

# Fluorescence Spectroscopy as a Non Invasive Tool to Follow *In Situ* the Polymerization in Miniemulsion

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**ABSTRACT:** Miniemulsion polymerization is a powerful technique to produce a whole variety of latexes with controlled colloidal and chemical properties, which has gained an increasing importance in the past years. For many applications, the following of the kinetics of polymerization is of crucial importance. In this study, we developed a technique based on the use of fluorescent probes that could be a very promising noninvasive method to follow the reaction *in situ*. It was possible to follow qualitatively the kinetics of methyl methacrylate (MMA) polymerization by measuring the photophysical properties of fluorescent probes sensitive to the modifica-

tion of the viscosity of the microenvironment along the reaction course. Two fluorescent sensors have been considered: 1,1-dicyano-4-(4'-dimethylaminophenyl)-1,3-butadiene and pyrene. In this article, we will show that using these two different fluorescent probes allow the detection of MMA polymerization in miniemulsion. The results will be compared with a classical NMR method. This method could be easily adapted to different monomers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 219–224, 2011

**Key words:** fluorescence spectroscopy; pyrene; molecular rotor; miniemulsion polymerization; kinetics

## INTRODUCTION

Miniemulsion polymerization is a powerful technique to produce a whole variety of latexes of controlled colloidal and chemical characteristics.<sup>1</sup> The particles are preformed as oil droplets with a size of 50–500 nm already from the beginning of the reaction by shearing a system containing oil, water, a surfactant and a highly water insoluble compound, the so-called hydrophobe. The surfactant stabilizes the droplets against collisions and mass exchange (Ostwald ripening) between the droplets is strongly reduced by the used of the hydrophobe.<sup>2,3</sup> Each droplet is thought to behave as a nanoreactor, and the polymer particles produced have ideally the same size as the monomer droplets (Fig. 1).<sup>4</sup> This makes the miniemulsion process suitable for many reactions. For the formulation of miniemulsions, a wide range of ionic and nonionic surfactants have been used, leading to differently charged and stables latexes.<sup>5</sup> The use of biocompatible surfactants allowed the synthesis of nanoparticles with a hydrophilic and biocompatible outer layer, which are well suited for biomedical application for instance.<sup>6,7</sup> It was shown that the miniemulsion process can be

applied on a much broader range than only conventional radical polymerization. For instance controlled radical polymerization<sup>8</sup> (RAFT,<sup>9</sup> ATRP<sup>10</sup>), ionic polymerizations,<sup>11,12</sup> and polyadditions<sup>13</sup> can be performed in the dispersed state after emulsification. Finally, miniemulsion polymerization was used to obtain structured particles such as hybrid nanoparticles<sup>14,15</sup> or nanocapsules.<sup>16,17</sup>

The kinetics of miniemulsion polymerization was studied for many systems.<sup>9,15,18</sup> Even though each nanodroplet can be considered as a mass nanoreactor, colloidal factors have to be taken into account to explain the global kinetics of miniemulsion polymerization.<sup>19,20</sup> In the case of radical polymerization, the rate of polymerization was found to strongly depend on the particle size,<sup>21</sup> the nature and amount of hydrophobe<sup>22</sup> used to suppress the Ostwald ripening and the nature of the initiator.<sup>23–25</sup> In particular, the solubility in the two phases of the initiator and of the radicals formed after its decomposition has to be considered.<sup>26</sup>

In most of the cases, kinetics of miniemulsion polymerization was followed by taking samples during the reaction course. The samples are analyzed by usual techniques such as NMR, size exclusion chromatography, or IR spectroscopy for instance. This procedure is however time consuming and invasive and can perturb the polymerization process. Few methods are available to follow the *in situ* polymerization in miniemulsion. The most widespread noninvasive technique is based on calorimetric

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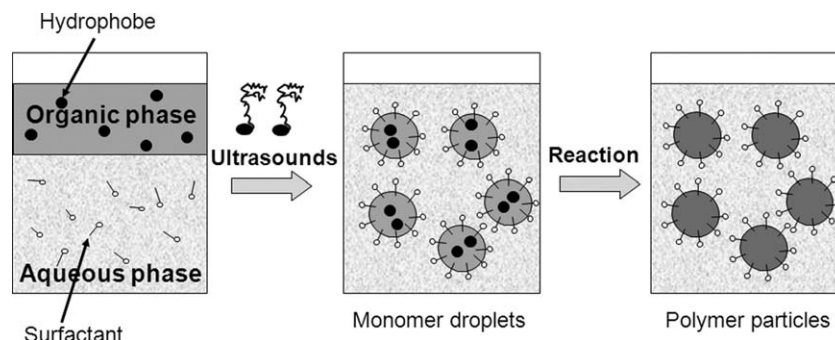


Figure 1 Principle of miniemulsion polymerization.

measurements.<sup>27</sup> However, this method requires some preliminary information such as the molecular heat of polymerization. In this study, we developed a technique based on the use of fluorescent probes that could be a very promising noninvasive method to follow the reaction *in situ*. It was possible to qualitatively follow the kinetics of miniemulsion polymerization by measuring the photophysical properties of fluorescent probes sensitive to the modification of the viscosity of the microenvironment along the reaction course. This technique does not require preliminary knowledge about the physical properties of the monomer (such as heat of polymerization for instance) and could be used for very different monomers and polymerization mechanisms.

Fluorescence spectroscopy is a powerful tool for imaging, sensing, and security applications.<sup>28</sup> Many teams are involved in the development of brighter, more stable and environmentally robust fluorescent probes such as quantum dots for biosensing and bioimaging.<sup>29</sup> Nevertheless, classical organic fluorescent probes are still used and can bring important information on the microenvironment of the probe. The use of a molecular rotor (1,1-dicyano-4-(4'-dimethylaminophenyl)-1,3-butadiene) and pyrene as fluorescent probes was proved to be of great interest to study macromolecules organization such as humic acids<sup>30,31</sup> or polymers.<sup>32</sup> Molecular rotors or pyrene as sensors for polymers have been used for example for the detection of the glass effect in the bulk polymerization of methyl methacrylate (MMA) taking advantage of the viscosity change,<sup>33</sup> to detect the hydrophobic microdomains in amphiphilic polymers due to the change in both polarity and the viscosity when the aggregation is performed.<sup>34</sup> Up to now, no data can be found concerning the use of these fluorescent probes to follow the kinetics of polymerization in miniemulsion. In this study, the change in the viscosity induced by the MMA polymerization in miniemulsion was followed by recording the variation of the photophysical properties of pyrene and molecular rotor. The fluorescent curves obtained were compared with the conversion curves obtained by analysis of aliquots by <sup>1</sup>H-NMR.

## EXPERIMENTAL PART

### Materials

Pyrene was purchased from Fluka and recrystallized at least 3 times from ethanol. The other chemicals were from Aldrich (St Quentin Fallavier, France). MMA was distilled under reduced pressure prior to utilization. The other chemicals were used as received. MilliQ water was used for all the experiments.

### Synthesis of the molecular rotor

The fluorescence rotor was synthesized by a Knoevenagel's reaction between (4-dimethylamino)-cinnamaldehyde and malonitrile.<sup>35</sup>

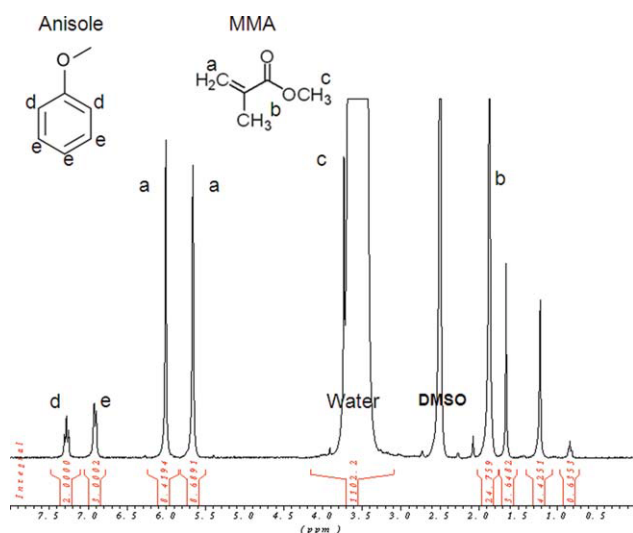
### Miniemulsion polymerization of MMA

250 mg of Lutensol (ethoxylated nonyl phenol) were dissolved in 18 g of MilliQ water. The organic phase always contains 2 g of MMA, 120 mg of hexadecane (6 wt % related to monomer), and 100 mg of AIBN (2,2'-azo-bis-isobutyronitrile). For fluorescence analysis, pyrene ( $[\text{pyrene}]_{\text{MMA}} = 10^{-3}$  M) or molecular rotor ( $[\text{rotor}]_{\text{MMA}} = 10^{-5}$  M) was added to the organic phase prior to emulsification. For NMR spectroscopy, anisole (20 wt % in MMA) was added to the organic phase. After stirring one hour, emulsification was achieved via sonication (pulsed mode, 10 W, 3 minutes) using a Vibracell model 600 W (Sonics & Materials, Danbury, CT). To avoid polymerization due to heating, the mixture was ice-cooled during sonication.

Polymerization was performed at different temperatures directly in the quartz cell of the spectrofluorimeter or in a nitrogen-flushed flask. In the last case, samples were taken during the reaction for <sup>1</sup>H-NMR analysis.

### Instrumentation

Steady-state fluorescence measurements were performed on a Fluorolog-2 spectrofluorimeter 1681



**Figure 2** Typical  $^1\text{H-NMR}$  spectrum of aliquots of MMA miniemulsion. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

(SPEX), equipped with a thermostated cell compartment, using 1.9 nm slits for both excitation and emission monochromators. Pyrene excitation wavelength was set at 342 nm and the emission was collected at 393 and 469 nm. Rotor excitation wavelength was set at 475 nm and the emission fluorescence measured at 565 nm.

Particles sizes were measured by dynamic light scattering at low concentration using a HPPS-ET from Malvern. Although this apparatus is able to measure relatively concentrated samples, the emulsions and latexes were diluted in pure water.

NMR spectra were performed on a Brüker Avance 300. Two to three drops on miniemulsion were directly diluted in  $d_6$ -DMSO for  $^1\text{H-NMR}$  analysis. Direct comparison of the integrals of the signals pertaining to anisole and integrals of singlet corresponding to the monomer double bond allows the determination of the conversion (Fig. 2).

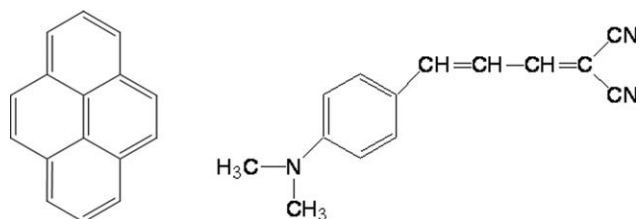
## RESULTS AND DISCUSSION

This study aims at developing a sensitive and easy technique for the on line monitoring of miniemulsion polymerization. Indeed, most of the techniques available nowadays are conducted off-line with a significant delay in information, mainly by analyzing aliquots taken from the reaction medium by NMR techniques or size exclusion chromatography measurements for instance. Fluorescence spectroscopy appeared to be a powerful tool to follow the kinetics of polymerization as we proved few years ago, by studying the mass polymerization of MMA with two fluorescent probes, pyrene and a molecular rotor (Fig. 3).<sup>33</sup>

Pyrene is a well-known fluorescent compound that can be used both as polarity and viscosity probe. It was already tested as a sensor for investigations of low-conversion polymerization of MMA<sup>36</sup> and it was proven that it did not affect the polymerization kinetics. Furthermore, the fluorescence remained unchanged even in the presence of other molecules such as AIBN or decomposition products. Vibronic structure of the monomer fluorescence depends on the polarity of the medium: the ratio  $I_1/I_3$  increases with an enhancement of the polarity ( $I_1$  and  $I_3$  are respectively the emission bands 1 and 3).<sup>37</sup> Moreover, the intermolecular formation of the excimer, which occurs at high-pyrene concentration, depends on the lateral diffusion in the medium: an increase of the local viscosity limits the diffusion of the ground state pyrene molecules toward the excited state pyrene ones leading to a decrease of the ratio  $I_{\text{ex}}/I_{\text{mon}}$ , where  $I_{\text{ex}}$  is the maximum fluorescence intensity of the excimer and  $I_{\text{mon}}$  the fluorescence intensity of the monomer.

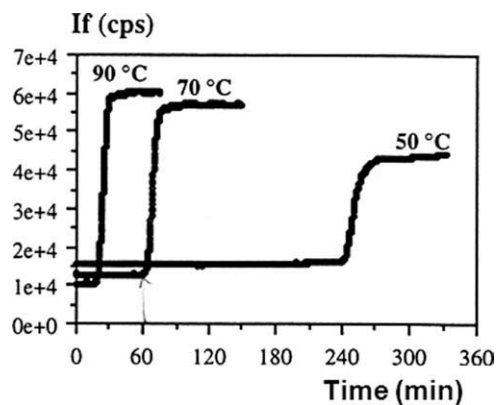
Molecular rotors of the type benzylidene or cinnamylidene can also be used both as polarity and viscosity probes. Indeed, their fluorescence maximum wavelength at the maximum is dependent of the polarity of the microenvironment: an increase of the polarity enhances the stability of the charge transfer state that lead to a red shift of the fluorescence spectrum. Moreover, their fluorescence quantum yield depends on the viscosity of the microenvironment: an increase of the local cohesion induces a diminution of the medium free volume with a decrease of the intramolecular rotor motion, thus an increase of the radiative deactivation processes. Because of the presence of unsaturated groups, the molecular rotors may be expected to combine themselves but it has been showed<sup>38</sup> that the rotor is in monomeric form below 0.03 M.

In the first set of experiments, performed few years ago,<sup>33</sup> mass polymerization of MMA was studied, simply by following the fluorescence data of a pyrene or molecular rotor solution in MMA, after the addition of AIBN initiator in the spectrofluorimeter cell. Figure 4 shows the time variation of the molecular rotor maximum fluorescence intensity for MMA mass polymerization at different temperatures. All three



**Figure 3** Chemical structure of pyrene (left) and molecular rotor (right).



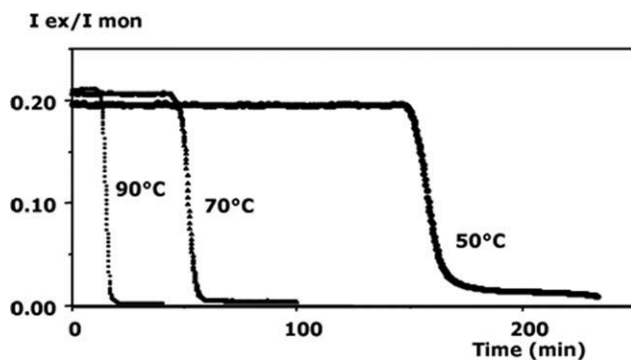


**Figure 4** Time variation of the fluorescence intensity of cinnamylidene rotor (in cycles per second) during the batch polymerization of MMA at three different temperatures.

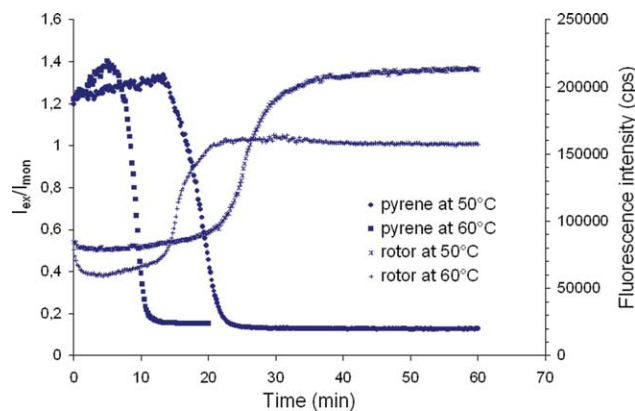
curves exhibited the same sigmoid shape: fluorescence intensity remained roughly constant in the first period, and then rose within few minutes before reaching a well-defined plateau. In mass polymerization, the intensity in the first period was observed to be lower for the higher bulk temperature. Indeed, higher temperature favors the intramolecular motions, such as rotations, to the detriment of fluorescence. The time of fluorescence intensity rose was shorter at higher temperature, which is consistent with an increase of polymerization rate at higher temperature.

Figure 5 shows the time variation of the ratio  $I_{ex}/I_{mon}$  intensity of pyrene for MMA mass polymerization at different temperatures. The first period of the kinetics is characterized by a high and roughly constant  $I_{ex}/I_{mon}$  ratio, followed by a sharp decrease to reach a low-residual level. Indeed, the increase of the medium viscosity hindered the formation of excimer.

In both cases, it is possible to correlate the abrupt change in the photophysical properties to a change in the local viscosity of the MMA mass polymerization medium. Nevertheless, it is interesting to notice that the change happens at different times considering py-



**Figure 5** Time variation of the ratio of excimer fluorescence intensity to monomer fluorescence intensity of pyrene (in cycles per second) during the batch polymerization of MMA at three different temperatures.



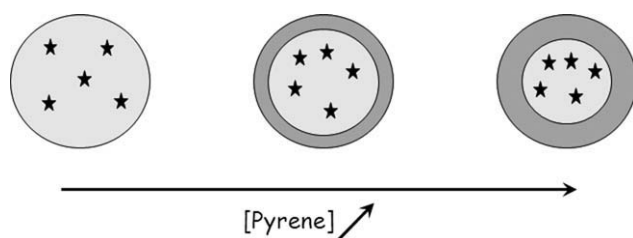
**Figure 6** Variation of (axis on the left) the ratio of excimer fluorescence intensity to monomer fluorescence intensity of pyrene (in cycles per second) during the miniemulsion polymerization of MMA at 50 and 60 °C. (axis on the right) the fluorescence intensity of cinnamylidene rotor (in cycles per second) during the miniemulsion polymerization of MMA at 50 and 60 °C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

rene or the molecular rotor. Indeed, concentration of pyrene excimer depends on the translation diffusion of two molecules. The free volume of solvent required for the excimer formation is thus greater than the free volume needed for the molecular rotor internal motions.<sup>39</sup> Therefore, a low increase of the viscosity could hinder the excimer formation without affecting the internal motion of the rotor.

This same strategy has been used to follow the MMA polymerization in miniemulsion. Miniemulsion of MMA was prepared by emulsifying a mixture of MMA, AIBN, and hexadecane in the surfactant solution by means of sonication. Pyrene or molecular rotor was added to the monomer prior to emulsification. Fluorescence emission could be followed as a function of time and temperature and reproducibility of experiments was checked.

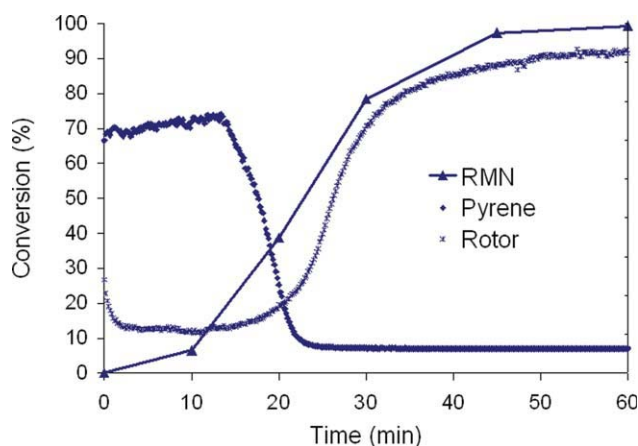
Figure 6 shows the variation of the ratio  $I_{ex}/I_{mon}$  intensity of pyrene and the variation of the molecular rotor maximum fluorescence intensity for MMA miniemulsion polymerization at 50 and 60 °C. When the molecular rotor was used, fluorescence intensity increased slowly in the first period then raised within a few minutes before reaching a well-defined plateau. The time of fluorescence intensity rose was shorter at higher temperature, which is consistent with an increase of polymerization rate at higher temperature. When pyrene was used, the  $I_{ex}/I_{mon}$  ratio first slightly increased, before sharply decreasing to reach a low-residual level. Once more, it is possible to correlate the abrupt change in the photophysical properties to a change in the local viscosity of the MMA mass polymerization medium.

However, a surprising effect was observed when pyrene was used as fluorescent probe. In the early

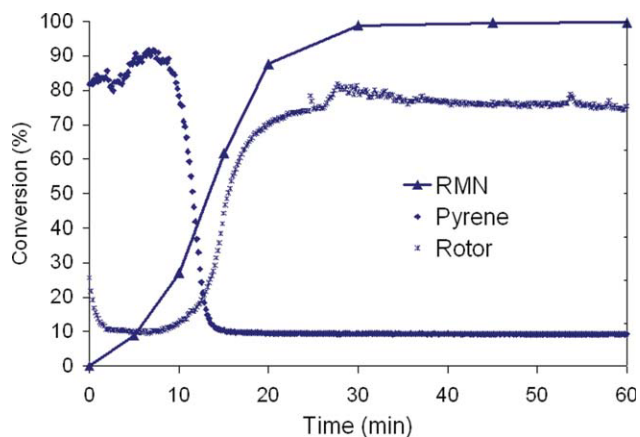


**Figure 7** Schematic representation of the early stage of the miniemulsion polymerization.

stages of the polymerization, an increase of the  $I_{ex}/I_{mon}$  ratio was observed. This was first attributed to an increase of the mobility of the pyrene molecules due to a slow stabilization of the temperature in the cell. However, this increase was not observed at the same temperature for a miniemulsion, which did not contain a polymerization initiator. The ratio  $I_{ex}/I_{mon}$  was constant in that case. The increase of the  $I_{ex}/I_{mon}$  ratio observed in the presence of an initiator has thus to be correlated to the polymerization mechanisms. Authors claimed that radicals produced by the thermal decomposition of AIBN go out of the droplets before entering the droplets again.<sup>25</sup> Polymerization could thus be initiated from the surface of the droplets, leading to a concentration of the pyrene in the unreacted liquid monomer. The apparent concentration of pyrene will thus increase. However, this process is only visible at the beginning of the polymerization (Fig. 7). To confirm this hypothesis, a water soluble initiator, KPS, was used to initiate the miniemulsion polymerization of MMA. In that case, radicals are directly produced in the aqueous phase and enter the droplets. The polymerization thus starts from the interface. In that



**Figure 8** Superposition of the conversion curve obtained by NMR, fluorescence intensity of the ratio of excimer to monomer fluorescence intensity of pyrene (in cycles per second) and fluorescence intensity of cinnamylidene rotor (in cycles per second) during the miniemulsion polymerization of MMA at 50°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9** Superposition of the conversion curve obtained by NMR, fluorescence intensity of the ratio of excimer to monomer fluorescence intensity of pyrene (in cycles per second) and fluorescence intensity of cinnamylidene rotor (in cycles per second) during the miniemulsion polymerization of MMA at 60°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

case, the increase of the  $I_{ex}/I_{mon}$  ratio at the beginning of the polymerization was indeed more pronounced (data not shown). Further experiments are however required to confirm this hypothesis.

To correlate the abrupt change in the photophysical properties observed to a monomer conversion, miniemulsion polymerization of MMA was performed in a nitrogen-flushed flask. Samples were taken during the polymerization and analyzed by  $^1\text{H-NMR}$  in DMSO without any purification (Fig. 2). The addition of an internal standard (anisole) in MMA allowed the quantification of the amount of reacted monomer. The obtained results were compared with the curve obtained by fluorescence spectroscopy (Figs. 8 and 9).

There is a direct correlation between the sharp increase of the fluorescence quantum yield of the molecular rotor and the increase of the monomer conversion. Molecular rotor is thus well suited to detect the end of the polymerization. On the contrary, the rapid decrease of the  $I_{ex}/I_{mon}$  ratio occurs for conversion below 50%. Pyrene cannot be used to detect the end of the polymerization. However, additional information could be obtained on the polymerization mechanism by using this fluorescent probe. Pyrene could thus be used to study in detail the mechanism of miniemulsion polymerization.

## CONCLUSION

To the best of our knowledge, this study reports for the first time the use of fluorescence spectroscopy to follow the *in situ* miniemulsion polymerization of MMA. For many applications, the following of the

kinetics of miniemulsion polymerization is indeed of crucial importance. In most of the cases, samples are taken during the reaction and quenched before analysis by methods such as NMR or GPC for instance. This procedure is invasive and can perturb the polymerization process. In this study, we developed a technique based on the photophysical properties of fluorescent probes sensitive to the modification of the viscosity of the microenvironment along the reaction course. This technique does not require preliminary knowledge about the physical properties of the monomer (such as heat of polymerization for instance) and could be used for very different monomers and polymerization mechanisms. Two sensors have been considered: 1,1-dicyano-4-(4'-dimethylaminophenyl)-1,3-butadiene and pyrene.

In the case of pyrene, polymerization led to a sharp decrease of the  $I_{\text{ex}}/I_{\text{mon}}$  ratio. In the case of molecular rotor, a sharp increase of the fluorescence intensity was observed with time. There is a direct correlation between the abrupt change in the photophysical properties observed and the monomer conversion. Molecular rotor is well suited to detect the end of the polymerization. On the contrary, the rapid decrease of the  $I_{\text{ex}}/I_{\text{mon}}$  ratio occurs for conversion below 50%. Pyrene cannot be used to detect the end of the polymerization. However, additional information could be obtained on the polymerization mechanism by using this fluorescent probe. Pyrene could thus be used to study in depth the mechanism of miniemulsion polymerization, which is still under discussion.

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