Communications to the Editor

Direct Measurement of Oligomers Entry Rate onto Latex Particles in an Emulsion Polymerization

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Although the general scheme of an emulsion is well established to be a three-interval process,[1] the intimate details of the mechanism are not yet fully understood. A key parameter to unravel the complex polymerization kinetics is the entry rate into the polymer particles of free radicals produced in the aqueous phase. Many interesting mechanisms have been postulated for this entry step, which have in turn generated numerous modeling works. For example, the diffusion control theory[2] implies that the radical diffusion to the particle determines the rate of entry. Another theory, the so-called displacement theory, connects the rate of entry to the surfactant desorption kinetics.[3] The colloidal entry theory predicts an entry rate related to the colloidal behavior of the oligomers, that is to say, their capacity to flocculate onto the latex particle.[4] In this case, it has been found, using semiempirical arguments, that the size of the MMA oligomers is between 53 and 82.[5]

The most recent and thoroughly accepted theory was proposed by Maxwell et al.[6] It states that an oligomer created in the aqueous phase reaches a critical size z before entering irreversibly the latex particle. In this case, the rate-determining step is the growth of aqueous radicals to a critical degree of polymerization z. Using theoretical considerations, these authors found it to be equal to 4 for MMA at 50 °C.

Albeit many theoretical works have been reported, experimental results are scarce, so that numerous questions remain unanswered.[7] Nevertheless, a complete knowledge of each step is necessary to have the whole process under control. Indeed, in industry, complex formulations involving numerous monomers and additives are used to produce polymers with precise features. As a mere modification in the process could lead to drastic changes in the quality of the product, there is a great endeavor for understanding each step of the mechanism and for accurately modeling the emulsion process.[8]

To our knowledge, there is no *direct* determination of the entry rate of aqueous oligomers prior to our work. The usual way to evaluate this rate consists of experimentally measuring the rate of polymerization and mathematically extracting the entry rate from a steady-state mass balance equation. This indirect determination lies upon many assumptions, which seem to be successfully verified for styrene.[9]

More work has been done about the nature of entrant oligomers. In a recent work, Poehlein et al.[10] presented the experimental determination of the critical size of vinyl acetate oligomers. The employed strategy involved 2,5-di-*tert*-butylhydroquinone as a water insoluble inhibitor, thus allowing an aqueous phase propagation but preventing any organic phase polymerization. The results ruled out a colloidal entry mechanism since the oligomer size found was significantly smaller than that expected from theory. Although this approach is really the first attempt to elucidate the entry mechanism, the authors admitted that the results do not allow one to conclude further since no kinetics of entry are presented. These authors have also characterized the nature of entrant oligomers styrene/MMA and styrene/AA by forcing these oligomers to transfer as soon as they enter into the particle.[11] In the styrene/MMA case, they found 0−1 styrene unit and 2−4 MMA units incorporated in the entrant oligomer. Finally, Rudin et al. have recently analyzed by MALDI TOF MS the oligomers located in the aqueous phase of an emulsifier-free MMA polymerization and found for them an average degree of polymerization between 5 and 9.[12]

In this paper, we propose a strategy allowing a direct measurement of the entry rate of critical size MMA oligomers generated in the aqueous phase as well as a complete characterization of these oligomers. For this purpose, we have synthesized a latex seed with radical traps covalently bound onto the particle surface. Then we have used this seed in an emulsion polymerization, whereby propagating radicals are initiated by thermal decomposition of potassium peroxodisulfate followed by addition onto aqueous monomer (MMA). When a carbon-centered radical formed in the aqueous phase reaches the particle surface, it is trapped by the scavenger, leading to a decreasing number of radical traps over time.

The initial latex seed is composed of polystyrene slightly cross-linked with divinylbenzene and functionalized with methacrylic acid. The obtained particles are monodisperse with a size of 50 ± 5 nm. To mainly incorporate carboxylic groups on the surface of the polystyrene−divinylbenzene particles, the methacrylic acid has been added in a semicontinuous way at 80% conversion of styrene.[13]

The choice of the radical trap fixed onto the particles relies on three points. First, it has to be selective toward entering carbon-centered radicals, as it should not react with oxygen-centered radicals produced by initiator decomposition. Second, it should induce very efficient trapping, with rates close to the diffusion limit. Third, the spin trap should be easily tagged by a spectroscopic

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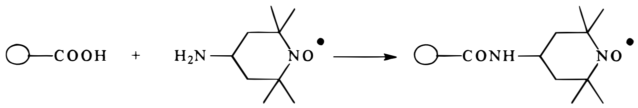
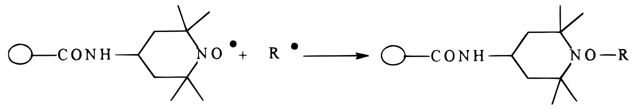
method (ESR in our case). Nitroxide stable radicals fulfill these different conditions.

The nitroxide was fixed onto the latex through an aqueous phase amidation reaction with the commercially available and water-soluble amino TEMPO (4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy, free radical), the latex seed-bearing surface carboxyl group, and a water-soluble carbodiimide as coupling agent.[14]



Then, the latex was thoroughly cleaned by ultrafiltration in order to eliminate the free amino TEMPO introduced in excess during the coupling reaction. Indeed, remaining amino TEMPO in the aqueous phase could propagate important errors in the entry rate measurements. During the ultrafiltration sequence, the filtrates were regularly collected and analyzed by ESR, fluorescence, and UV spectroscopy.[15] The three methods showed a sharp decrease of the signal at the beginning, followed by a nearly horizontal plateau, likely corresponding to an equilibrium between aqueous and organic solubilized amino TEMPO. After an exhaustive filtration (more than 30 times the latex initial volume), the concentration of free amino TEMPO in the aqueous phase dropped to a virtually negligible amount (3.6%), relative to the nitroxide amount covalently bound onto the latex. In a typical experiment, at least 50% of the COOH groups fixed on the latex were reacted with the amino TEMPO (the amount of COOH covalently bound was determined by conductometric assays).[16] This corresponds to 9700 TEMPO grafted per particle. This functionalized latex was found to be stable over time, as we observed no decomposition or decrease of the ESR signal, even after prolonged heating periods at 70 °C.

The functionalized latex seed was then used in an emulsion polymerization. MMA was used as monomer, potassium persulfate (KPS) as initiator, and sodium dodecyl sulfate as surfactant.[17] The quantity of monomer introduced in the reactor was calculated to be sufficient for swelling the seeds and forming monomer droplets in the medium. Thus, the aqueous phase is saturated with MMA. When an aqueous propagating radical entered into a particle, the nitroxide moiety led to the formation of a stable alkoxyamine.



Thus, the kinetics of entry of the radicals was followed by monitoring the decay of the ESR signal of the nitroxide. Samples were extracted from the reactor and analyzed by ESR. Figure 1 shows a net decrease of the ESR signal and of the amino TEMPO concentration bound to the latex. For the first 60 min, trapping occurs rapidly and at a constant rate. During this period, the monomer conversion is very low, so we infer that all the oligomers created in the aqueous phase are trapped on the latex. Later on, in the time range 60−400 min, MMA begins to polymerize and spin trapping becomes less and less efficient, as the concentration of surface TEMPO is not sufficient to trap all the oligomers entering the particle. The coefficient of entry, ρ, that is to say, the number of entering radicals per unit time and per particle, is directly read from the decay kinetics, at short times (when the capture is very efficient).[18]

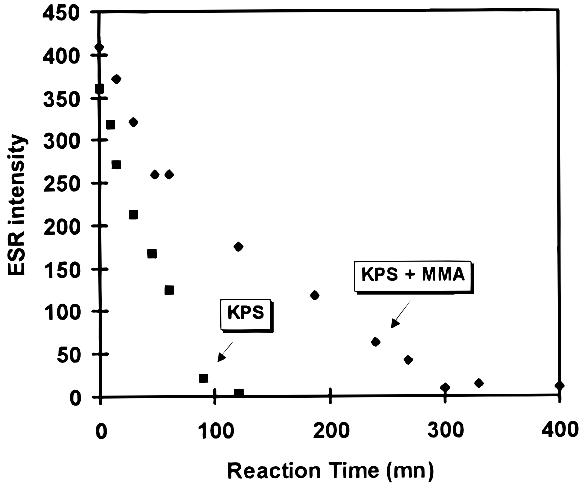


Figure 1. ESR signal during the decomposition of KPS in the absence and in the presence of monomer. The coefficient of entry of MMA-containing oligomers is 1.5 s^{-1}. Each 86 nm latex particle is covered with 9700 nitroxides.

The rate of entry was calculated to be $\rho N_p = 3.49 \times 10^{16}$ (entries/s)/L. In our experiment, the rate of initiator decomposition was $2fk_d[I]N_a = 9.7 \times 10^{16}$ (rad/s)/L.[19] Thus, in this particular case, we found an efficiency (ratio of entrant to produced radicals) of 36%. It is important to note that the rate of radical entry must be calculated at initial times, when no polymerization occurs. At longer times, the rate of nitroxide quenching decreased, as a fraction of the aqueous oligomers crossed the particle interface without being quenched. During the 400 min reaction times, there were 9 times more radicals created than quenched nitroxides.

It is clear that the previous experiment is only valid if the decrease of the ESR signal does actually correspond to the trapping of entrant radicals. When the experiment was repeated in the absence of monomer, everything else being kept identical, the ESR signal was observed to decrease sharply and linearly. The total amount of the initial grafted nitroxides disappeared within 1 h of reaction. This decrease could be assigned to direct oxidation of the nitroxide moiety by KPS.[20] We believe that, in the presence of monomers, oxidation did not take place for the following reasons. Contrary to what was observed in the presence of monomers, the rate of nitroxide oxidation was equal to the rate of persulfate decomposition. Moreover, it is known that persulfate is an oxidizing agent; but, in the presence of monomers, oxidation occurs to a lesser extent.[21] In our case, trapped oligomers that should not be present if oxidation took place were collected and analyzed (see below). In addition, at the beginning of the reaction, polymerization inhibition was complete, which ensures that, despite a putative oxidation, nitroxide was still present to trap radicals. Finally, the trapping experiment was repeated without potassium persulfate, but using the so-called V50 water soluble diazo-initiator (2,2′-azobis(2-methylpropionamidine) dihydrochloride).[22] As previously described, samples were regularly taken from the reactor and analyzed by ESR. During the reaction, the ESR signal decreased, as shown in Figure 2.

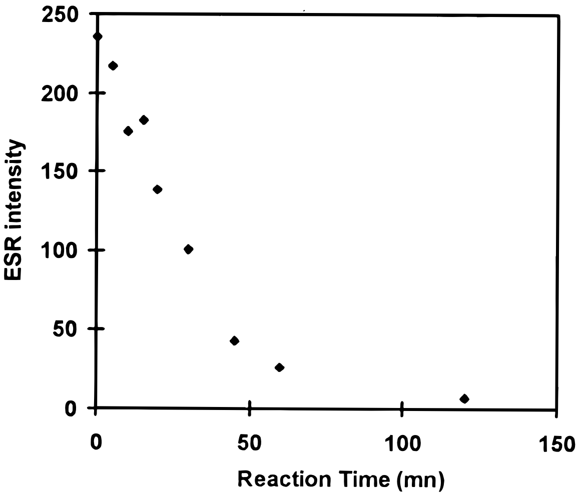
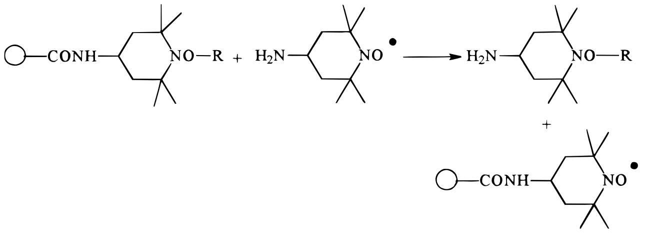


Figure 2. ESR signal during the polymerization of MMA. V-50 is used for initiator. The coefficient of entry for this experiment is $\rho = 1.9\ s^{-1}$. The pH is constant around 5. Each 92 nm particle is covered with 5960 nitroxides.

The coefficient of entry measured is $\rho = 1.9\ s^{-1}$, which is very similar to the value obtained in the former experiment. Furthermore, in this case, the rate of entry $\rho N_p = 8.72 \times 10^{16}$ (entries/s)/L, is of the same order of magnitude as in the first experiment. By assuming a k_d of $1.15 \times 10^{-4}\ s^{-1}$ at 70 °C for V-50,[23] and with an initial initiator concentration of 3.82×10^{-3} mol·L^{-1}, the trapping efficiency is 33%.

The analysis of the rate of entry would be incomplete without a determination of the nature of entrant oligomers. For this purpose, several aliquots of latex were withdrawn from the reaction and analyzed by two different methods. First, the precipitated latex was washed several times with water, methanol, and THF, and extensively dried in vacuo. The solid white powder then contained only cross-linked polystyrene with grafted MMA oligomers. Quantitative IR spectroscopy allowed us to determine the relative amounts of PMMA and PS.[24] In the experiment above cited, we found that the critical size *z* of oligomers was 5. Another way to analyze the sample latex consisted of recovering entrant oligomers by adding a significant excess of free (i.e., unanchored) amino TEMPO to the *dried* latex sample and by heating this reaction medium to 130 °C in chlorobenzene. Under such conditions, the thermoreversible C−O bond led to a homolytic scission, thus liberating oligomeric radicals in the medium. These carbon-centered radicals were immediately trapped by the free TEMPO introduced in excess.



Afterward, a simple filtration was achieved to remove the polymer and collect the TEMPO-terminated oligomers, which were then analyzed by GPC.[25] The average resulting polystyrene equivalent mass is about 733 g/mol. This value cannot be transformed into real PMMA molecular mass as the Mark−Houwink relation is no longer reliable for such low molecular weights. Nevertheless, this result confirms the infrared experiment, since the molecular mass of the 5-mer would be 806 g/mol.

It has been shown in this paper that it is possible to measure directly the entry rate of oligomers onto latex particles and to determine the size of entering oligomers by two independent methods (IR and GPC). It would be now interesting to focus on the influence of various factors (particle size, e.g.) on the coefficient of entry and on the nature of entrant oligomers. Using these results, it will then be possible to clearly understand the determining factors that control the entry, as well as to use these data in the modeling of the emulsion polymerization kinetics. In addition, these latex particles are currently used to produce controlled radical polymerization in emulsion, as well as to produce core−shell particles by a two-step process.

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(12) Thomson, B., Wang, Z.; Paine, A.; Lajoie, G.; Rudin, A. *J. Polym. Sci., A: Polym. Chem.* **1995**, *33*, 2297.

(13) Polystyrene latex slightly cross-linked with divinylbenzene and functionalized with methacrylic acid was synthesized through a two-step process. The core of the particle was obtained by a batch process. The conversion evolution was determined by gravimetry. When the styrene conversion reached 80%, a mixture of methacrylic acid and styrene (1/1.8) was added in a semicontinuous way. The polymerization was initiated by thermal decomposition of potassium persulfate (0.08% in weight), at 70 °C. The amount of monomer introduced was calculated for obtaining a final 10% solid content. The DVB amount introduced was 4% of the total styrene quantity used. Monodisperse particles of 50 ± 5 nm diameter were obtained.

(14) 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (1.45 g) and amino TEMPO (1.32 g) were dissolved in a 4 g/L sodium dodecyl sulfate solution and introduced in a PS−DVB−methacrylic acid latex, previously washed with an equimass mixture of anionic and cationic ion-exchange resins. The coupling reaction was pursued at room temperature overnight, under agitation. Lewis, S. D.; Shafer, J. A. *Biochim. Biophys. Acta* **1973**, *303*, 284.

(15) ESR measurements were made on a Varian ESR spectrometer, with a classical cylindrical Suprasil-quartz cell at −198 °C. The entire study was made with the same ESR cell, for signal quantification. Fluorescence measurements were

performed on a Perkin-Elmer LS50 fluorometer, equipped with a microtiter plate reader and Elisa type 96 well plate. 4-Phenylspiro[furan-2(3*H*), 1′-phthalan]-3,3′-dione (fluorescamine) was used to assay the primary amine moiety of the amino TEMPO fluorescent. A 100 μL aliquot of a solution composed of 100 mL of serum containing amino TEMPO, 2900 μL of 0.2 M borate buffer adjusted with 10 N NaOH (pH = 9.2), and 1000 μL of a fluorescamine solution in 0.3 g/L acetone were analyzed (421 nm excitation, 477 nm emission) as prescribed in: Ganachaud F.; Mouterde G.; Delair, Th.; Elaissari A.; Pichot C. *Polym. Adv. Technol.* **1994**, *6*, 455. UV assays were realized on a 922 Uvikon double-beam spectrophotometer.

(16) Van den Hul, H. J.; Vanderhoff, J. W. *J. Electroanal. Chem.* **1972**, *37*, 161.

(17) Methyl methacrylate (MMA) polymerization was carried out under a nitrogen atmosphere, in a 250 mL reactor. MMA (2.07 g) was added to 141.6 g of PS−DVB−TEMPO latex seed (0.93 g of polymer/100 g of latex, $N_p = 2.37 \times 10^{16}$ part·L^{-1}). The polymerization (70 °C) was initiated with 148 mg of $K_2S_2O_8$ introduced in 12.3 g of H_2O. Conversion was followed by gravimetry.

(18) Radical concentrations were calculated by double integration of the signal and comparison with standard solutions containing known concentrations of free amino TEMPO and SDS (4 g/L). We found the following relationship: ESR intensity (in arbitrary unit) = 3028.6[amino TEMPO (g·L^{-1})]. Thus, the slope of the kinetics plot at initial times corresponds to the concentration of trapped radicals (in g·L^{-1}) per unit time. The coefficient of entry is then obtained by dividing by the particle number.

(19) $k_d = 5.5 \times 10^{-5}$ s^{-1}, according to: Santos, A. M.; Vindevoghel, Ph.; Graillat, C.; Guyot, A.; Guillot, J. *J. Polym. Sci., Part A* **1996**, *34*, 1271.

(20) Nitroxides are known to be oxidized into oxammonium salts. For example, see: Endo, T.; Miyazawa, T.; Shiihashi, S.; Okawara, M. *J. Am. Chem. Soc.* **1984**, *106*, 3877.

(21) Kolthoff et al. have shown that decomposition of KPS is catalyzed by acids. In the absence of monomers, the decomposition of KPS generates sulfate radicals, which further react with water, giving the extremely reactive hydroxyl radical and HSO_4^- (p$K_a \sim 2$). The decomposition of KPS is thus self-catalyzed (see, for example: Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055. House, D. A. *Chem. Rev.* **1962**, *62*, 185). Accordingly, the pH continuously decreases from 6 to 2, when KPS is decomposed in the sole presence of our functionnalized latex. In the presence of monomers, the pH only decreases to 4 since sulfate radicals are trapped by MMA before transferring to water. Since 100 times less protons are created, we can roughly conclude that sulfate radicals are trapped by monomers in 99% of the cases and that oxidation occurs only to the extent of 1%. Notably, separately heating the functionalized latex with hydrochloric acid (pH = 2) did not result in nitroxide decomposition.

(22) Methyl methacrylate (MMA) polymerization was carried out under a nitrogen atmosphere, in a 250 mL reactor. MMA (11.65 g) was added to 100 g of PS−DVB−TEMPO latex seed (2.7 g of polymer/100 g of latex). $N_p = 4.59 \times 10^{16}$ part·L^{-1}. The polymerization (70 °C) was initiated with 104 mg of V-50 introduced in 2.79 g of H_2O. Conversion was followed by gravimetry.

(23) Wako Chemicals, Technical Information furnished with the product.

(24) The latex has been analyzed using the 696 cm^{-1} polystyrene band as the internal standard and the 1730 cm^{-1} C═O ester band. The quantity of grafted PMMA onto the polystyrene particles was evaluated by comparison with a calibration curve established with different known ratios of PS/PMMA standards.

(25) MALDI TOF MS results are pending.

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