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Nitroxide Mediated Living Radical Polymerization of Styrene in Emulsion

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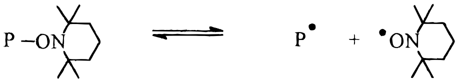
Because of the stringent technological regulations required in industry, controlling molecular weight distribution and chain topology in order to develop novel materials cannot be done at the expense of environmental and safety rules.[1] Much work has been devoted to "living" or "controlled" polymerizations, for example in the field of anionic[2] and cationic[3] polymerizations, or group transfer polymerization.[4] Nevertheless, the drastic conditions necessary for these polymerizations (monomer purity and reactivity, presence of water and oxygen, unfriendly solvents, and viscosity buildup) strongly limit the implementation of such processes on a large scale.

As radical polymerization necessitates much less restricting conditions and is employed for a wide range of monomers, there has been a strong impetus to design strategies allowing to control this kind of polymerization. Up to now, different processes have been employed. One of the pioneer work, developed by Rizzardo et al., consists of moderating the free radical reactivity by reversible termination with a nitroxide.[5] This discovery has stirred a lot of interest, as shown by the ever growing number of reports about this novel polymerization.[6] Soon after, it was realized that it is possible to tune the reactivity of a free radical via the mediation of organometallic compounds. The use of organometallic compounds has appeared to be an attractive strategy,[7] since it allows a greater tunability of the adduct formed by the metal and the free radical, but it can create some compatibility issues with reaction media such as water.

For the reversible termination scheme, the organic compound acts as a counter-radical which leads to a dormant polymer chain (Scheme 1).

Scheme 1



In this case, there is an equilibrium between the dormant polymer chain and the growing free radical, resulting in a net decrease of the growing chain concentration compared to conventional radical polymerizations. Therefore, as termination reactions are bimolecular processes in radical concentration, they become negligible compared to the propagation rate. Polymerization can thus be considered as living. Accordingly, the synthesis of monodisperse polymers in bulk homopolymerization[6] and block copolymerization,[7] as well as suspension and dispersion polymerization, has been possible.[8] Furthermore, particular strategy has employed by Hawker *et al.*[9] in order to design monodisperse, controlled molecular weight polymers with structural properties such as star-shaped, grafted, and telechelic polymers.

Although these recent advances are extremely promising, there could be a strong limitation if convenient suspension and emulsion processes are not found. Indeed, most of the work has been made in bulk or solution, whereas radical polymerization is most commonly carried out in emulsion or suspension. In a conventional emulsion polymerization, the use of water as continuous phase allows one to work at reduced viscosity at high volume concentration and high molecular weight, with fast reaction rates. It is also environmentally safe, and because of its high specific heat capacity, it can absorb easily the heat of polymerization. For these reasons, it would be therefore very interesting to obtain living radical polymerizations in emulsion. Nevertheless, the "living" character is expected to strongly impact on the typical features of emulsion polymerization, such as kinetics, nucleation, and colloid stability.

As far as we know, no attempt has been reported to describe a living radical polymerization in emulsion, ab initio. During this work, German *et al.*[10] reported a preliminary communication about seeded emulsion polymerization and showed that the molecular weight was increasing with conversion. Living character was thus preserved during the polymerization. Nevertheless, there were no data about the stability of the resulting emulsion, the particle size obtained, and the mechanism of particle growth. We concentrate here on these features, and we report the first ab initio living radical emulsion polymerization of styrene. The intrinsic difficulty in achieving such an experiment relies on several points.

First of all, temperatures as high as 130 °C are required for the polymerization to be possible. Indeed, lower temperatures only lead to inactive dormant chains. Emulsion polymerization is typically carried out under pressure, in a 200 mL stainless steel Schlenk tube or in a thick glass Schlenk tube, thermostated at 130 °C, with magnetic stirring being kept at 900 rpm.[11] A second aspect concerns the stability of such an emulsion. Indeed, a living polymerization is usually characterized by a slow propagation rate and therefore long reaction times. Most commonly used surfactants decompose under harsh conditions (high temperatures combined to long reaction times). We have observed that SDS was hydrolyzed during the polymerization, giving rise to dodecanol.[12] Other surfactants, such as dioctyl sulfosuccinate, sodium dodecyl benzenesulfonate (SDBS), Aerosol MA 80 and dodecyltrimethylammonium bromide are less prone to rapid decomposition, but give rise to latex flocculation and/or very low monomer conversions. Surprisingly, combination of amino TEMPO (**5**) and SDS give the best results. We infer that stabilization is offered by quaternary amino groups of amino TEMPO (and by the residual surfactant) since the pH in the emulsion is consistently found between 4 and 8, below the pK_a of an amine. Moreover, we suspect that the presence of dodecanol is a key factor to latex stabilization.[13] By introducing ab initio a fatty alcohol in the medium, the results obtained are better than those without any long alkyl chain alcohol (Table 1). A mixture of SDS, hexadecanol (1/1), **5**/KPS (3/1), and 100 equiv of styrene produces a stable emulsion (37.5% conversion corresponding to 5% solid contents emulsion after 36 h). Particle size distribution, as measured

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Table 1. Results Obtained with Different Nitroxides[a]

nitroxide	conversion (%)	$M_n \times 10^3$	PDI	reaction time (h)
Tempo	<1	9.8	1.31	47
hydroxy Tempo	<1	32.4	1.33	36
tert-butoxy Tempo	<1	47.4	2.3	78
carboxy Tempo	<1	1.4	1.19	12
amino Tempo				
expt a	0	1.84	1.23	23
	5.8	1.86	1.28	29
	37.6	2.1	1.34	44
expt b	9	1.5	1.14	16
	26	3.1	1.68	25
	37	4.7	1.78	36
expt c	61	5.4	1.76	47
	69	6.0	1.7	55
expt d	20.9	2.4	1.4	43
	40.6	3.9	1.4	109
expt e	0			18
	44.3	7.0	1.2	86
anionic alkoxyamine **A**	69	42	1.7	15

[a] Key: experiment a, without hexadecanol; experiments b and c, with hexadecanol; experiment d, V-50 as initiator; experiment e, preformed miniemulsion.

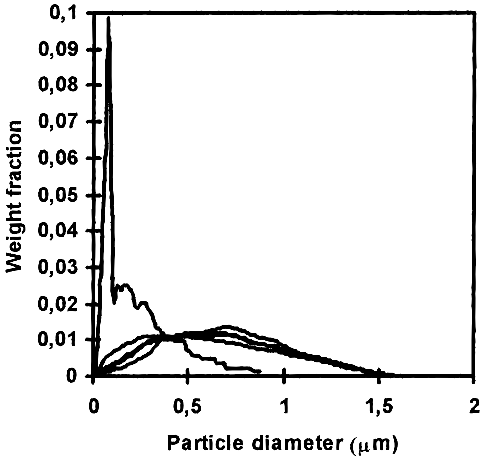


Figure 1. Particle size distribution of living latices, measured by FFF, using UV and on-line light-scattering detection. Plain lines: runs a–e (similar particle size distribution) Key: experiment a, weight average diameter d_w = 503 nm, PDI = 1.30; experiment c, d_w = 581 nm, PDI = 1.20; experiment d, d_w = 431 nm, PDI = 1.42; experiment e, d_w = 501 nm, PDI = 1.33. Dotted line: run with alkoxyamine A (bimodal particle size distribution).

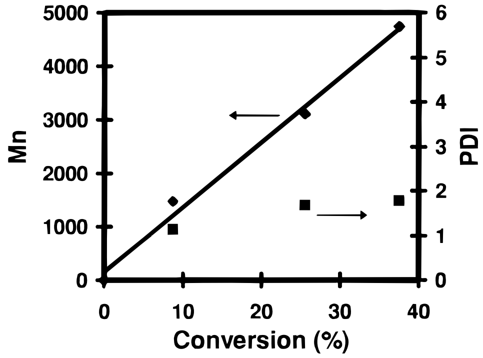
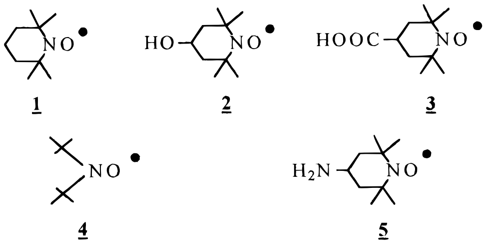


Figure 2. Variations of number average molecular weight and polydispersity index (PDI) with conversion.

Chart 1



separately by electron microscopy, photon correlation spectroscopy, and field flow fractionation (FFF), is not monodisperse (Figure 1) (weight average diameter = 540 nm, PDI = 1.3[14]). This emulsion is stable and can be stored at room temperature for several days. GPC analysis of different samples withdrawn from the reactor allows one to prove that molecular weight is increasing linearly with conversion and PDI remains low, which are characteristic of a living polymerization (Figure 2).

This experiment is reproducible, although final particle size, conversion, and molecular weight may slightly depend from sample to sample, likely because of the evasive nature of the nucleation process, which is dependent upon stirring rate. To date, it has been possible to reach 70% conversion after 55 h reaction, with no measurable floc. For this sample, the number average molecular weight is 6000, and the particle size distribution is broad, centered around 500 nm. In the presence of hexadecanol, it is also possible to obtain satisfying results when SDS is replaced by SDBS, which is less prone to hydrolysis.

We believe that these polymerizations offer interesting similarities with a miniemulsion process. Miniemulsion polymerization requires the formation of a stable submicrometer dispersion of monomer in water. The dispersion is only stable in the presence of a cosurfactant and is obtained by furnishing the system enough energy to rearrange in a miniemulsion state. We believe that these two characteristics are present in our recipes, since the usual mechanical energy applied to the system to reach a thermodynamically stable miniemulsion state is probably unnecessary at temperatures as high as 130 °C. Thus, we have conducted a living polymerization starting from a stable miniemulsion[15] which has been brought up to 130 °C. After 85 h of reaction, a stable latex is collected (5.4% solids, conversion greater than 45%), as well as a small amount of coagulated polymer. GPC analysis of both latex and coagulated polymer gives $M_n \approx 7000$ (PDI = 1.2). The particle size distribution of this miniemulsion latex is similar to that for the other latices (Figure 1).

To investigate whether the nature of the radical scavenger has an influence on the process, we have effected polymerizations with different nitroxides, keeping everything else unchanged (Chart 1).[12]

Nitroxides **1**, **2** and **3** are not satisfying as little polymer is produced (less than 1% conversion) before the latex completely coagulates. It is worth noting that, afterward, polymerization can proceed in a living fashion in bulk, up to high conversion. Typically, 32% conversion is obtained for the experiment realized with **1** and 61% conversion when using **2** in 36 h. With **4**, the reaction is performed at lower temperatures, which leads to a longer lifetime emulsion. Polymerization is nevertheless extremely slow; high molecular weights and large PDI values are reached. **5** is the only nitroxide which gives rise to a real emulsion. After 44 h of reaction, it is possible to isolate a latex with particle size in the range of 400 nm. GPC analysis on the dried polymer indicates a molecular weight of 8700, with a

Scheme 2

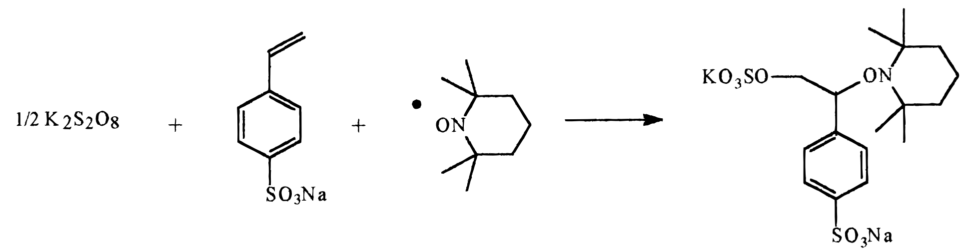


Table 2. Partition of Hydroxy and Amino TEMPO between Aqueous and Organic Phases in a Latex[a]

nitroxide	initial latex	aqueous phase (1 h)	aqueous phase (24 h)	aqueous phase (24 h with SDS)
hydroxy TEMPO	6.5	6.5	5.9	6.4
amino TEMPO	6.6	5.3	5.2	5

[a] The latex was composed of 153 nm monodiperse particles (4.9% solids) of polystyrene, cross-linked with divinylbenzene and carrying surface carboxyl functionalities.

narrow polymer index (PDI = 1.27). Obviously, the balance between aqueous and organic solubility of each nitroxide is to play a critical role in the nucleation process, which itself determines the outcome of the reaction. We believe that amino TEMPO offers the best compromise between aqueous and organic phase. Indeed, amino TEMPO is highly soluble in water (the solubility of pure hydroxy TEMPO and amino TEMPO are greater than 108 g·L^{-1} and 150 g·L^{-1}, at 25 °C). The polymer chains, created in water, rapidly end up in the organic phase, so that the spin trap must be able to follow the radical from aqueous to organic phase, in order for the polymerization to be living. With more hydrophobic spin traps, the polymerization is uncontrolled in the aqueous phase, where many radicals die. This translates into a departure from stoichiometry between spin trap and polymer chains in the organic phase and, ultimately, an extreme decrease of the polymerization rate. This phenomenon is observed by using TEMPO, for example, which solubility in water is far lower (the saturation concentration, as measured by UV-spectroscopy, is 10.6 g·L^{-1}). Despite its high water solubility, amino TEMPO is also soluble into polymer particles. This is demonstrated by the study of nitroxide partition between aqueous and organic phases in a latex (Table 2). For this purpose, nitroxide has been added to a cleaned latex. Upon analysis of the aqueous phase (by EPR), it has been observed that most hydroxy TEMPO is located in the aqueous phase, whereas a significant amount of amino TEMPO is present in the organic phase. The partition between both phases is not significantly affected either by the presence of additional surfactant (SDS) or by the delay between nitroxide addition and aqueous and organic phases separation.

Finally, the nature of initiator has little influence on the polymerization (experiment d, Table 1). This is totally expected, as, at these temperatures, the decomposition of typical emulsion intiators is instantaneous.

Although suitable spin trap and surfactant are now unraveled, it is still necessary to improve the colloidal stability in order to reach higher conversions. Thus, we have prepared an anionic alkoxyamine, **A**,[16] to improve the electrostatic stabilization of each living chain.

Using compound **A** for an initiator, it is possible to obtain a "living" latex in the absence of added surfactant. The polymer molecular weight distribution is narrow ($M_n \approx 10000$, PDI $\approx$ 1.2), yet above 2% solids, noticeable amounts of floc are observed along the emulsion. Using SDS or SDBS as additional surfactant, a living polymerization is obtained, which in all respects, is identical to the polymerization initiated by KPS.[17] However, it is possible to reach 69% conversion without flocculation. The average molecular weight of the polymer is 42000, and the PDI is 1.7. Moreover, the particle size distribution is bimodal, one peak being constituted of 70 nm monodisperse particles, accounting for 50% in weight of the latex, and the other being broad, centered around 200 nm. As expected, if 0.3 equiv of free amino TEMPO is added to the medium prior to polymerization, the PDI decreases to 1.2, but the polymerization rate drops appreciably.

In this paper, we describe the features of a living radical polymerization in emulsion. Although latices are usually obtained, the features of the polymerization do not resemble those characteristic of a conventional emulsion polymerization. In particular, the kinetics of the reaction is very different from a classical emulsion polymerization because of the presence of radical scavengers in the medium.

Amino TEMPO seems to be a suitable candidate for this polymerization, since it provides additional electrostatic stabilization and an optimized balance between hydrophilic and hydrophobic character. Evidently, further work needs to be done in this field, as many questions remain unanswered. For example, how would it be possible to reach conversions greater than 99% without flocculation? To bring a possible answer, we have synthesized an anionic alkoxyamine, which appears to be a suitable initiator for living emulsion polymerization. Current work concentrates on this issue, as well as on the synthesis of block copolymers in emulsion.

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(11) In a typical experiment, 69 g of water, 126.1 mg of amino TEMPO, 100.4 mg of KPS and 344.8 mg of SDS are added to 7.12 g of styrene in a metallic Schlenk tube. After three freeze−pump−thaw cycles, the mixture is stirred at 135 °C for 36 h, giving a latex. The resulting light scattering particle size is 430 nm. The average number molecular weight is 15000. PDI = 1.3. Conversion is followed by solid content analysis of samples withdrawn from the reactor during the course of the reaction. For this purpose, the temperature is slowly decreased to about 50 °C. At this temperature, the polymerization cannot proceed any more as the NO−C bond becomes unlabile.

(12) 21 h of reaction are necessary for dodecanol to be observed (GC analysis).

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(14) Polydispersity index of particle size distribution is defined here as the squared ratio of standard deviation to average plus one. This definition and the more classical one (M_w/M_n) are equivalent for molecular weight distribution.

(15) We thank a reviewer for suggesting this experiment. The miniemulsion was obtained by mixing with an ultra-turrax homogenizer the usual emulsion recipe components, AIBN instead of KPS, hexadecanol in equimolar amount relative to SDS, and TEMPO as nitroxide.

(16) The alkoxyamine was prepared by reacting 1 g of TEMPO, 1.3 g of KPS, and 1.63 g of styrene sulfonate in 10 mL water at 80 °C for 4 h. The resulting compound is recrystallized from hot ethanol. ^{1}H NMR (D_2O): 7.9 (2, H*aryl*), 7.6 (2, H*aryl*), 5.2 (0.8, Hα), 4.4 (1.2, Hβ), 1.5−0.7 (18, H*cyclohexyl*). ^{13}C 143.4, 142.4, 128.6, 125.8, 83.5, 70.1, 61.5, 39.8, 32.5, 20.7, 16.8. MS parent peaks: 474.3 g/mol ($A - Na^+$), 458.3 g/mol ($A - K^+$).

(17) In a typical experiment, 50 g of water, 57.1 mg of **A**, and 203 mg of SDBS are added to 5.3 g of styrene in a metallic Schlenk tube. After three freeze−pump−thaw cycles, the mixture is stirred at 135 °C for 15 h, and the emulsion is collected after cooling.

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