsion polymerization may be more important than in the corresponding bulk free-radical polymerization. A methodology is derived for finding the locus of spontaneous polymerization in emulsion polymerization, through use of spin traps and catalysts which can accelerate decomposition of peroxides. Applying this to both styrene and chloroprene (chlorobutadiene), it is found that this generation occurs to some degree within all phases present. The rate of spontaneous initiation is relatively small in styrene emulsion polymerization but large in chloroprene. A means of including this effect in modeling rates and molecular weight distributions is derived, which also shows how rate parameters for the process may be obtained from experimental molecular weight distributions. This methodology is applied to these two monomers, with a series of seeded emulsion polymerizations using polystyrene host seeds for both. For styrene polymerization, the spontaneous initiation rate is low and varies with latex preparation; consistent values for this rate coefficient for a given latex are obtained by independent measurements involving two different techniques, thereby verifying the methodology. Applying this methodology to chloroprene, it is found that the effect of spontaneous initiation is much larger and probably arises from peroxides formed by exposure to oxygen. For chloroprene, spontaneous radical generation occurs both within the particles and in any monomer droplets present, with different chain-stopping mechanisms occurring in these two phases. It is a major influence on rates and molecular weight distributions, even in the presence of large amounts of added initiator; chain stoppage in droplets is largely by transfer to monomer, whereas chain stoppage within particles is by termination with short radicals formed by spontaneous initiation. Arrhenius parameters for the rate coefficient for transfer to monomer are obtained from the molecular weight distributions for the chloroprene system: $k_{\mathrm{tr}}/\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1} = 10^{4.3} \exp(-30.9\ \mathrm{kJ\ mol}^{-1}/RT)$.

Introduction

Spontaneous polymerization is that which occurs in the absence of an added radical source and has been observed to occur in many different systems.[1−10] Most studies have been performed on bulk and solution systems, with far fewer being performed on emulsion polymerizations. There are circumstances in which the spontaneous rate in emulsion polymerizations can be significantly greater than in the corresponding bulk system.[1] While the spontaneous rate in emulsion polymerizations is often small (e.g., for styrene[1,2]) or negligible (e.g., for MMA[11] and vinyl acetate[12]), this is by no means always the case.

Formation of radicals in different phases (water, particle, monomer droplet, and, during nucleation, micelles) of an emulsion polymerization system may lead to qualitatively different effects on polymerization behavior. The aims are (a) to identify which of the several phases spontaneously generated radicals are produced in styrene and 1,3-chlorobutadiene (chloroprene) emulsion polymerizations, (b) to identify possible origins of spontaneous radical formation in these systems, (c) to quantify the effects on overall rates and molecular weight distributions, and thus (d) to deduce values for the rate coefficients for spontaneous initiation in those phases in which it is significant.

In this study, we employ seeded emulsion polymerization (polymerization in the presence of preformed particles under conditions chosen so that no new particle formation occurs) to avoid the complexities of particle nucleation. Now, while seeded emulsion polymerization is a standard technique for styrene systems, it poses a challenge for chloroprene, because it is not a simple matter to create a sufficiently monodisperse seed of convenient size for accurate studies, while at the same time maintaining conditions so that new particle formation does not occur. This can be overcome by a variant denoted “heteroseeded emulsion polymerization”,[13] in which one grows a seed of appropriate size and monodispersity using a convenient monomer such as styrene, where the second-stage monomer (in this case chloroprene) will swell the seed polymer (polystyrene). Seeded studies are then carried out in the normal way. The kinetic techniques used in the present paper depend only on data obtained over a relatively small range of conversion, and hence the formation of a relatively small amount of second-stage polymer (polychloroprene) in the presence of excess monomer which is soluble in both polymers is unlikely to cause phase separation based on incompatibilities between the two polymers. Moreover, the presence of excess polystyrene minimizes the likelihood of branching and cross-linking[14,15] occurring. This heteroseeded technique has been applied to a polystyrene/chloroprene system previously.[16]

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Heteroseeded emulsion polymerization data were obtained with different seed sizes, so that the kinetics could be either zero-one or pseudo-bulk. A zero-one system is where entry of a radical into a particle already containing a growing radical results in "instantaneous" termination, in which case the average number of radicals per particle, $\bar{n}$, is always $\leq {}^1/_2$.[17] In such systems, production of a pair of radicals in a particle leads to their rapid termination, and therefore no polymerization will be observed due to particle-phase radical production. A pseudo-bulk system[17] shows no effect of compartmentalization of radicals into particles and thus particle-phase pairwise radical production will have an effect. Radical production in the droplet phase, if present (Interval 2), will always have an effect in both zero-one and pseudo-bulk systems. For styrene, conditions were chosen to ensure both zero-one (small seed) and pseudo-bulk (large seed) conditions, while for chloroprene, the seed size was sufficiently small in each case to comfortably ensure zero-one conditions. The means of choosing a particle size so that zero-one conditions will be satisfied have been given elsewhere.[18]

An Interval 3 system is an emulsion polymerization where no monomer droplets are present, and an Interval 2 system is where both droplets and particles are present. Studies were performed under both types of conditions to identify in which phase(s) spontaneous radical production was significant.

A range of initiation systems was used: no added initiator to study spontaneous polymerization in isolation, added persulfate initiator, and also using γ-radiolysis initiation, which produces a steady flux of radicals at low temperatures.

Locus of Spontaneous Polymerization

The approach used is to isolate the phases. In this manner, the effect(s) of spontaneous radical formation occurring in each of the phases may be observed in the environs of an emulsion polymerization system, but so that the presence of the other phases does not affect the phenomenon occurring in the phase of interest. The concentrations of surfactant (sodium dodecyl sulfate, SDS) used for kinetic experiments in this work were such that the micellar phase was not present.

Aqueous Phase. It seems possible that a component of the spontaneous polymerization is due to peroxides, many of which are known to undergo redox reactions with various transition metal ions[19,20] to form reactive oxy-centered radicals, e.g.

$$\mathrm{R{-}O{-}O{-}R'}_{(aq)} + \mathrm{Fe}_{(aq)}{}^{2+} \rightarrow \mathrm{R{-}O}^{\bullet} + \mathrm{R'{-}O}^{-} + \mathrm{Fe}_{(aq)}{}^{3+} \quad (1)$$

Thus, addition of $\mathrm{Fe}_{(aq)}{}^{2+}$ to an emulsion polymerization system that contains aqueous-phase peroxides would increase the polymerization rate. A concentration of $[\mathrm{Fe}_{(aq)}{}^{2+}] = 10^{-4}$ mol dm^{-3} was used for these studies. Another possible source of spontaneously generated radicals is polymeric peroxides formed by exposure of the emulsion to oxygen. In the cases of chloroprene and styrene, such a polymeric species would be insoluble in water. Confirmation of aqueous-phase spontaneous radical generation would therefore imply that the species undergoing decomposition to form the radicals were not polymeric.

Oil Phases. Determining whether spontaneously generated radicals are formed in the oil phases (particles and droplets) is made simpler by eliminating contributions to the total spontaneously generated radical flux from aqueous-phase spontaneous radical formation using a radical trap that is only soluble in the aqueous phase, viz., $\mathrm{K_2(SO_3)_2NO}$ (Frémy's salt, FS).[21] It has been found that FS does not interact with SDS-stabilized micelles[21,22] and hence by inference for droplets and particles. One means of testing whether the concentration of FS is sufficient to trap all aqueous-phase radicals is to observe its effect upon an Interval 3 zero-one polymerization system, in which the only avenue by which polymerization may proceed is radical production in the aqueous phase followed by entry into the particle phase. Provided that all radicals in the aqueous phase are trapped by the FS, then no polymerization will be observed.

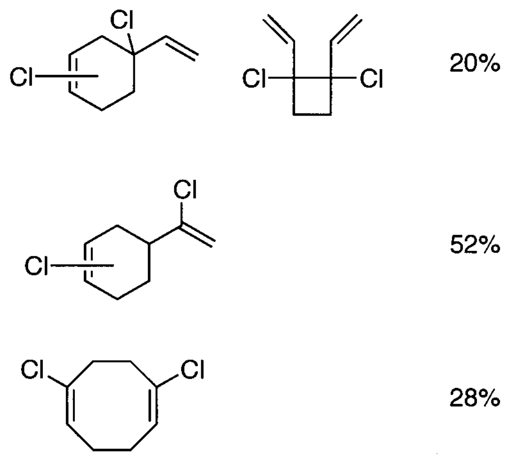

Figure 1. Structures and amounts of chloroprene dimers.

Some control of the presence of various phases is afforded by controlling the amount of monomer present in a seeded polymerization, i.e. whether the system is in Interval 2 (monomer droplets present) or 3 (no monomer droplets).

Experiments To Establish Locus of Spontaneous Radical Generation. Determination of the phase(s) in which spontaneous production occurs was accomplished via seeded polymerization of styrene and chloroprene using well-characterized polystyrene seed latices. Styrene seeds of various sizes were prepared by conventional recipes with persulfate initiator and AMA80, sodium dioctyl sulfosuccinate, as surfactant.[1,23,24] Particle size was determined by transmission electron microscopy (TEM) and capillary hydrodynamic fractionation (CHDF). TEM and CHDF were also used to determine whether secondary particle formation had occurred during a given seeded polymerization. Polymerizations during which secondary particle formation occurred were not used for quantitative kinetic analysis.

Measurement of the conversion rate was by automated dilatometry. Styrene (Aldrich, 99%) was purified by distillation at reduced pressure, and chloroprene (DuPont, 50% in xylene containing 1% phenothiazine as an inhibitor) was purified by distillation at reduced pressure (200−300 mmHg) and in a nitrogen atmosphere. The surfactant (AMA80), buffer ($\mathrm{NaHCO_3}$), initiator ($\mathrm{K_2S_2O_8}$) and n-decane (Merck) were used as received. A mixture of chloroprene dimers shown in Figure 1 was prepared and characterized by Dr. S. D. Arthur (DuPont Experimental Station, Wilmington, DE) using gas chromatography.

Table 1. Type and Main Feature(s) of Experiments To Elucidate Loci of Spontaneous Radical Generation

phenomenon under investigation	monomer	distinguishing feature/additive	result
spontaneous production of radicals	styrene	seeded emulsion polymerization, 50 °C	very slow rate
spontaneous production of radicals	chloroprene	seeded emulsion polymerization, 30 °C	rate almost the same as with added chemical initiator
spontaneous production of radicals in aqueous phase	chloroprene	Fe^{2+} addition	rate reduced
spontaneous production of radicals in oil phase	styrene	large particles, no droplets	rate reduced, but $\neq 0$
spontaneous production of radicals in oil phase	chloroprene	droplets present; FS addition	rate reduced, but $\neq 0$
effect of chloroprene dimers upon spontaneous radical formation	chloroprene	chloroprene dimer addition	no significant effect
spontaneous radical generation by species in seed latex	chloroprene	use of heat-treated seed latex	no significant effect

An emulsion of monomer in water was made by addition and subsequent agitation of the surfactant, monomer, and water. To this was added the seed latex, which was allowed to swell with monomer for ~12 h for the styrene/polystyrene system and 3−5 h for chloroprene/polystyrene. The system was purged of dissolved gas(es) by bubbling with nitrogen or argon, and subsequently partially degassed by exposing the reaction emulsion to vacuum using a water pump for 3−5 min, and then placed in the dilatometer and further warmed to 5 °C above the reaction temperature to degas further.

Addition of the FS (Aldrich) and iron(II) sulfate (Ajax, 99%) solutions (preheated to reaction temperature) to the reaction was effected using a syringe and needle by injection of the solutions through a rubber septum attached to a sidearm of the dilatometer. Chloroprene dimer addition was to the monomer prior to emulsification (0.5% w/w dimer:monomer).

For GPC experiments, polymer isolated from each of the samples was dissolved in distilled tetrahydrofuran (THF) to yield a polymer solution (0.05−0.10% w polymer/w THF). Molecular weight distributions (MWDs) were measured on a Waters instrument with a combination of Ultra-Styragel (Waters) packed-bed columns in series: 10^3, 10^4, and 10^5 Å. Detection of the polymer eluting from the GPC was by two methods: (i) differential refractive index and (ii) measurement of the absorbance of the eluting solution at 254 nm. The method with the higher signal-to-noise ratio was found to be the 254 nm absorbance method and was therefore used for the determination of most of the MWDs.

Results

Table 1 summarizes the experiments performed for the elucidation of the phases in which spontaneous radical formation occurs. Initial experiments, shown in Figure 2, were performed to ascertain the significance of the spontaneous polymerization rate of chloroprene and styrene. Spontaneous polymerization of styrene was very slow, as seen elsewhere.[1] However, spontaneous polymerization of chloroprene was found to be very fast and indeed comparable in rate with the polymerization of chloroprene with added initiator. At first, it might be conceived that this difference is due to the value of the chloroprene propagation rate coefficient (k_p) being[25] ~3 times that for styrene.[26] However, as seen later in this paper, $\bar{n}$ in a zero-one polymerization of styrene is typically a factor of 3−10 larger than that for chloroprene. (Of course, the actual value of $\bar{n}$ depends on many factors such as initiator concentration, particle size, particle number, etc., and is therefore generally not constant from experiment to experiment.)

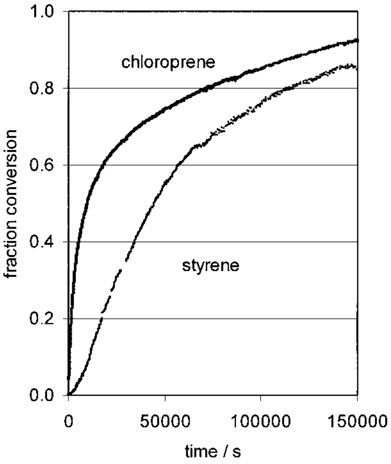

Figure 2. Conversion as a function of time for the polystyrene-seeded spontaneously initiated polymerization of styrene and chloroprene. Styrene polymerization: swollen particle radius $r_s = 62$ nm, particle number $N_c = 10^{17}$ dm^{-3}, $T = 50$ °C. Chloroprene polymerization: $r_s = 57$ nm, $N_c = 1.7 \times 10^{16}$ dm^{-3}, $T = 30$ °C.

To ensure that peroxides arising from the preparation of the polystyrene seed were not responsible for spontaneous initiation in chloroprene, the seed latex was also heat-treated at 83 °C for 3 days; use of this latex as seed made no noticeable difference in the rate of spontaneous initiation in chloroprene.

Aqueous-Phase Radical Formation. Lacík et al.[27] found that styrene spontaneous emulsion polymerization under zero-one conditions was suppressed by addition of FS, consistent with spontaneous production of radicals in the aqueous phase and/or on the particle surface. Figure 3 shows fractional conversion x and rate as a function of time for a polystyrene-seeded polymerization of chloroprene at 30 °C, started in Interval 2. As is seen in the figure, the rate is approximately constant[17] in Interval 2. The decrease in rate at ca. 900 s may be attributed to the polymerization entering Interval 3. Addition of $Fe_{(aq)}{}^{2+}$ (at $t = 1100$ s) led to an increase in the polymerization rate by a factor of ca. 3. This increase is attributed to an increase in radical flux, caused by reaction of the $Fe_{(aq)}{}^{2+}$ with the initiating species (i.e., the species that produces radicals spontaneously). Further evidence for redox conversion of $Fe_{(aq)}{}^{2+}$ to $Fe_{(aq)}{}^{3+}$ was that the initially opaque, white latex was slightly tinged with brown/orange a few minutes after the addition of $Fe_{(aq)}{}^{2+}$. Approximately 200 s after the addition of $Fe_{(aq)}{}^{2+}$, the rate of polymerization decays, which is consistent with the disappearance

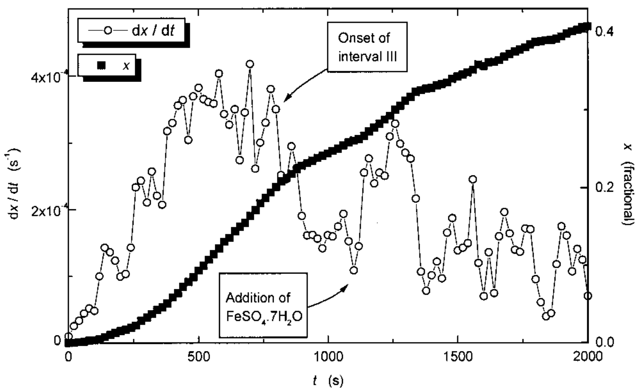

Figure 3. Fractional conversion and rate of fractional conversion as a function of time for the spontaneously initiated heteroseeded emulsion polymerization of chloroprene with added $\mathrm{Fe}^{2+}_{(aq)}$. Reaction conditions: $r_s = 57$ nm, $N_c = 6 \times 10^{16}$ dm^{-3}, $T = 30$ °C, Interval 2, $[\mathrm{Fe}^{2+}_{(aq)}] = 10^{-4}$ mol dm^{-3}.

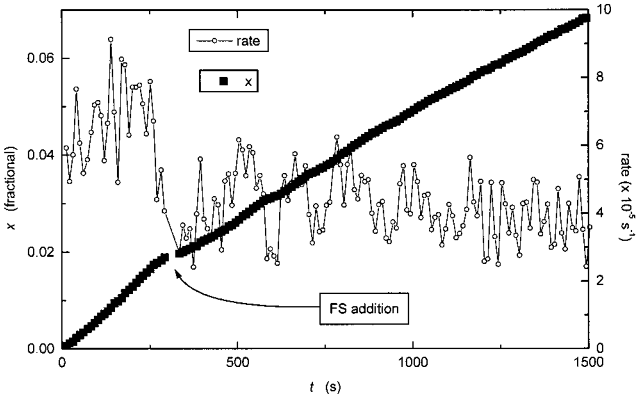

Figure 4. Fractional conversion and rate of fractional conversion as a function of time for the spontaneous polymerization of chloroprene with added FS. Reaction conditions: $r_s = 57$ nm, $N_c = 5.8 \times 10^{16}$ dm^{-3}, $T = 30$ °C, Interval 2, [FS] = 1.9×10^{-4} mol dm^{-3}.

either of the species that yields the spontaneously generated radicals or of the $\mathrm{Fe_{(aq)}}^{2+}$ species. However, it was not possible to distinguish between these two kinetic pathways from this experiment.

Oil-Phase Radical Formation. As stated, it has been found[27] that spontaneous polymerization in a zero-one system is essentially stopped by the addition of FS, implying that the radical-generating species are either on the surface of the particles or in the aqueous phase. However, this does not preclude the possibility of extensive spontaneous generation of radicals in the oil phase (droplets or particles), since it is expected that extensive geminate recombination occurs in zero-one systems. Since systems containing droplets cannot be well characterized, it is convenient to use a pseudo-bulk system as a model for droplets. (Any polymerization within the droplet phase will be pseudo-bulk.) A seeded emulsion polymerization of styrene under pseudo-bulk conditions (50 °C, [FS] = 10^{-4} mol dm^{-3}, unswollen radius = 130 nm, Interval 3, and with $\bar{n} > {}^1/_2$; experiments kindly provided by Dr. Hank de Bruyn) showed diminished but still significant polymerization, implying significant spontaneous radical generation in the particle phase.

Figure 4 shows that the effect of adding FS to a seeded chloroprene polymerization system in an Interval 2 system is to decrease but not eliminate the polymerization rate. This is consistent with the $\mathrm{Fe_{(aq)}}^{2+}$ studies, in that both sets of experiments indicate the formation of radicals in the aqueous phase. Since radicals are trapped in the presence of FS, then it may be concluded that radicals are also formed in a phase that does not contain FS (i.e., an oil phase). Since this chloroprene polymerization is zero-one (which would mean that geminate recombination would eliminate any significant spontaneous radical production in the particles leading to subsequent polymerization), then the observed polymerization with added FS must be due to droplet-phase polymerization.

Chemical Origin of Spontaneously Formed Radicals. To examine the possibility that chloroprene dimers lead to spontaneous polymerization, experiments were performed that involved the addition of chloroprene dimers to the polystyrene-seeded initiator-free seeded emulsion polymerization of chloroprene at 30 °C. No change in the polymerization rate was observed upon addition of the dimers, thus indicating that dimers are not directly responsible for the spontaneous formation of radicals. It was thought that exposure of the chloroprene dimers to oxygen might induce peroxide formation (possibly by displacement of labile hydrogen atoms), so a second experiment was performed by adding the same mixture of dimers to the polymerization system, but where the dimers had been stirred under air (and therefore oxygen) for 15 h. No significant change in the rate of polymerization was observed. Hence, any presence of dimers in the reaction system is not directly related to spontaneous radical formation.

It is likely that the species which gives rise to the spontaneous radicals in chloroprene are peroxidic, since the rate is accelerated by addition of $\mathrm{Fe_{(aq)}}^{2+}$. Furthermore, it is known that some monomers (including styrene and especially chloroprene) form organic peroxides, this being the case particularly after removal of inhibitor (following purification of these monomers). However, even though a peroxide would seem to be the most probable origin of the spontaneity, other species may not be eliminated.

Chemical Origin of Spontaneous Polymerization. *Styrene.* In addition to their purported ability to undergo transfer, it has been suggested that Diels–Alder dimers of styrene are responsible for the spontaneous polymerization of styrene,[28,29] at least for bulk polymerization at elevated temperatures (≥60 °C);[29–33] any effects of these at lower temperatures are significantly smaller.[34] Since experiments presented here were performed at 50 °C, and furthermore were emulsion polymerizations, no conclusions may be drawn regarding the nature of the initiating species for spontaneous styrene polymerization.

Chloroprene. Chloroprene also readily undergoes dimerization reactions[35] at a rate significantly faster than for the dimerization of styrene. These may lead to radical species (involving dissociation either of the dimer directly or possibly of a peroxide of the dimer). It would seem that the species responsible for forming radicals spontaneously in the chloroprene system are at least sparingly soluble in the aqueous phase, since radicals are produced in the aqueous phase of the polymerization system. In addition to this, since styrene and chloroprene both spontaneously polymerize in bulk (particularly chloroprene[9]), at least one of the species responsible for spontaneous polymerization derives from the monomer.

Including Spontaneous Polymerization in Models for Rates and Molecular Weight Distributions. There are extensive, experimentally verified models for quantifying the effect of conventional initiation on the rates and molecular weight distributions (MWDs) of emulsion polymerizations.[17] These models are now extended to take into account the preceding inferences about the loci of spontaneous radical production. The radicals so produced are assumed to be monomeric in size and solubility and therefore partitioned between the aqueous and nonaqueous phases according to monomer solubility in these phases. The species that give rise to these radicals may also be present in both oil and water phases.

Pairwise spontaneous radical production within a particle occurs with a rate of spontaneous radical production, τ, defined as

$$\tau = 2f_{\mathrm{T}}k_{\mathrm{d}}^{\mathrm{T}}C_{\mathrm{P}}^{\mathrm{T}}N_{\mathrm{A}}V_{\mathrm{s}} \qquad (2)$$

where f_{T} is the efficiency of formation of the spontaneous radicals (analogous to an initiator efficiency), $k_{\mathrm{d}}^{\mathrm{T}}$ is the first-order rate coefficient for decomposition of the species T that gives rise to two spontaneously generated radicals, N_{A} is Avogadro's constant, V_{s} is the swollen volume of a particle, and $C_{\mathrm{P}}^{\mathrm{T}}$ is the particle-phase concentration of species T. Providing that the values of f_{T} and $k_{\mathrm{d}}^{\mathrm{T}}$ are commensurate in the particle and aqueous phases, then the pseudo-first-order rate coefficient for entry of spontaneously generated radicals into particles from the aqueous phase, ρ_{T}, is given by

$$\rho_{\mathrm{T}} = \frac{2f_{\mathrm{T}}k_{\mathrm{d}}^{\mathrm{T}}C_{\mathrm{W}}^{\mathrm{T}}N_{\mathrm{A}}}{N_{\mathrm{c}}} \qquad (3)$$

where $C_{\mathrm{W}}^{\mathrm{T}}$ is the aqueous-phase concentration of species T and N_{c} is the number of particles per unit volume of the water phase.

Radicals generated spontaneously in the particle phase of a zero-one system would lead to the formation of a pair of radicals which may either undergo (i) mutual annihilation of the pair of spontaneously generated radicals or (ii) termination of the preexisting radical with a spontaneously generated radical. Spontaneous radical formation in a particle that contains a preexisting radical is assumed to result in one of two possible outcomes. Termination via the first mode will occur between the two short radicals formed by spontaneous radical generation ("short−short" termination[24]). This termination mode leads to no change in either the MWD of polymer or in the rate of polymerization, as the original preexisting radical remains in the particle. Termination by the other mode leads to one of the two short radicals formed by spontaneous radical generation undergoing short−long[24] termination with the preexisting radical (which will, on average, be much greater in length than the short radical produced by spontaneous means). The effect of this termination mode on the polymer MWD is to decrease the molecular weight of the polymer by premature termination of the preexisting radical. The effect of this mode upon the polymerization rate is not as straightforward and is dependent upon the type of exit kinetics that the polymerization system exhibits. Exit involves the production of a small radical within a latex particle and the radical's subsequent desorption from the latex particle. Conversely, the small free radical resulting from this mode may propagate within the particle before being able to undergo desorption, when the average number of radicals per particle will not change. Providing that the small radical propagates to a significantly higher degree of polymerization, then the effect of chain length on the propagation rate coefficient will be negligible, and therefore the rate of polymerization will not change as a result of this mode. The kinetic effect of spontaneous radical production in a particle that does not contain a radical is negligible.

Spontaneous formation of a pair of radicals within a particle that already contains a (polymeric) radical results in the formation of a particle that contains one *long* (on average), relatively immobile radical and two *short*, mobile radicals. Now, it was noted above that a zero-one system is, by definition, one in which two radicals will coexist for a negligible time inside the same particle. However, when one considers the present case of *production* of two radicals within a particle already containing a growing chain, then "negligible" needs quantitative elaboration, as follows. The probability, ϵ, of the (long) polymeric radical undergoing termination with one of the two (short) spontaneously derived radicals may be defined in terms of the rates of *short−long* and *short−short* termination:

$$\epsilon = \frac{R_{\mathrm{t,SL}}}{R_{\mathrm{t,SL}} + R_{\mathrm{t,SS}}} \qquad (4)$$

where $R_{\mathrm{t,SL}}$ and $R_{\mathrm{t,SS}}$ are respectively the rates of termination between a short and a long species and between two short species. It is well-established[23,36−38] that these rates are diffusion-controlled in emulsion polymerizations. Since a long chain is much less mobile than a short one, then one simply has $R_{\mathrm{t,SL}} = R_{\mathrm{t,SS}}$. This is because there are two modes of short−long termination and only one of short−short. Hence $\epsilon = {}^{1}/_{2}$.

Spontaneous production of radicals within a particle that contains no radicals results in the mutual termination of the spontaneously generated radicals, whence this kinetic pathway affects neither the polymer MWD nor the rate of polymerization, as assumed by Nomura et al.[39] However, Nomura et al. also applied this assumption (incorrectly) to particles that contained a radical. In other words, Nomura et al. assumed that termination of the pair of radicals formed in the particle was much faster than other processes, including that of termination of one of the pair of radicals with a preexisting long radical. As seen in the preceding section, the production of a pair of radicals within a particle that contains a radical may lead to the annihilation of the preexisting radical. (The probability of such an encounter is given by $\epsilon = {}^{1}/_{2}$.) This will be seen to affect the polymerization through both the rate and the polymer MWD.

It is important to note that spontaneous production of radicals within a latex particle has a qualitatively different effect to that of entry of spontaneously generated radicals from the aqueous phase. Entry of a radical into a particle that contains a preexisting radical will result in mutual termination of the radical species. For the case in which a spontaneously generated radical enters a particle that does not contain a radical, there exist two possible kinetic outcomes: (i) propagation of the spontaneously generated radical within the particle to form a species that is unlikely to desorb from the particle (due to decreased aqueous-phase solubility) or (ii) desorption of the spontaneously generated radical from the particle to the aqueous phase. Spontaneous generation of a radical in the aqueous phase leads to entry of the radical into the particle phase (given that it does not undergo termination in the aqueous phase), wherein the radical undergoes rate-determining termination with a preexisting radical.

Spontaneous generation of radicals in the particle phase of pseudo-bulk polymerization systems leads to effects that are similar to those exhibited by the case of spontaneous aqueous-phase radical formation. Production of radicals in the aqueous and/or oil phase leads to an increase in the average number of radicals per particle. This in turn leads to an increase in the termination rate, which affects both the polymer MWD and the polymerization rate. This will also be applicable to any polymerization that occurs in droplets.

The overall result of these inferences about spontaneous radical production is the following additions to the standard[17] evolution equations for rates and MWDs in zero-one and pseudo-bulk emulsion polymerizations. The derivations will not be given in detail, but they are straightforward additions to the corresponding derivations[17] in systems with ordinary initiators. In a zero-one system where aqueous-phase termination of exited radicals can be neglected (an excellent approximation), the overall rate is found using the so-called[17] "Limit 2" expression:

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho_{\mathrm{init}} + \rho_{\mathrm{T}})(1 - 2\bar{n}) - 2\tau\epsilon\left(\frac{k_{\mathrm{dT}}\bar{n}}{k_{\mathrm{dT}}\bar{n} + k_{\mathrm{p}}^{\mathrm{T}}C_{\mathrm{P}}}\right)\bar{n} - 2k_{\mathrm{tr}}C_{\mathrm{P}}\left(\frac{k_{\mathrm{dM}}\bar{n}}{k_{\mathrm{dM}}\bar{n} + k_{\mathrm{p}}^{1}C_{\mathrm{P}}}\right)\bar{n} \quad (5)$$

where ρ_{init} is the component for the entry rate coefficient for radicals into particles from ordinary (chemical) initiator, k_{dM} and k_{dT} are those for desorption of monomeric radicals resulting from transfer to monomer and spontaneously generated radicals which lead to exit, k_{p}^{1} is that for propagation of these radicals, and k_{tr} is that for transfer to monomer. In the common case ("Limit 2a") where exited radicals reenter a particle and remain there, eq 5 reduces to

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = (\rho_{\mathrm{init}} + \rho_{\mathrm{T}})(1 - 2\bar{n}) - 2\left[\left(\frac{k_{\mathrm{tr}}k_{\mathrm{dM}}}{k_{\mathrm{p}}^{1}}\right) + \left(\frac{\tau\epsilon k_{\mathrm{dT}}}{k_{\mathrm{p}}^{\mathrm{T}}C_{\mathrm{P}}}\right)\right]\bar{n}^{2} \quad (6)$$

Equations 5 and 6 are nothing more than the usual equation for zero-one kinetics with the inclusion of an extra term, that involving $\tau\epsilon$. The desorption terms are given by $k_{\mathrm{dM}} = 3D_{\mathrm{W}}C_{\mathrm{W}}/r_{\mathrm{s}}^{2}C_{\mathrm{p}}$, where D_{W} is the diffusion coefficient of the radical in water and r_{s} is the swollen particle radius.

The inclusion of spontaneous radical production for pseudo-bulk kinetics is simply a matter of using the arguments leading to eq 5 in the term for entry in the coupled integrodifferential equations describing these kinetics:[17]

$$\rho_{\mathrm{total}} = \rho_{\mathrm{init}} + \rho_{\mathrm{T}} + \tau + \rho_{\mathrm{re}}^{\mathrm{M}} + \rho_{\mathrm{re}}^{\mathrm{T}} \approx \rho_{\mathrm{init}} + \tau \quad (7)$$

where the terms with subscript "re" refer to reentry of the corresponding radicals and where it has been assumed that the solubility of the spontaneously generated radicals is much greater in the particle than the water phase; one has $\rho_{\mathrm{re}}^{\mathrm{M}} = k_{\mathrm{dM}}\bar{n}$. The pseudo-bulk kinetic equation to be used with eq 7 is[17]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho_{\mathrm{total}} - k\bar{n} - 2\frac{\langle k_{\mathrm{t}}\rangle}{N_{\mathrm{A}}V_{\mathrm{s}}}\bar{n}^{2} \quad (8)$$

Here $\langle k_{\mathrm{t}}\rangle$ is the average termination rate coefficient, where the average is that of the chain-length-dependent microscopic rate coefficients $k_{\mathrm{t}}(N,N')$ over the distribution of radicals of all degrees of polymerization. The integrodifferential equations used to obtain $\langle k_{\mathrm{t}}\rangle$ again explicitly incorporate spontaneous radical generation through eq 7. The quantity k in eq 8 is the phenomenological exit rate coefficient; for chloroprene, intraparticle polymerization is almost invariably zero-one, and hence pseudo-bulk kinetics will normally only be important for droplets, for which exit can be neglected because[17] of their large size.

The same arguments leading to eq 5 also lead to a simple modification for the expression for the instantaneous number MWD in a zero-one system:

$$P(M) = \exp\left[-\left(\frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} + \frac{\tau\epsilon + \rho_{\mathrm{total}}}{k_{\mathrm{p}}C_{\mathrm{P}}}\right)N\right] \approx \exp\left[-\left(\frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} + \frac{\tau\epsilon + \rho_{\mathrm{init}}}{k_{\mathrm{p}}C_{\mathrm{P}}}\right)N\right] \quad (9)$$

where N is the degree of polymerization (an arbitrary normalization constant has been omitted for convenience in eq 9). $P(M)$ is the instantaneous distribution of the number of chains with molecular weight M, which is related to the instantaneous GPC distribution $w(\log M)$ by[40,41]

$$P(M) = \frac{w(\log M)}{M^{2}} \quad (10)$$

The experimentally observable MWD is the cumulative distribution, from which a (pseudo-) instantaneous distribution may be inferred by subtracting appropriately normalized cumulative MWDs obtained at successive conversions.[42] Note that $w(\log M)$ is the GPC trace corrected for nonlinear calibration[40,41] (a facility which exists in most current GPC software).

The instantaneous MWD in a pseudo-bulk system with inclusion of spontaneous radical generation is identical to that in normal systems:

$$P(M) = \exp\left\{-\frac{k_{\mathrm{tr}}C_{\mathrm{P}} + (\langle k_{\mathrm{t}}\rangle\,\bar{n}/N_{\mathrm{A}}V_{\mathrm{s}})}{k_{\mathrm{p}}C_{\mathrm{P}}}N\right\} \quad (11)$$

(Again, a normalization constant has been omitted, and it is noted that eq 11 is invalid for very short chains, say with $N \lesssim 10$.)

Equations 9 and 11 are useful because they indicate how one can obtain rate data from MWDs.[23] Specifically, these equations predict that the logarithm of the instantaneous number MWD should always be linear. The slope of this is denoted Λ_{01} and Λ_{PB} for the zero-one and pseudo-bulk cases, and one then has[23]

$$\Lambda_{01} = \frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} + \left(\frac{\rho_{\mathrm{total}} + \tau\epsilon}{k_{\mathrm{p}}}\right)\frac{1}{C_{\mathrm{P}}} \qquad (12)$$

$$\Lambda_{\mathrm{PB}} = \frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} + \left(\frac{\langle k_{\mathrm{t}}\rangle}{N_{\mathrm{A}}V_{\mathrm{s}}}\right)\left(\frac{\bar{n}}{k_{\mathrm{p}}C_{\mathrm{P}}}\right) = \frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} + \rho_{\mathrm{total}}\left(\frac{1}{2R_{\mathrm{P}}}\right) \qquad (13)$$

where $R_{\mathrm{p}} = k_{\mathrm{p}}\bar{n}C_{\mathrm{P}}$ is the polymerization rate. Hence, for the zero-one case, a plot of Λ_{01} as a function of $1/C_{\mathrm{p}}$ should, if the various rate coefficients are independent of conversion, give a straight line from whose slope and intercept from which the entry rate coefficient (including $\tau\epsilon$) and transfer rate coefficient can be extracted. Similarly, plotting Λ_{PB} against $1/R_{\mathrm{p}}$ for the pseudo-bulk case should yield the transfer rate coefficient, $\langle k_{\mathrm{t}}\rangle$, and the entry rate coefficient (including ρ_{T}). These data reduction techniques will be applied in the next sections.

Results for Styrene. Rate and MWD data for styrene zero-one and pseudo-bulk seeded emulsion polymerizations have been presented elsewhere,[23] including plots of the cumulative and pseudo-instantaneous number MWDs, and the gradients Λ_{01} and Λ_{PB}. Here, these data are re-processed to yield information about spontaneous polymerization. The determination of the molecular weight region over which the gradient is measured is not a trivial matter. First, polymer formation by chain-length-dependent termination may be significant at lower molecular weights, which induces curvature in a plot of ln $P(M)$ as a function of M. Theory[41] suggests that the effect of this chain-length dependence upon the gradient of ln $P(M)$ vs M becomes negligible for higher molecular weights ($\gtrsim 10^4$). However, for very high molecular weights, the amount of polymer from which the MWD is measured is very small, thereby inducing error in the MWD, particularly for pseudo-instantaneous MWDs. Measurement of the gradient of ln $P(M)$ vs M in such regions of the MWD should therefore be avoided. For the same reason, there frequently exists a large error in ln $P(M)$ at lower molecular weights. To be consistent with the analysis of others,[43,44] the lower bound to the molecular weight range over which the gradient was measured was the peak molecular weight in $w(\log M)$, and the upper bound as the molecular weight at which $w(\log M)$ was 10% of its value at the peak.

Figure 5 shows Λ_{01} and Λ_{PB} for zero-one and pseudo-bulk systems, using previously published data.[23] The data are consistent with the predictions of eqs 12 and 13, although the uncertainty is too great to see whether true linearity is actually obtained. The pseudo-bulk data have been treated elsewhere[23] to determine $\langle k_{\mathrm{t}}\rangle$, yielding values that were in accord with those obtained from a quite different technique, that of γ-radiolysis relaxation kinetics; these $\langle k_{\mathrm{t}}\rangle$ values were also in adequate, although imperfect, agreement those predicted from diffusion theory.

Here, both sets of data are used as suggested by eqs 12 and 13 to determine the total entry rate coefficient; the results are shown in Figure 6. Also shown in this figure are the predictions from a model[45] that has had considerable success in predicting the value of ρ for chemical initiator, which assumes that entry involves oligomers $^{\bullet}\mathrm{M}_n\mathrm{SO}_4^-$ arising from propagation of the $\mathrm{SO}_4^{-\bullet}$ radical with aqueous-phase monomer and that entry occurs only, and irreversibly, when the oligomer attains a critical degree of polymerization z. The parameters used in the fit are those given in the literature,[17] including $z = 3$, except that the initiator dissociation rate coefficient k_{d} was increased slightly (1.67×10^{-6} s^{-1}), and $k_{\mathrm{t,aq}} = 3.5 \times 10^9$ dm^3 mol^{-1} s^{-1}; the propagation rate coefficients $k^n_{\mathrm{p,aq}}$ of $^{\bullet}\mathrm{M}_n\mathrm{SO}_4^-$ are given by $k^1_{\mathrm{p,aq}} = 10k_{\mathrm{p,aq}}$, $k^2_{\mathrm{p,aq}} = 4k_{\mathrm{p,aq}}$, and $k_{\mathrm{p,aq}} = 2.4 \times 10^2$ dm^3 mol^{-1} s^{-1}.[26] The accord with experiment is no particular cause for congratulation, because there is significant latitude in a physically reasonable choice of parameters such as

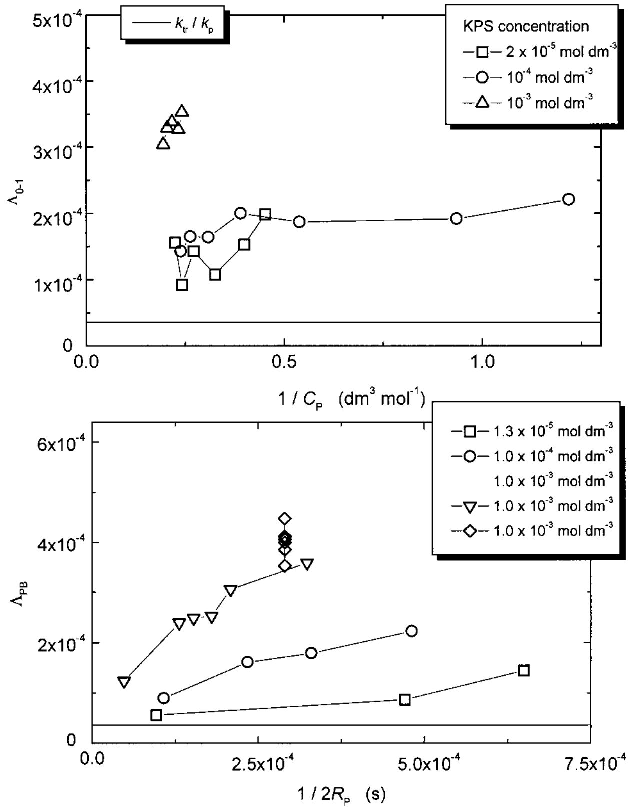

Figure 5. Gradients Λ_{01} and Λ_{PB} for zero-one and pseudo-bulk systems (unswollen radii 44 and 130 nm, $N_{\mathrm{c}} = 2 \times 10^{16}$ and 1×10^{15} dm^{-3}, respectively) for seeded emulsion polymerization of styrene at 50 °C, for a range of concentrations of initiator ($\mathrm{K_2S_2O_8}$), plotted as suggested by eqs 12 and 13. The literature value[51] of the transfer constant $k_{\mathrm{tr}}/k_{\mathrm{p}}$ is also shown, which should be the value of Λ at the intercept in both cases.

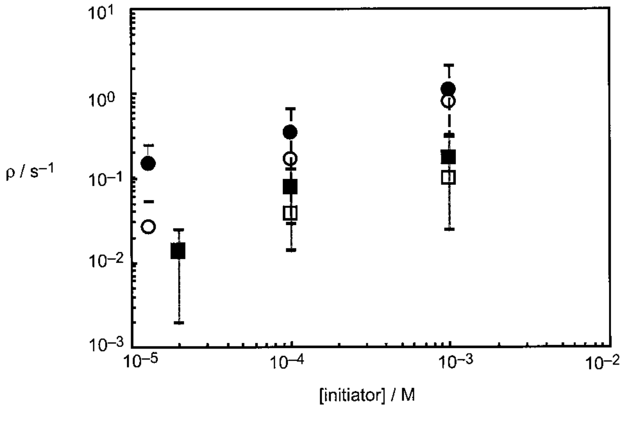

Figure 6. Overall entry rate coefficients for various initiator concentrations obtained from the data of Figure 5: filled points, experiment; open points, model predictions for component arising from chemical initiator; circles, pseudo-bulk; squares, zero-one.

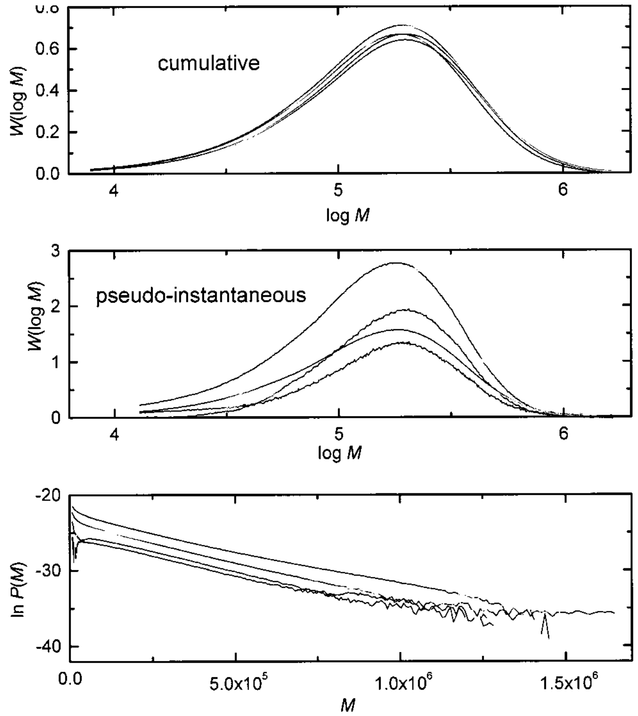

Figure 7. MWDs obtained from the heteroseeded emulsion polymerization of chloroprene in a polystyrene seed: (i) total (seed and new-growth polymer) *w*(log *M*), normalized to conversion (i.e., the total area is proportional to conversion), (ii) pseudo-instantaneous *w*(log *M*) obtained by subtraction, and (iii) pseudo-instantaneous ln *P*(*M*). Reaction conditions: Interval 3, $r_s = 57$ nm, $N_c = 1.3 \times 10^{17}$ dm^{-3}, $T = 40$ °C. Values of fraction conversion are 0.024, 0.027, 0.033, 0.038, 0.042, 0.054, and 0.057.

$k^1_{p,aq}$. However, it is significant that the same parameters fit the values of ρ_{init} for pseudo-bulk and zero-one systems; entry rate coefficient data for styrene pseudo-bulk systems have not been reported hitherto.

Equations 9 and 11 show that one can obtain the values of $\epsilon\tau$ (for the zero-one case) and τ (for the pseudo-bulk case) from the limiting value of the overall entry rate coefficient at low initiator concentration, as given in Figure 6. Now, to compare these values, one first uses $\epsilon = {}^1/_2$ (see above). Next, τ refers to the rate per particle, and the particles have different volume; one can then convert the values of τ to an initiation rate per unit volume ($f_T k_d^T C_P^T$ in eq 2) to obtain $(1.9 \pm 1.6) \times 10^{-8}$ and $(0.9 \pm 0.5) \times 10^{-8}$ mol dm^{-3} s^{-1} for the zero-one and pseudo-bulk systems, respectively. Although these values are subject to a large uncertainty, they are consistent.

The consistency obtained for styrene, which is a well-studied system, supports the correctness of the overall methodology. Now, spontaneous radical production is not very important in styrene, but it will be seen to quite a different situation when the same methodology is applied to chloroprene.

Results for Chloroprene. The experimental technique used to obtain MWD data for polychloroprene formed in the heteroseeded emulsion polymerization with polystyrene seed is as given elsewhere,[23,42] except that allowance was made during the subtraction procedure for polystyrene having a different extinction coefficient at the detector wavelength used (254 nm) to that of polychloroprene. The results for the case of Interval 3 polymerization (no droplets) are presented first, followed by data for Interval 2 polymerization, where there are two organic phases (droplets as well as particles). Data were obtained between 2 and 50 °C, both with external initiator (persulfate and γ) and without any external initiator (i.e., spontaneous polymerization only). Figures 7 and 8 show the cumulative and pseudo-instantaneous *w*(log *M*) and pseudo-instantaneous *P*(*M*) from one set of experiments with only spontaneous initiation and with initiation by γ radiolysis (which was used to generate a constant radical flux at low temperatures).

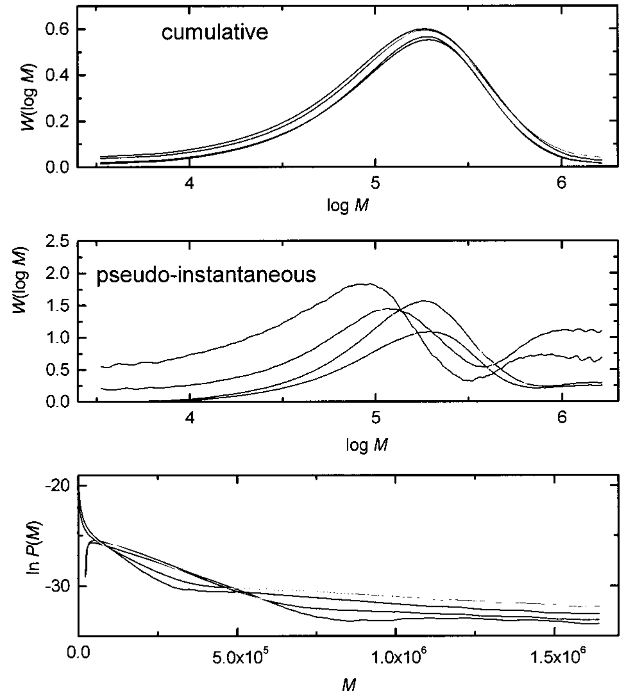

Figure 8. As for Figure 7, except for $N_c = 5.6 \times 10^{16}$ dm^{-3}, $T = 2$ °C, initiation by γ radiolysis; fractional conversions are 0.09, 0.10, 0.13, 0.15, 0.17, and 0.19.

The MWDs of the Interval 3 data in Figure 7 and other temperatures are consistent with the form of eq 9, in that ln *P*(*M*) is linear with *M*. In addition, it is evident from these data that chain transfer is not the only chain-stopping mechanism in the particles, as the gradient of each ln *P*(*M*) is significantly greater than that predicted by the literature value[46] k_{tr}/k_p at the only temperature for which such data are available, viz. 50 °C. The total rate of chain stoppage ($\rho_{total} + \tau\epsilon + k_{tr}C_p$) may be deduced from the gradient of ln *P*(*M*); however, this does not enable the determination of the individual rate coefficients ρ_{total}, τ, and k_{tr}. Indeed, chain stoppage by termination with a spontaneously generated radical is kinetically very similar to that by transfer.

The data for Interval 2, exemplified in Figure 8, are qualitatively different from those for Interval 3: for each sample there exists two linear regions. Moreover, it is found that, within experimental error, the lower-*M* slope of one of these regions corresponds to that observed in the absence of droplets. The various slopes are independent of both conversion and radical flux for a given temperature. This observation indicates that polymer is formed by more than one mechanism during Interval 2. This is especially obvious in the instantaneous distributions, as both *w*(log *M*) and *P*(*M*).

It is postulated that the two components arise from droplet polymerization occurring simultaneously with particle-phase polymerization in Interval 2. Droplet

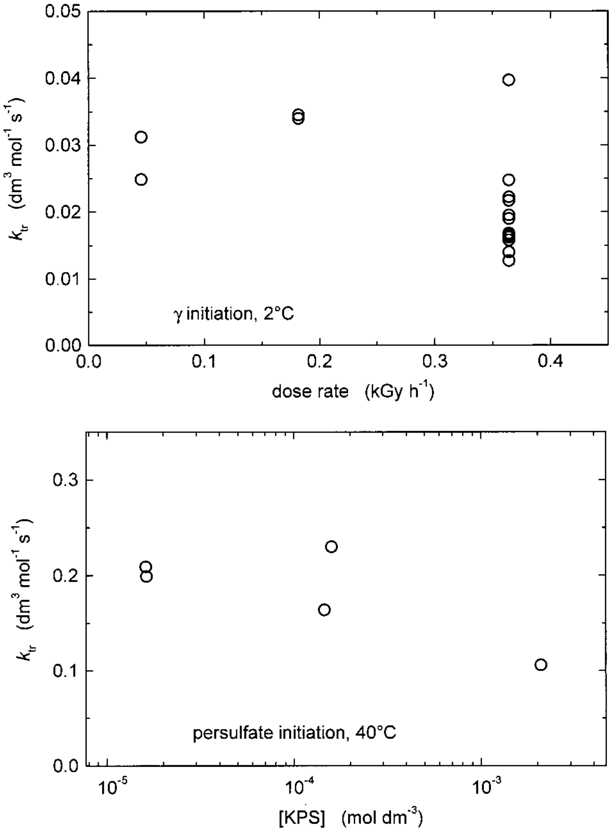

Figure 9. Value of rate coefficient for transfer to monomer calculated from the high-M region of a plot of ln $P(M)$ vs M in Interval 2 as a function of radical flux (varying γ-radiation dose rate at 2 °C and persulfate initiator concentration at 40 °C).

polymerization is expected to give rise to polymer with a transfer-dominated MWD. This is inferred from model calculations using eq 11 for chloroprene, which show that, for all except unphysically high radical fluxes, the MWD is dominated by the k_{tr}/k_p term. (To be more precise, chain stoppage is predominantly by termination between long and short radicals, the latter arising from transfer to monomer.)

A test of this inference is that the region of the MWD which corresponds to the polymer produced by droplet polymerization should be independent of radical flux. (This condition is achieved experimentally by changing the initiation rate.) Figure 9 shows k_{tr}, inferred from the high molecular weight region of the above MWDs, as a function of radical flux. At 2 °C, initiation was by γ radiolysis, and radical flux was varied by inserting lead shielding between the γ source and the reaction vessel. For experiments conducted at 40 °C, radical flux was varied by changing the initiator (potassium persulfate) concentration. It can be seen that the value of k_{tr} calculated from the high molecular weight region of the MWD is independent of radical flux (within experimental error). Therefore, it is probable that the MWD of polymer formed in monomer droplets is determined principally by transfer to monomer, not by termination processes. Further evidence that the MWD of polymer formed in droplets is transfer-dominated is that the value of k_{tr}/k_p determined at 50 °C in this work, $(2.36 \pm 0.08) \times 10^{-4}$, compares favorably with previous work[46] ($k_{tr}/k_p = 2.32 \times 10^{-4}$).

The preceding data suggest that the high-M component of the MWD in Interval 2 arises from polymer formation in droplets by transfer to monomer. Hence, the slope of this linear portion of the ln $P(M)$ plot should give k_{tr} directly, using eq 9. Figure 10 is an Arrhenius plot of the rate coefficients so inferred, along with the joint 95% confidence interval[47] for the values of the frequency factor and activation energy obtained from a least-squares fitting of these data to the Arrhenius equation. The best-fit values are k_{tr}/dm^3 mol^{-1} s^{-1} = $10^{4.3}$ exp(−30.9 kJ mol^{-1}/RT), with the uncertainties in the frequency factor and activation energy expressed by the joint confidence interval given in Figure 10.

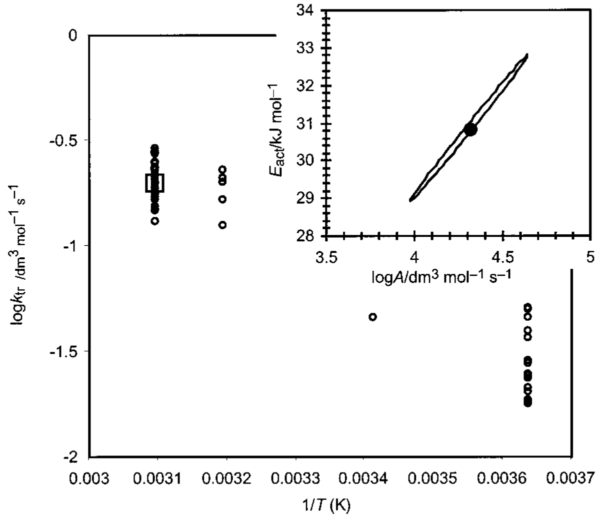

Figure 10. Arrhenius plot of k_{tr} inferred from the high-M portion of the MWDs for Interval 2 polymerization of chloroprene. Also shown (as open square) is the literature value[46] for k_{tr}. Inset: contour plot of joint 95% confidence interval for the Arrhenius frequency factor (A) and activation energy (E_{act}), with the best-fit value as the filled point.

The frequency factor and activation energies are both much smaller than those few reliable data in the literature for transfer to monomer, e.g., for MMA,[3] k_{tr} = $10^{5.3}$ exp(−45.9 kJ mol^{-1}/RT) dm^3 mol^{-1} s^{-1}. (These Arrhenius parameters are reprocessed from the original data, which were reported as k_{tr}/k_p, using the IUPAC-recommended values[48] for k_p.)

A proper analysis of the mechanism for this transfer process must await further data, such as identifying the end groups involved. However, some reasonable postulates can be made. ^{13}C NMR studies of the microstructure of polychloroprene have shown[49,50] that the monomer adds to form a predominantly 1,4-trans microstructure. At reaction temperatures of interest (0−50 °C), the amount of polymer formed by 1,4-trans addition is in the range 80−90%. Polymer formed by 4,1-trans addition accounts approximately for a further 5−10% of the total polymer, with the remainder is comprised of 1,4-cis, 4,1-cis, 1,2, and 4,3 addition. The actual ratios of the various types of addition are dependent upon the polymerization temperature but not highly so in the temperature range of interest in these studies. As there are many types of addition that constitute propagation, the value of k_p measured from experiment,[25] $10^{7.89}$ exp(−30.7 kJ mol^{-1}/RT) dm^3 mol^{-1} s^{-1}, will therefore be an average k_p. A possible mechanism for the *transfer* process involves cyclization (backbiting) through one of the “minor” propagation products, followed by elimination of a chlorine atom which can then reinitiate; this is given in Figure 11. If the first step, “minor-product” propagation, is the only rate-

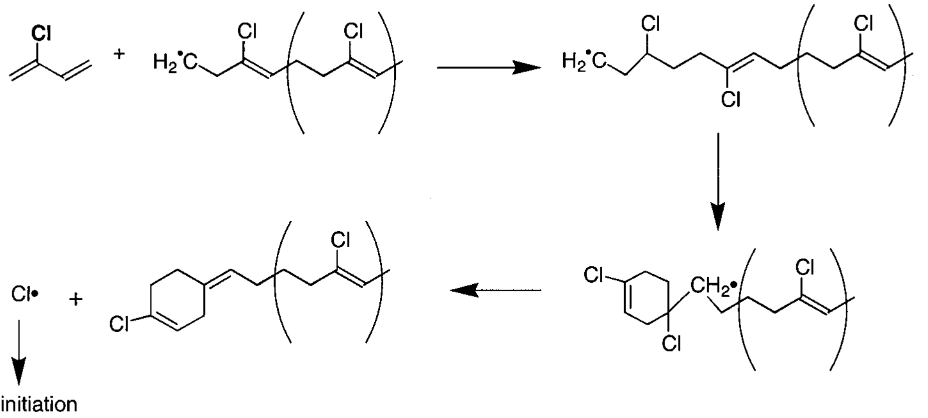

Figure 11. A possible mechanism for transfer to monomer in chloroprene that is consistent with the experimental Arrhenius parameters.

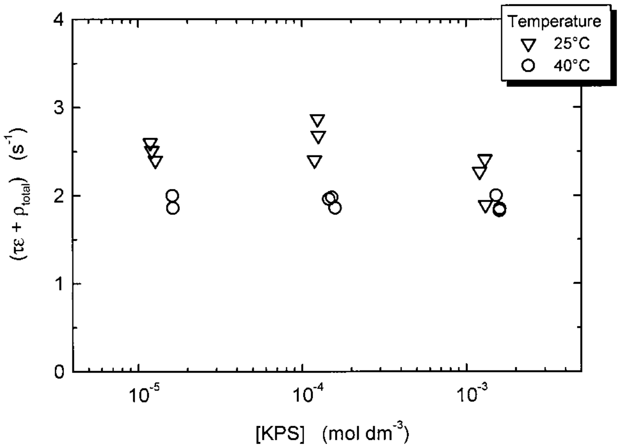

Figure 12. Rate of chain stoppage, with transfer component removed, as a function of potassium persulfate concentration for the heteroseeded polymerization of chloroprene.

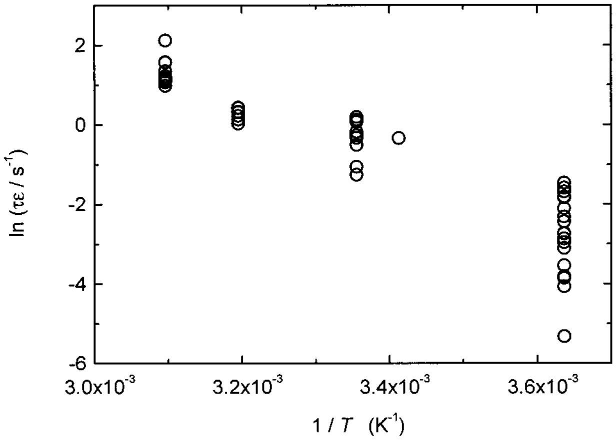

Figure 13. Arrhenius plot of $\tau\epsilon$, calculated from the low-M portion of the polychloroprene MWDs. Experimental conditions: various N_c and $r_s = 57$ nm.

determining one, then it is not unreasonable to assume that the activation energy might be similar to that of the overall average k_p (~30 kJ mol^{-1}, much less than that for a hydrogen transfer which is the assumed mechanism for transfer with other monomers). If this addition is somewhat more hindered than the "majority" addition step (explaining why this conformer is a minor product), then one would expect a frequency factor that is significantly smaller than that for the overall average k_p. This mechanism is therefore consistent with the observed low values of the activation energy and frequency factor for transfer to monomer. It is however emphasized that while this suggestion is consistent with the observed Arrhenius parameters for the transfer process, it requires considerably more data to test it adequately.

By subtracting the transfer component from the slope of the ln $P(M)$ using eq 9, information about the spontaneous and chemically initiated components of radical generation, $\tau\epsilon + \rho_{\text{total}}$, can be obtained, using both the Interval 3 data and the lower-M slope of the Interval 2 data; recall it is assumed that the chain-stopping event in both these cases is rapid termination with newly generated radicals. The inferred value of $\tau\epsilon + \rho_{\text{total}}$ is plotted as a function of radical flux in order to determine whether the MWD is dominated by intraparticle spontaneous radical production or by radicals directly arising from added initiator: if the MWD is determined principally by spontaneous radical formation, then no dependence of the MWD upon radical flux (by varying initiator concentration or γ-radiation dose rate) will be observed. Figure 12 shows this quantity as a function of potassium persulfate concentration. It is seen there and in γ-initiation data that this component of the MWD does not depend on radical flux (within experimental error). It may therefore be concluded that radical entry is not a major factor in the determination of the zero-one polychloroprene MWD under the conditions studied. The corollary to this is that spontaneous radical production dominates polychloroprene chain stoppage within the particles.

These data are given as an Arrhenius plot in Figure 13. This fits $\tau\epsilon/\text{s}^{-1} = 10^{10.4} \exp(-61 \text{ kJ mol}^{-1}/RT)$. The activation energy is somewhat lower than is typical for a peroxide bond-breaking process. It is not possible to comment upon the magnitude of the frequency factor, as the rate coefficient that describes the above process (τ) is pseudo-first-order, and without knowing the concentration of species responsible for spontaneous radical production, it is not possible to calculate the frequency factor for the true microscopic rate coefficient. The data of Figure 13 exhibit a wide scatter at each temperature over a larger range than for the rate coefficient for transfer to monomer. This is expected, as spontaneous radical production is a highly variable process. The origin of spontaneous radical production in chloroprene emulsion polymerization is an obvious area for future study.

Conclusions

Spontaneous radical formation in the polystyrene-seeded emulsion polymerizations of styrene and chloroprene occurs in all phases (water, particles, and droplets) present in the polymerization systems used here. While the effect is small for styrene, it dominates the rate and MWD for chloroprene, at least for the systems studied here.

The following inferences are made for chloroprene emulsion polymerization. There are two major loci of polymerization in Interval 2 polymerization: particles and monomer droplets. It was found that the polymer produced in droplets is of higher molecular weight than that produced in particles. The molecular weight distribution of polymer produced in the particles is governed by contributions from (a) spontaneous radical generation within the particles and (b) transfer to monomer. The MWD of polymer produced in the droplets is governed by transfer to monomer. During Interval 3, polymerization occurs in the particles, wherein spontaneous radical generation and transfer to monomer are the rate-determining mechanisms of polymer formation.

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