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Emulsion Polymerization of Chloroprene in the Presence of a Maleic Polymerizable Surfactant: Control of Gel Formation at Low Conversion

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ABSTRACT: Chloroprene was polymerized in emulsion, using a redox system as initiator. With a rosin derivative as surfactant, gel formation was avoided until ca. 70% conversion, but when a reactive maleic hemiester surfactant was used, gel could appear at conversions as low as 5%. The purpose of this paper is to show how this problem of early gel formation can be controlled via the flux of radicals entering the particles. Using more initiator leads to shorter polymer chains, a delayed onset of gel formation, and paradoxically to slower polymerizations.

Introduction

Flory, who pioneered the science behind gel formation, used to define gel as the result of the formation of infinitely large three-dimensional molecules.[1−3] Many terms are used nowadays to describe the presence of gel, such as macrogel, insolubles, microgel, or nanogel. In emulsion polymerization, compartmentalization limits the formation of a network to the frontiers of particles, and nanogel is the most convenient term. The network is necessarily restricted to the particle volume, and it has no consequence on the latex rheology. Although polychloroprene has been produced commercially since the beginning of the 1930s,[4] few authors have published on the polymerization mechanisms of this monomer as well as on its gel formation.[5−8] Like any difunctional monomer, chloroprene leads to branching and cross-linking as the reaction proceeds to high conversion. On a theoretical point of view, it is admitted that gel formation in chloroprene polymerization may result from either additions to the residual double bonds of polychloroprene chains or transfer to polymer, followed by termination.[9] As Flory[1−3] demonstrated, transfer to polymer cannot result in network formation if termination occurs only by disproportionation. In chloroprene, termination occurs mostly by coupling, and transfer to polymer may lead to network formation, but, as for other diene monomers, most of the cross-links are generated by the reaction of a propagating radical with a pendant 1,2 double bond.[10] Internal double bonds, resulting from a 1,4 addition of the monomer unit, can be neglected because of their very low reactivity in radical polymerization.[11−13]

For both mechanisms of gelation (via transfer to polymer or pendant double bond insertion), the probability of cross-link formation can be expressed as follows:

$$P_{\text{cross-link}}(t) = \frac{k[\mathrm{P}]}{k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{tr,X}}[\mathrm{X}] + k_{\mathrm{t}}[\mathrm{R}^{\bullet}] + k[\mathrm{P}]} \quad (1)$$

with [P], [M], [X], and [R•] represent respectively the polymer, monomer, transfer agent, and radical concentrations, and k_p, $k_{tr,X}$, k_t, and k represent respectively the rate constants for propagation, transfer (to monomer, solvent, and chain transfer agent), termination, and cross-link formation.

Propagation reactions dominating all other reactions, the probability to create a network increases with the volume fraction of polymer in particles. This probability is therefore constant during the second interval of emulsion polymerization because the polymer-to-monomer ratio inside the particles remains constant,[14] but it increases with the conversion in the third stage of the process.

The presence of gel influences the main characteristics of polychloroprene such as crystallinity and mechanical and adhesives properties.[9] Therefore, a precise control of gel content is essential. Chloroprene is usually polymerized batchwise at medium or low temperature, using a redox initiating system. A chain transfer agent, generally sulfur containing, is used to control molecular weight, and a short stop is usually added to stop conversion before gel formation around about 70% conversion.[9] The chain transfer agent reduces the kinetic length of the growing polymer chains. Therefore, when a cross-link is formed in the presence of chain transfer agent, it links two short chains, whereas in the absence of chain transfer agent, it links two high molecular weight chains. The gel point occurs with the apparition of infinite molecular weight chains, and this event is hence retarded by the use of chain transfer agents. We recently published a series of papers about the use of polymerizable surfactants in emulsion.[15−17] These surfactants are efficient stabilizers of latexes, and they cannot diffuse in films formed with these latexes. Surfactant diffusion (blooming) is responsible for the formation of film defects, eventually causing blistering and adhesion problems. In this report, we present results about the emulsion polymerization of chloro-

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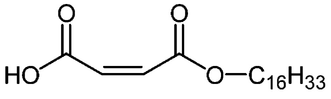
Table 1. Typical Recipe for the Emulsion Polymerization of Chloroprene

	parts by weight
organic phase	
chloroprene	100
n-dodecyl mercaptan (n-DDM)	0.23
aqueous phase	
deionized water	90
HEC_{16}	3.4
$NaHCO_3$	1.64
initiators	
sodium persulfate, $Na_2S_2O_8$ (aq soln 1% w:w)	variable
sodiun dithionite, $Na_2S_2O_4$ (aq soln 1% w:w)	variable

prene in emulsion using a polymerizable surfactant. Classical recipes for the emulsion polymerization of chloroprene often use a terpenic surfactant such as rosin. When replacing the terpenic surfactant by a hemimaleic polymerizable surfactant, the gel formation occurred at very low conversion. We were very surprised by this observation, as gel formation is a priori not affected by the nature of surfactant. The applications of polychloroprene latex stabilized by a polymerizable surfactant are treated in another paper.[18] In this paper, we endeavor to understand the nature of this premature gel formation. We also devise a way to control gel formation below 70% conversion in chloroprene emulsion polymerization on the basis of the control of free radical lifetime in particles.

Experimental Section

Chloroprene was supplied by Enichem. Chloroprene cannot be purchased, nor can it be stored or purified. It is produced in situ in the production plant and polymerized immediately. Because the monomer was of "industrial" grade, amounts of inhibitors changed from day to day, giving induction periods which span from a few minutes to 1 h. *n*-Dodecyl mercaptan (nDDM) and buffer salts were purchased from Acros Chemicals (reagent grade). Sodium dithionite was purchased from Clariant (88 ± 2%), and sodium persulfate from Peroxid Chemie GmbH (>98%). The reactive surfactant HEC16 (hexadecylmaleic acid) was supplied by Sidobre-Sinnova under the name of Sinnoester HMP. Water was deionized and degassed prior use.



HEC16

Particle sizes were measured by dynamic light scattering with a Beckman Coulter N4 PLUS at 90°.

Polymerizations All surfactant amounts are given in weight percent relative to the monomer (noted p in Tables 1−3). Polymerizations were carried out in a 3 L stainless steel reactor at 12 °C. The recipe can be found in Table 1. Trials A−F were performed with continuous addition of sodium persulfate and sodium dithionite aqueous solutions. Addition profiles were varying during the polymerization, depending on the evolution of conversion and the reaction exothermy. Trials G−Q were performed with a single shot addition of sodium dithionite at $t = 0$ and a continuous addition of a 4% aqueous solution of sodium persulfate at constant rate. The components of the aqueous phase were first solubilized at 90 °C for 45 min. The mixture was cooled in the reactor under stirring (50 rpm) and under N_2 pressure (0.3 bar). The organic phase was then introduced, and the mixture was cooled at 12 °C. The introduction of the redox initiators triggered the polymerization. Conversion was measured gravimetrically at several time intervals. Polymerization rates (Figures 1 and 5) were calculated by taking the derivative of the conversion.

Table 2. Relation between Gel Formation and the Flux of Radical ($T = 12$ °C; Buffer: $NaHCO_3$; n-DDM: 0.23 p at $t = 0$; Continuous Addition of an Aqueous Solution of Sodium Persulfate (4% w:w) and Sodium Dithionite (4% w:w)

	HEC16 at $t = 0^a$	gel content in chlorobenzene (%)	conv (%)	time (min)	N_p (L^{-1})	$[R^\bullet]^b$ (radicals/(s L))
A	2.86	85	9	30	3.8×10^{17}	1.1×10^{17}
B	2.44	68	15	60	2.7×10^{17}	1.7×10^{17}
B	2.44	90	27	90	2.7×10^{17}	1.7×10^{17}
C	2	70	16	60	3.2×10^{17}	2.6×10^{17}
C	2	92	28	90	3.2×10^{17}	2.6×10^{17}
D^c	1	3	33	120	5.3×10^{17}	5.9×10^{17}
D^c	1	43	58	180	5.3×10^{17}	5.9×10^{17}
E^d	1	5	69	240	1.8×10^{17}	9.1×10^{17}
F^d	1	13	75	260	1.9×10^{17}	1.1×10^{18}

[a] In weight percent relative to the weight of chloroprene. [b] Average free radicals flux, calculated as the average of the rate of addition of the default reagent, sodium dithionite, during the first 30 min of the polymerization. [c] Initial addition of surfactants: 1 p of HEC16 and 2 p of Triton X405 (octylphenol with 40 units of ethylene oxide, to help stabilization at high solids). Continuous addition of surfactant in 4h30: 2 p of HEC16 and 1 p of Triton X405. [d] Initial addition of surfactant: 1 p of HEC16 and 2 p of NP30 (nonylphenol with 30 units of ethylene oxide, to help stabilization at high solids). Continuous addition of HEC16 in 5h: 2 p.

Table 3. Relation between Gel Content and Average Flux of Radicals ($T = 12$ °C; $[HEC16]_0$: 1 p; Buffer: $NaHCO_3$; n-DDM: 0.23 p)

	$[R^\bullet]_0{}^a$ (radicals/(s L))	$[R^\bullet]_{poly}{}^b$ (radicals/(s L))	$t_R{}^c$ (min)	time (min)	gel content (%)	conversion (%)
G	1.3×10^{18}	4.0×10^{17}	30	270	<20	74
H	1.2×10^{18}	4.0×10^{17}	30	240	0	60
I	1.3×10^{18}	2.0×10^{17}	61	60	2	9
				90	60	20
J	1.3×10^{18}	4.0×10^{16}	61	60	0	9
				120	50	25

[a] Average radical flux, calculated as the average of the rate of addition of the default reagent, sodium persulfate, during the interval [0, t_R]. [b] Average radical flux, calculated as the average of the rate of addition of the default reagent, sodium persulfate, during the interval [t_R, ∞]. [c] Instant corresponding to the reduction of the rate of persulfate addition, i.e., time at which the average free radicals flow changes from $[R^\bullet]_0$ to $[R^\bullet]_{poly}$.

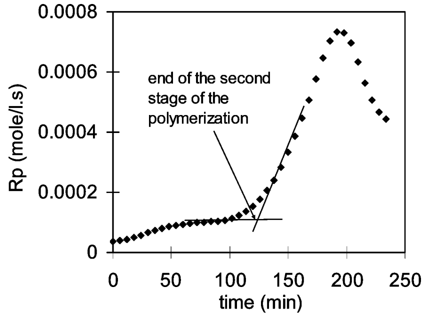


Figure 1. Evolution of rate of polymerization, R_p, vs time for the emulsion polymerization of chloroprene.

Gel Content. The latex (2 mL) was laid on a glass plate to form a 0.5 mm thick damp film and was dried overnight at ambient temperature. A given amount of the dry polymer was put in a metallic mesh basket (100 mesh diameter). The basket was immersed in toluene or chlorobenzene for 24 h. The insoluble part of the polymer remained in the basket, whereas the soluble part diffused in the solvent phase. After filtration and evaporation, the solid content of the solvent phase was determined to calculate the weight content of insoluble poly-

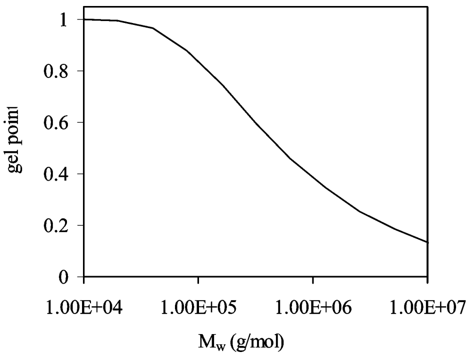


Figure 2. Gel point vs molecular weight. The gel points were calculated using eq 2, using C_p of 5×10^{-4}, which corresponds to the chain transfer constant to polychloroprene.[25]

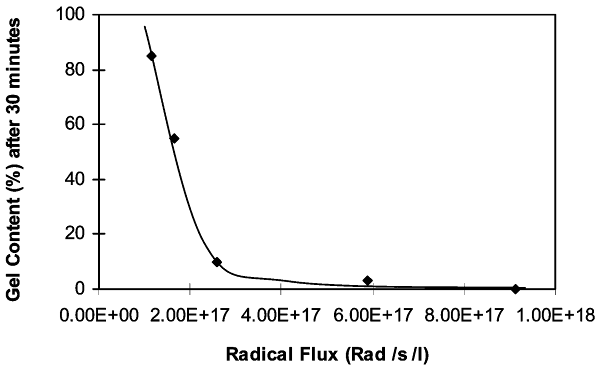


Figure 3. Evolution of gel content at time $t = 30$ min vs the average radicals flow, calculated during the first 30 min of the polymerization.

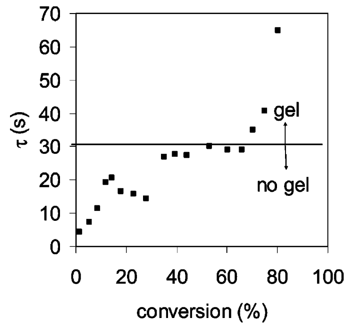


Figure 4. Evolution of the free radical lifetime in particles vs conversion for an industrial polychloroprene latex.

mer in the material, following the equation:

$$\text{gel content (\%)} = \frac{m_{\text{initial}} - m_{\text{dissolved}}}{m_{\text{initial}}}$$

where m_{initial} is the initial amount of dry polymer and $m_{\text{dissolved}}$ is the amount of polymer dissolved in the solvent phase after 24 h.

Results and Discussion

Generalities about the Polymerization. The reactive surfactant HEC16 is a very hydrophobic surfactant[17] (cmc in basic water: 0.1 g/L) that can only be used in basic medium, under the deprotonated form. Using a Maron titration,[19] the specific area of HEC16 adsorbed on a polychloroprene latex (18.6 g/L) was found to be 30 A^2/molecule (pH 8.5). At pH 12, the ester group of HEC16 is slowly saponified. Thus, the polymerizations were run in a NaHCO$_3$ buffer, which maintains the pH at 8.5 ± 0.5.

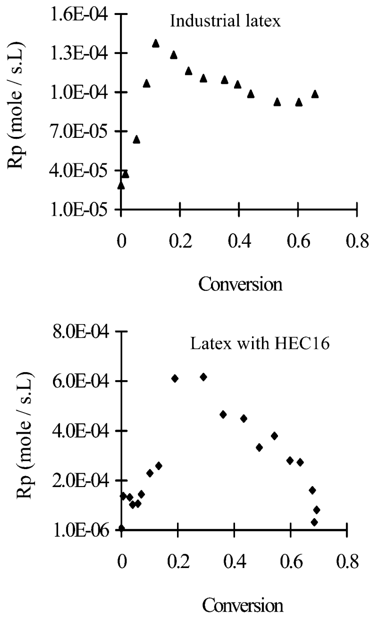


Figure 5. Evolution of the polymerization rate R_p vs conversion for two polychloroprene latices: (a) top, stabilized by a rosin derivative ($T = 10$ °C, buffer NaOH, n-DDM: 0.1 p); (b) bottom, stabilized by HEC16 ($T = 12$ °C, buffer NaHCO$_3$, n-DDM: 0.23 p)

The typical rate profile of a polymerization is shown in Figure 1. The transition from interval 2 to 3 is clearly seen at the onset of the Trommsdorff effect. If the solubility of chloroprene in water is neglected, then the concentration of chloroprene in the particles during interval 2, $[M]_p$, can be estimated from the concentration of residual monomer during the transition from interval 2 to 3. For a series of five different batch polymerizations, this concentration was found to be 10.3 ± 0.3 mol/L, corresponding to a volume fraction of monomer in the particles, ϕ_m, of 0.95. This value is very elevated compared to other monomers ($\phi_m = 0.60$ for styrene, $\phi_m = 0.72$ for MMA, $\phi_m = 0.75$ for vinyl acetate).[20] However, it is highly recognized that this method of obtaining $[M]_p$ is not very precise.[20] The exact value of $[M]_p$ is not very important, as our results are to be interpreted on a relative scale. For example, a decrease of 20% in the value of $[M]_p$ translates into an increase of 20% in the lifetime of the radicals. To conclude this section on $[M]_p$, because the transition from interval 2 to 3 occurs very rapidly in chloroprene polymerization, it is likely that gel effect also occurs early in the polymerization. This early gel formation phenomenon will be revisited below.

Molecular Weight Control with a Chain Transfer Agent. In a previous study, the molecular weight of polychloroprene latex was shown to be highly dependent on the choice of surfactant.[21] In the emulsion polymerization of chloroprene, molecular weight is controlled by a chain transfer agent, n-DDM. When rosin is used as surfactant, n-DDM is efficiently reducing the molecular weight of the polymer, whereas with HEC16, gel occurs very rapidly. This phenomenon was attributed to a difference in the rate of transport of n-DDM though the aqueous phase with the various surfactants. HEC16 does not transport well n-DDM, and the chain transfer reaction becomes diffusion limited.

The appearance of a premature gel effect in the HEC16 stabilized particles has been attributed to the low local concentration of n-DDM. The probability of cross-link formation, as given in eq 1, does not depend on the molecular weight of the polymer, but on the polymer content. At identical conversions, the number of branches per 1000 C should be identical in the HEC16 and in the colophane stabilized polymers. This could not be checked experimentally, as in one case the polymer is solid, and the number of branches is typically estimated via the swelling ratio of the gel, whereas in the other case, the polymer is soluble, and the number of branches is often measured via ^{13}C NMR. If the probability of cross-link formation does not depend on the molecular weight, by contrast, the gel point, that is to say the onset of gel formation, is highly molecular weight dependent. According to Flory, the gel point in the bulk polymerization of chloroprene in batch is given by

$$-2C_p\left[1+\frac{1}{\theta_c}\ln(1-\theta_c)\right]=\frac{1}{X'_w} \tag{2}$$

where X'_w is the weight-average degree of polymerization of the polymer, counting monomers as polymers of degree of polymerization 1, C_p is the chain transfer constant to polymer, and θ_c is the gel point. [22] X'_w is dependent on the conversion and can be calculated as the weight average of the polymer, of degree of polymerization X_w, and of the monomer (degree of polymerization 1):

$$X'_w=\theta_c X_w+(1-\theta_c) \tag{3}$$

Combining eqs 2 and 3 defines an implicit equation in θ_c which can be numerically solved for known values of C_p and X_w. As shown in Figure 2, the gel onset can be significantly retarded by lowering the molecular weight of the polymer. Since n-DDM is transported less efficiently to the growing particles in the case of HEC16 than in the case of rosin, very high molecular weight is formed in the case of HEC16, resulting in the premature formation of gel.

Control of the Gel Content by the Radical Flux. When the use of chain transfer agent is not appropriate to regulate the molecular weight, a convenient method for lowering the kinetic chain length of the polymer consists of increasing the radical flux on the particle. In the case of the chloroprene emulsion polymerization, we show below that using more initiator results in delaying the gel effect and, paradoxically, in having lower polymerization rates.

A redox initiator, composed of sodium persulfate and sodium dithionite, is used in this work. We demonstrated that the reaction of dithionite with persulfate is instantaneous and quantitative (see Supporting Information). Thus, when sodium persulfate and sodium dithionite are introduced in equimolar amounts in a continuous addition, the rate of radical generation is equal to the rate of addition. Because a molar excess of sodium persulfate is introduced, this rate is equal to rate of addition of the default reagent, sodium dithionite. Table 2 reports the correlation between the rate of gel formation and the rate of radical formation for six experiments. The correlation between the radical flux and the gel content at 30 min is illustrated in Figure 3. The gel content does not seem to be correlated to the number of particles, as shown in entries 2 and 5 of Table 2, but all these experiments have nearly the same number of particles. A minimum radical flux seems required to avoid gel formation at the beginning of the polymerization. Moreover, it has been observed that gel, when formed at the beginning of the reaction, persists all over the polymerization, whatever the subsequent radicals flux. This may be due to the initial formation of very viscous primary particles, in which termination is more difficult. Therefore, the kinetic length of the growing polymer chains therefore increases as well as the probability to initiate a network. These results show the major importance of a high radical flux at the beginning of the polymerization. The onset of gel formation is delayed as long as the radical flux is high.

In another series of experiments (Table 3), sodium dithionite is added in a single shot at the beginning of the polymerization, and sodium persulfate is added continuously. The rate of free radicals generation is thus directly related to the decomposition rate of persulfate. Each polymerization is started with the same free radical flux. After 30−60 min, the persulfate addition rate is reduced, and the corresponding values of free radical flux varies between 4 × 10^{16} and 4 × 10^{17} rad/(s L). Table 3 presents the evolution of the gel content with the average free radical flux in the polymerization medium. A high flux is sufficient to avoid gel formation until 60−70% conversion. Below a value of approximately 2 × 10^{17} rad/(s L), gel formation is systematic as can be seen for trials I and J, where gel is formed immediately after the persulfate addition rate has been reduced. Taking these results into account, increasing the free radicals flux seems to be the best way to control gel formation in chloroprene emulsion polymerization.

Gel Content and Lifetime of the Radicals in the Particles. When working with a variable number of particles, the kinetic chain length of the polymer does not only depend on the free radical flux. Instead of using the concept of radical flux per particle, we have calculated the radical lifetime in the particle, named τ, which seems a more tangible notion. Obviously, the kinetic chain length is directly related to τ. Let ρ be the number of radical entries per particle and per second (ρ is usually referred as the coefficient of entry). If we consider a particle at time t as a nanoreactor containing n radicals, ρ is the frequency at which radicals are generated in this nanoreactor (rad/s). During a certain interval time x, $2n$ radicals will be generated ($\rho x = 2n$). Out of these $2n$ radicals, n of them will terminate with the existing ones, and the other n will renew the terminated ones. During the interval of time x, $2n$ radicals have died and have been replaced; therefore, $x = 2\tau$. As a result, it can be deduced that

$$\tau=\frac{\bar{n}}{\rho} \tag{4}$$

Nowadays, the theory developed by Gilbert et al. is the most widely accepted one to account for the radical entry phenomenon.[23] It states that an aqueous radical enters the latex and starts to propagate only when growing chains have reached a given degree of polymerization, noted z. On the basis of a steady-state hypothesis, Gilbert et al. developed an expression of ρ. The average free radicals lifetime in particles τ can easily be obtained from the expression of ρ:

$$\tau=\frac{R_p}{k_{p,aq}[M]2k_d[I]}\left\{\frac{\sqrt{k_d[I]k_{t,aq}}}{k_{p,aq}Cw}+1\right\}^{z-1} \tag{5}$$

where R_p is the polymerization rate (mol/(s L)), $k_{p,aq}$ is

Table 4. Average Free Radical Lifetime in Particles for a Series of Trials Presenting or Not the Formation of Gel at Low Conversios (T = 12 °C; [HEC16]$_0$: 1 p; Buffer: NaHCO$_3$; n-DDM: 0.23 p; Sodium Dithionite Added in Single Shot at t = 0; Continuous Addition of an Aqueous Solution of Sodium Persulfate)

trial	[R$^\bullet$] (radicals/(s L))	$\tau_{\mathrm{conv}=10\%}$(s)	τ_{av} (s)
trials with gel at low conv			
K	4×10^{16}	19	58
L	2×10^{17}	15	47
M	2×10^{17}	20	44
trials without gel until 70% conv			
industrial latex with rosin derivative	3×10^{16}	11	21
N	4×10^{17}	10	22
O	4×10^{17}	10	30
P	4×10^{17}	10	28

the aqueous phase propagation rate constant (105 mol/(L s) at 10 °C[1]), [M] is the monomer concentration in particles (mol/L), $2k_d$[I] is the initiation rate (mol/(L s)), $k_{t,aq}$ is the aqueous phase termination rate constant, not given in the literature for the chloroprene and estimated equal to 10^8 mol/(L s) at 12 °C, C_w is the monomer solubility in the aqueous phase (saturation:13 mmol/L at 20 °C), and z is the critical size of the oligoradicals entering particles. This expression allows to calculate the average free radical lifetime even at the very beginning of the polymerization where gelation occurs. In our calculations, the value of C_w is taken as the saturation value which is reached only during interval 2. Because of this approximation, lifetime values should only be taken for comparison purposes, not on an absolute scale. Interestingly, the radical lifetime does not depend on the number of particles (but the rate of polymerization, R_p, does). Morrison et al.[24] developed a method for the determination of the critical size z on the basis of thermodynamic calculations. This model leads to z = 3.17 for chloroprene at 12 °C. Using this value, it was possible to calculate τ for different experiments (Table 4).

Two values of τ have been determined, from a series of trials presenting or not the phenomenon of gel formation at low conversions: a value at early conversion ($\tau_{\mathrm{conversion}=10\%}$) and an average value calculated on the whole polymerization duration (τ_{average}). The emphasis must be put on the relative nature of the τ values presented in Table 4. First, it was admitted that the persulfate decomposition rate can be directly correlated to the free radical flux. Second, the aqueous phase termination rate constant, not given in the literature, was estimated. Third, the monomer concentration in water was taken as the saturation concentration, which is not the case in stage III of the polymerization. In such conditions, τ values presented in Table 4 are only relative. By comparing the trials presenting or not gel at low conversions, it appears that gel forms when free radicals remain twice longer in the particles. This qualitatively correlates well with the findings of Figure 2, where an increase in molecular weight results in an early gel point.

Comparison between Rosin Derivative (Colophane) and HEC16 Surfactant. The gel data obtained with the nonterpenic HEC16 polymerizable surfactant differ drastically from those obtained with the rosin derivative found in industrial latices (Table 5). In the latter case, a much smaller free radical flux is sufficient to maintain the particles without gel formation before 60−70% conversion. This observation can be explained by the smaller number of particles in the case of the industrial latex.

Table 5. Free Radicals Lifetime in Particles for Two Polychloroprene Latices, One Stabilized by a Rosin Derivative (Industrial Latex) and One Stabilized by HEC16 (Trial Q), for a Given Value of Conversion

	conv (%)	N_p (L^{-1})	[R$^\bullet$] (radicals/(s L))	τ (s)
industrial latex	5.2	2.5×10^{16}	3.9×10^{16}	7.4
trial Q	5.9	2.0×10^{17}	4.4×10^{17}	7.5

Table 6. Average Number of Radicals per Particle and Radical Lifetime for Two Experiments: One with Gel (BU-129) or One without Gel (BU-116) (T = 12 °C, HEC16: 1 p, Buffer NaHCO$_3$, n-DDM: 0.23 p; Addition of Dithionite at Time Zero and Continuous Addition of Persultate)

BU-129: no gel up to 70% conv			BU-116: with gel[a]		
conv (%)	$\bar{n}$	τ (s)	conv (%)	$\bar{n}$	τ (s)
1	0.3	4.5	2.3	2	11.5
6.7	0.15	11	8.7	2.7	15
12.2	0.3	11	14.9	3.3	33

[a] Gel content = 52% at 25% conversion.

For the industrial latex, the initiation rate allows to maintain the free radicals lifetime in particles below a critical value until approximately 65% conversion. Above this value of the conversion, the concentration of the transfer agent is not important enough to regulate the kinetic length of the growing chains, resulting in gel formation. Free radical lifetime in particles increases rapidly as well as the polymer chains kinetic length and the probability to form gel. These results explain why most of the industrial chloroprene emulsion polymerizations are short-stopped around 65−70% conversion to avoid gel formation. We fund that HEC16 was very efficient to nucleate particles in chloroprene emulsion polymerization.[18] Therefore, the polymerization rate is greater and, according to eq 5, the lifetime of the radicals longer. Thus, the presence of early gel in the HEC16 containing latexes is a consequence of the capacity of this surfactant to nucleate particles.

Trommsdorf Effect. Because of the low aqueous phase solubility of chloroprene and its ability to swell the polymer particles, the Trommsdorf effect occurs at conversions as low as 10% (Figure 5a). The Trommsdorf effect is observed systematically, even in the absence of gel, as in the case of the industrial latex (Figures 4 and 5a). Thus, in our experiments, the Trommsdorff effect can appear largely before the gel point. This might explain why we overestimated the monomer concentration in the particles (see above). Obviously, when the gel point is reached, a Trommsdorff effect must be observed (if already not present) as the internal viscosity in the particle is very high.

Despite the absence of correlation between the Trommsdorff effect and gel formation, we found that decreasing the rate of polymerization was a convenient method to delay the gel point and to shorten the kinetic length of the polymer (see eq 5 for the relation between rate of polymerization and kinetic length). For example, for experiments BU 129 and BU 116, the radical flux and the particle numbers are the same, but the average number of radicals per particle is smaller in the experiment BU 129 (Table 6). Thus, the polymerization is slower for BU-129, and the radical lifetime is longer for BU 116. As a result, the chains generated in the slower experiment are shorter than those generated in the faster one, and the gel point is delayed.

The difference of polymerization rate between BU 116 and BU 129 can be explained by the presence at different levels of inhibiting impurities in the monomer (see Experimental Section). Therefore, the onset of gel formation can also be retarded by adding (purposefully or not) inhibitors.

Conclusion

In our previous work, it was shown that the replacement of rosin by HEC16 often causes a premature gel formation.[21] This was putatively attributed to the decreased efficiency of the chain transfer agent. Another possible cause was the efficiency of the nucleation observed in the presence of this kind of surfactant.[15] In the case of chloroprene polymerization, the number of generated particles is high, resulting in a long lifetime of the radicals and large kinetic chain length. This increase in molecular weight is directly correlated with the early onset of gel formation.

The possibility tocontrol the gel formation through the flux of radicals has been explored. For this purpose, we have proposed an expression for the lifetime of the radicals in the particles. If the lifetime of the radicals is short, no gel is formed. Thus, using more initiator results in delaying the appearance of gel and, paradoxically, in having lower polymerization rates. Similarly, gel onset can be delayed by using monomer with a higher level of inhibitor.

Supporting Information Available: Kinetics of initiator decomposition. This material is available free of charge via the Internet at http://pubs.acs.org

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