

A sensitive fluorescence method for monitoring the kinetics of microemulsion polymerization

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Abstract: We present a fluorescence method that allows one to monitor the kinetics of microemulsion polymerization of very low monomer contents (water-to-monomer ratio can readily be superior to 1000). The microemulsion polymerization of methyl methacrylate (MMA) was investigated using *N*-(2-anthracene)methacrylamide (AnMA) as the probe whose fluorescence emission intensity was proportional to the conversion of MMA into the polymer. The real-time-measurement results show that in the regime of very low monomer contents, the surfactant exerted a profound effect on the kinetic process. In a microemulsion containing 0.1 wt% of MMA with respect to water, with the anionic surfactant of sodium dodecyl sulfate (SDS), the fast polymerization was preceded by an induction period whose length increased with reducing the concentration of the water-soluble initiator of potassium persulfate (KPS). By contrast, with the non-ionic surfactant of polyoxyethylene (20) oleyl ether (Brij98), the induction period was short and the decrease in the KPS concentration mainly resulted in a decrease of the reaction rate. The unprecedented sensitivity of this fluorescence method made it possible to access kinetic data of microemulsion polymerization with very low monomer contents for the first time, providing new insight into the effects of surfactant and initiator on this heterophase polymerization process.

Key words: microemulsion polymerization, reaction kinetics, fluorescence spectroscopy, characterization method.

Résumé : On a mis au point une méthode de fluorescence qui permet de suivre la cinétique de polymérisation en microémulsion à des teneurs très faibles de monomères dans lesquelles le rapport d'eau à monomère peut facilement être supérieur à 1000. On a étudié la polymérisation en microémulsion de méthacrylate de méthyle (MAM) en utilisant le *N*-(2-anthracène)méthacrylamide (AnMA) comme sonde dont l'intensité d'émission de fluorescence était proportionnelle à la conversion du méthacrylate de méthyle en polymère. Les résultats de mesures en temps réel montrent que dans le régime impliquant de très faibles teneurs en monomère, l'agent de surface exerce un effet important sur le processus cinétique. Dans une microémulsion contenant 0,1 % en poids de MAM par rapport à l'eau et du dodécylsulfate de sodium (DSS) comme agent de surface anionique, la polymérisation rapide est précédée d'une période d'induction dont la longueur augmente avec la réduction de la concentration du persulfate de potassium (PSK), l'initiateur soluble dans l'eau. Par opposition, avec l'éther oléyle du polyoxyéthylène (20) (Brij98), un agent de surface non ionique, la période d'induction est courte et une diminution de la concentration de persulfate de potassium conduit à une réduction de la vitesse de réaction. La sensibilité sans précédent de cette méthode de fluorescence permet d'obtenir pour la première fois des données cinétiques pour la polymérisation en microémulsion avec de très faibles teneurs en monomère et d'en tirer des conclusions sur les effets des agents de surface et de l'initiateur sur le processus de polymérisation en hétérophase.

Mots-clés : polymérisation en microémulsion, cinétique de la réaction, spectroscopie de fluorescence, méthode de caractérisation.

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Introduction

The kinetics of microemulsion polymerization has been extensively investigated.^{1–10} Generally, to monitor the kinetics, aliquots of the oil (monomer) in water (o/w) reaction mixture are removed over the course of polymerization at

various time intervals; by measuring the polymer concentration formed over time, kinetic data can be obtained. Using this method, understandably, one needs a large volume of the reaction solution and a high monomer content (e.g., > 3 wt% with respect to water) to obtain data with an appreciable precision. There are also several real-time monitoring

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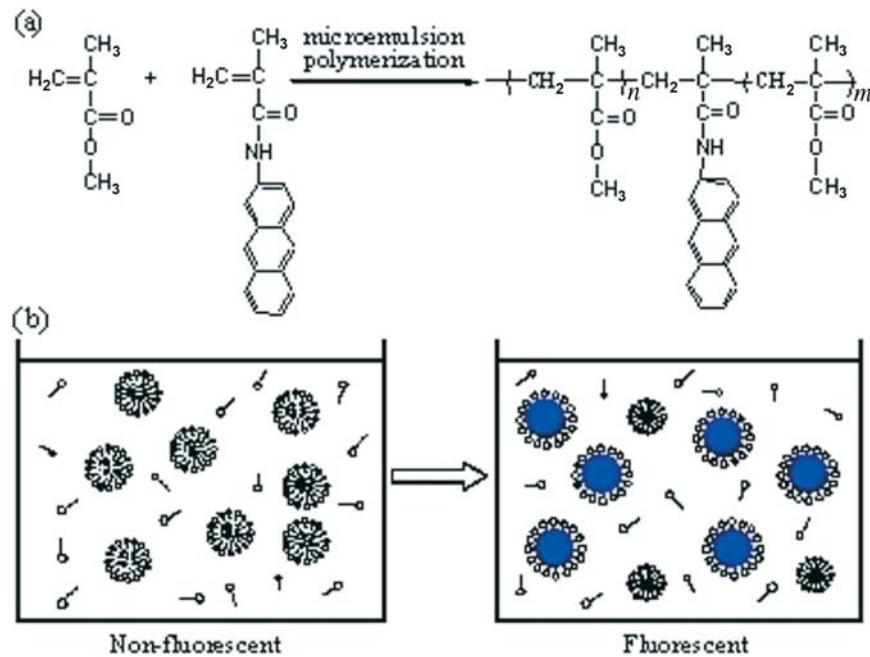
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Fig. 1. Chemical structures of the monomers and schematic illustration of the microemulsion-polymerization-induced fluorescence emission.



techniques that have been utilized to study the kinetics of microemulsion (and miniemulsion) polymerizations. These include the dilatometry that measures the volume change of the reaction liquid in a capillary upon polymerization,³ the reaction calorimetry that measures the heat released from the polymerization over time,^{8,9} and the laser Raman spectroscopy that probes the breaking of C=C double bonds in a vinyl polymerization.² In terms of sensitivity, the calorimetric method is better, allowing the use of low monomer contents around 0.5 wt%.⁸

Although a microemulsion is a thermodynamically stable, transparent solution, the polymerization is a heterophase reaction process, since it takes place inside nanometer-sized monomer droplets (~5–10 nm) stabilized by a large number of surfactant molecules. In a microemulsion, there are also empty micelles, dissolved surfactant molecules, and either a water-soluble or monomer-soluble initiator.^{1–10} It is of fundamental interest to know what happens when the monomer content becomes very low. For instance, is the polymerization kinetics affected by reducing the monomer concentration while keeping the same concentrations of surfactant and initiator? Can the kinetics reveal some sort of transition from a heterogeneous to homogeneous polymerization when the monomer concentration is extremely diluted? The above-mentioned experimental techniques cannot access this regime of very low monomer contents. In this paper, we report a very sensitive fluorescence-based method that can yield kinetic data on microemulsion (or miniemulsion) polymerization using monomer content as low as 0.0035 wt% (or water-to-monomer ratio of 28 000)!

The method used is based on previous reports of Warman and co-workers.^{11–14} They have developed a series of fluorescent probes and used them to study radiation-induced polymerization. The fluorescent probes are polymerizable monomers (with a C=C double bond) and have the distinct feature to be completely nonfluorescent in the monomer

form but become fluorescent upon polymerization as the double bond is saturated. In particular, Frahn et al. showed that *N*-(2-anthracene)methacrylamide (AnMA) could be used as a fluorescent probe to monitor the Gamma-ray induced free-radical polymerization of methyl methacrylate (MMA) in bulk and in solution, and found that the ratio of the chain-propagating rate constants for the reactions of an MMA free radical with AnMA and with MMA is 0.96.¹⁴ This means that the increase in the fluorescence emission intensity over time could reflect closely the kinetic process of the free-radical polymerization of MMA. In the present study, we used AnMA as the probe to investigate the microemulsion polymerization of MMA with very low monomer contents. The great sensitivity of the fluorescence appearing upon polymerization, as schematically illustrated in Fig. 1, allowed us to access kinetic data in this regime for the first time. Among the results, the real-time measurements show a more important effect of the used surfactant on the kinetics with very low monomer content than with relatively high monomer content.

Experimental

Materials

Unless otherwise stated, all chemicals were purchased from Aldrich. For the monomers, methyl methacrylate (MMA, 98%) was passed through a basic alumina column prior to use. *N*-(2-Anthracene)methacrylamide (AnMA) was synthesized using a literature method,¹³ it was purified by recrystallization from a methylene chloride/hexane mixture (4:1, v/v). The two used surfactants were sodium dodecyl sulfate (SDS, 99%), which is an anionic surfactant, and polyoxyethylene (20) oleyl ether (Brij98, 99%), which is a non-ionic surfactant. For the free-radical initiators, the water-soluble potassium persulfate (KPS, 99.99%) was used as received, and the water-insoluble 2,2'-azobis(isobutyronitrile) (AIBN) (from Polysciences) was recrystallized twice from ethanol. For

other chemicals, tetrahydrofuran (THF, 99%) was distilled from sodium benzophenone, while hexadecane (99%) and hexyl alcohol (98%) were used without further purification.

Preparation and monitoring of microemulsion polymerization

An example of experiment is detailed as follows: SDS (0.3 g, 1.04 mmol) was dissolved in 10 g of deionized water (0.56 mol) in a 25 mL round-bottom flask. AnMA (0.15 mg, 0.00057 mmol) was dissolved in a solution of hexyl alcohol, a costabilizer, (0.03 g, 0.29 mmol), and MMA (0.3 g, 3 mmol). Then, the liquid mixture of monomers containing AnMA was added dropwise into the aqueous solution at room temperature. After 5 min ultrasound sonication (60 W, 40 KHz), KPS (5 mg, 0.0185 mmol) was added. After another 1 min sonication, an aliquot of the microemulsion was transferred into a standard quartz fluorescence cuvette (1 cm × 1 cm × 3 cm), purged with argon gas for 15 min and sealed with a Teflon stopper and a Parafilm tape. Afterwards, the cuvette was placed in the spectrometer's sample holder, pre-heated to 60 °C, and the fluorescence emission (whole spectrum or intensity at a wavelength) was recorded after 1 min required for thermal equilibrium of the solution.

In case where Brij98 was the surfactant, hexadecane was used as costabilizer (10 wt% with respect to Brij98). In all reactions, the same extremely low fluorescent-probe concentration was used (0.19 mmol AnMA in 1 mol MMA) to ensure that AnMA remained part of the monomer even with a very low monomer content in the microemulsion. In the control test using relatively high monomer content, the increase in the amount of polymer over time was determined by using the conventional method. Aliquots of the reaction solution were taken at various time intervals, poured into cold methanol (cooled by ice), and the precipitated polymer was filtered, dried under vacuum, and weighed to calculate the monomer conversion defined as: Conversion (%) = $W_p/W_m \times 100\%$, where W_p is the mass of the obtained PMMA and W_m is the known mass of the monomer. In this paper, the monomer content and the surfactant concentration are mass-percentages with respect to water, while the concentration of initiator is mass-percentage with respect to the monomer.

Characterizations

Steady-state fluorescence emission spectra were recorded using a fluorescence spectrophotometer (Varian Cary Eclipse). The excitation and emission slit widths were set at 5 nm, and the scan rate was 10 nm s⁻¹. Real-time monitoring of the emission intensity at a chosen wavelength could also be carried out. For all measurements, the excitation wavelength was 337 nm; and for the kinetic data, the emission intensity at 425 nm was measured. Unless otherwise stated, the reported fluorescence intensities were not scaled. They were recorded under the same conditions (same volume of reaction solution, same excitation and emission slit widths). Since the concentration of AnMA was kept constant in MMA, the different fluorescence intensities result from different monomer concentrations in the microemulsion.

Results and discussion

We first attempted to validate the fluorescence method by

using a microemulsion containing 3% of the monomer, with which the conventional method can be utilized to determine the reaction kinetics. Figure 2 shows the results, together with the composition of the solution. In Fig. 2a, the fluorescence emission spectra of the solution were recorded as a function of time. While the solution was virtually nonfluorescent before the reaction, the fluorescence emission increased over time, indicating a growing number of AnMA monomers polymerized with MMA. In Fig. 2b, the plot of fluorescence intensity, f , at 425 nm vs. time is given, showing a fast increase within the first 10 min before reaching a plateau. The first derivative of the plot, df/dt , yielded the change of the reaction rate over time (the profile of the rate curve is better seen from the smoothed line). The result is typical of a microemulsion polymerization, showing that the polymerization rate rose to a maximum value and then decreased to zero without an interval of constant reaction rate. Shown in Fig. 2c is the conversion curve obtained by measuring the polymer concentrations at various reaction times. It is seen that within experimental error, the plot of fluorescence intensity vs. time corroborates well the kinetics measured using the conventional method. However, it should be emphasized that the fluorescence result represents better the reaction kinetics due to its sensitivity. Using the conventional method, oligomers can be washed away upon polymer precipitation, while with the fluorescence method, they can be detected. Apparently, the maximum fluorescence intensity corresponds to a monomer conversion of about 60%. These results indicate that this fluorescent probe reveals correctly the kinetics of microemulsion polymerization of MMA. We mention that for the experiments with very low monomer contents to be discussed below, we were mainly focused on the kinetic aspects. Due to the few nanoparticles formed, the characterizations of actual conversion, molecular masses, and particle morphology could not be performed with certainty.

Before discussing the results obtained with low monomer contents, Fig. 3 is meant to emphasize that, with the used surfactant concentration, all polymerizations were performed with a microemulsion. The highest MMA content used was 3%, and with 3% of either SDS or Brij98, the solutions are basically transparent (Fig. 3, images A and B), in contrast with, for comparison, a solution with only 0.3% of SDS (Fig. 3, image C). However, the microemulsion with the non-ionic surfactant Brij98 appears less transparent than the solution with the anionic surfactant SDS, reflecting the difference between the two surfactants. The surfactant concentration was kept the same with lower MMA contents.

In a microemulsion, with the same concentrations of surfactant and water-soluble initiator, what could be the effect on the kinetics by diluting the monomer to a very low concentration? Fig. 4 shows the results obtained with a set of experiments designed to answer the question, using two different surfactants and, for each of them, three monomer concentrations (actual compositions of the solutions are shown in the figure). The fluorescence curves obtained with 0.5% and 0.1% of MMA are magnified by a factor as indicated in the figure, since a lower monomer content means less fluorescent AnMA units in the polymer. While the kinetics appears similar with the two surfactants at the rather high monomer content of 3%, it is drastically different at the low

Fig. 2. (a) Fluorescence emission spectra ($\lambda_{\text{ex}} = 337 \text{ nm}$) recorded at various polymerization times; (b) plots of fluorescence emission intensity at 425 nm, (f) and the first derivative (df/dt) vs. time; and (c) plot of conversion (%) vs. time for a microemulsion containing 3 wt% of MMA with respect to water (the composition of the reaction solution is indicated).

MMA (g)	H ₂ O (g)	KPS (mg)	Brij98 (g)	Hexadecane (g)	MMA/H ₂ O (wt %)
0.3	10	5	0.3	0.03	3

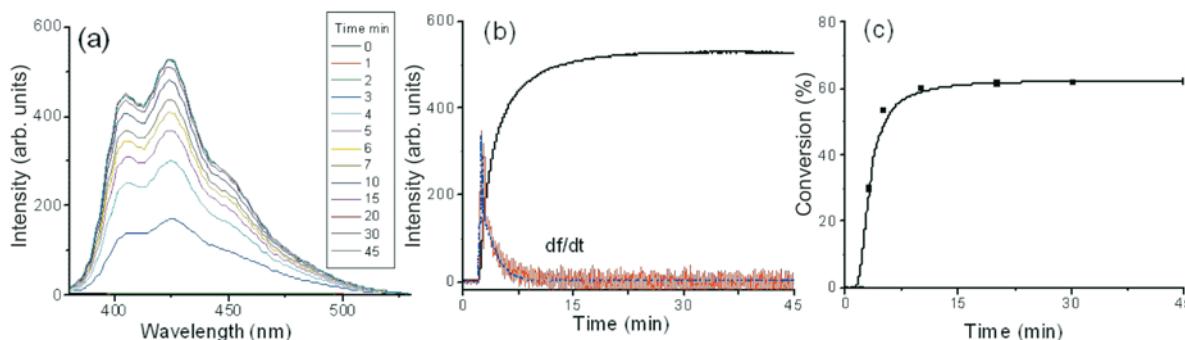
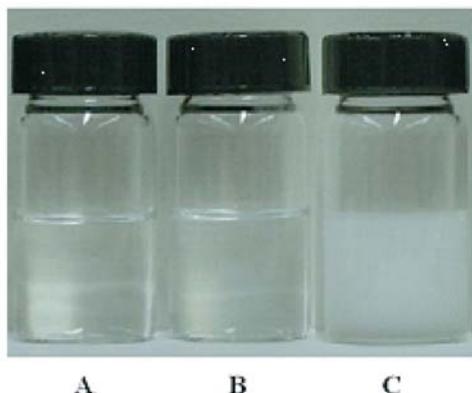


Fig. 3. Photographs of a microemulsion containing 3% MMA with 3% SDS (image A), a microemulsion containing 3% MMA with 3% Brij98 (image B), and an emulsion containing 3% MMA and 0.3% SDS (image C).

Sample	MMA (g)	Water (g)	SDS (g)	Brij98 (g)	Hexyl alcohol (g)	Hexadecane (g)
A	0.3	10	0.3	0	0.03	0
B	0.3	10	0	0.3	0	0.03
C	0.3	10	0.03	0	0.003	0



contents of 0.5% and 0.1%. With SDS as the surfactant, there appeared an induction period before the reaction took place, which became longer with reducing the monomer concentration. By contrast, using Brij98 as the surfactant, the reduction of the monomer concentration resulted in a decrease in the rate of polymerization. In all cases, the polymerization rate profiles (dotted lines) are also shown. A couple of analyses can be made. On the one hand, with the same surfactant, if only the number of monomer droplets was diminished with lower monomer content (more empty micelles in the solution), each droplet would be surrounded by initiator molecules of the same concentration and, consequently, the kinetics should not be changed. The results in Fig. 4 show that this is not the case, suggesting that at a very low concentration of monomer, the monomer droplet

size and the concentration of surfactant molecules adsorbed at the interface may be different, which changes the dynamic nature of the monomer-swollen micelles and the entry of primary free radicals in the droplets to initiate the polymerization. On the other hand, the very different kinetic behaviours observed with the two surfactants should reflect, among others, their different micellization abilities and interaction natures with MMA. The kinetic results indicate that the initiation of polymerization takes place more rapidly with Brij98 than with SDS, but after the initiation, the polymerization rate is slower with the former than with the latter. With SDS, the monomer droplets are covered by an outer layer of anionic sulfate groups, while with Brij98, they are surrounded with nonionic ethylene glycol units. The two surfactants are also very different in size (molar mass of 288 g for SDS as compared with about 1150 for Brij98), which means, at the same mass-based concentration, very different numbers of surfactant molecules interacting with the monomer droplets. These differences could affect the number and size of monomer droplets and the entry of primary radicals required to initiate the polymerization. It may appear more reasonable to use the same molar concentration for the two surfactants, but still this may just have a different effect on the number and size of monomer droplets, and on the density of adsorbed surfactant molecules. Clearly, it is the combination of those factors that dictates the reaction kinetics. At this point, we can only speculate the reasons for the observed differences; a clear understanding requires further studies by varying systematically the reaction conditions.

We then investigated the effect of the initiator concentration on the kinetic process with a very low monomer content of 0.1%, while keeping the surfactant concentration unchanged. Again, the two surfactants were utilized, and the results are shown in Fig. 5. With SDS as surfactant, the decrease of the water-soluble initiator concentration resulted in an increase in the induction period preceding the starting of polymerization and a slight decrease in the polymerization rate as well. At the lowest KPS concentration (2% with respect to the monomer), no polymerization was observed

Fig. 4. Fluorescence emission intensity at 425 nm ($\lambda_{\text{ex}} = 337 \text{ nm}$) vs. reaction time for microemulsions containing 3%, 0.5%, and 0.1% MMA with (a) SDS and (b) Brij98 as surfactant. All solutions have the same surfactant and initiator (KPS) concentrations. The curves obtained at lower monomer contents are magnified by a factor as indicated in the figure.

MMA (g)	H ₂ O (g)	SDS (g)	Hexylalcohol (g)	Brij98 (g)	Hexadecane (g)	KPS (mg)	MMA/H ₂ O (wt %)
0.3	10	0.3	0.03	0	0	5	3
0.05	10	0.3	0.03	0	0	5	0.5
0.01	10	0.3	0.03	0	0	5	0.1
0.3	10	0	0	0.3	0.03	5	3
0.05	10	0	0	0.3	0.03	5	0.5
0.01	10	0	0	0.3	0.03	5	0.1

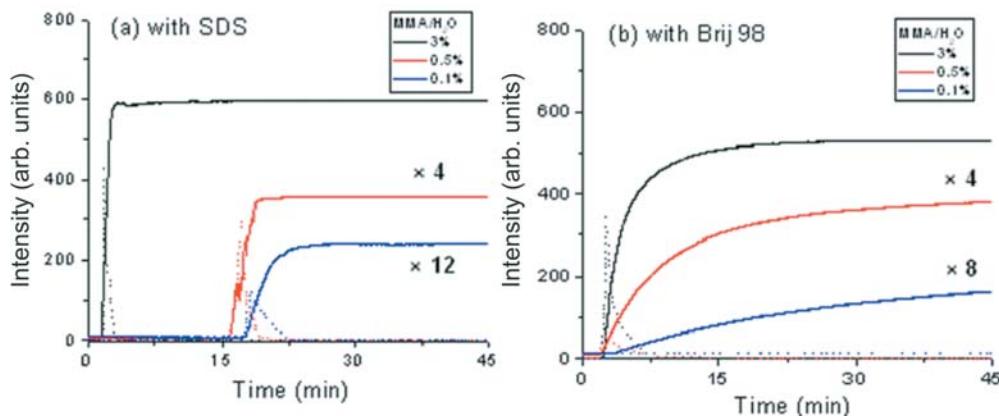
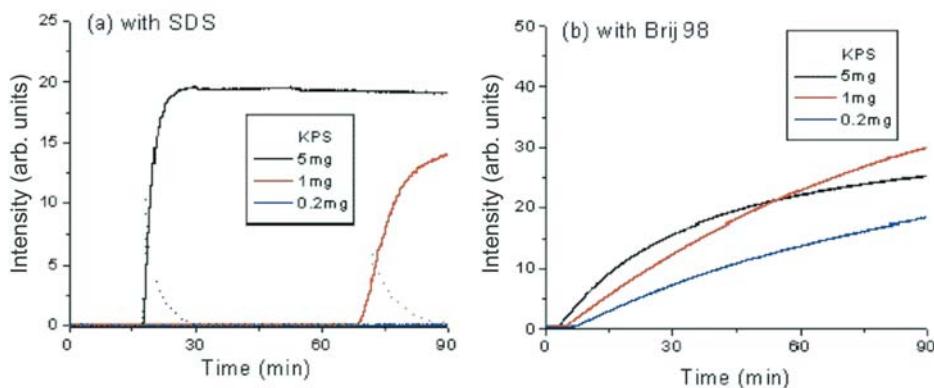


Fig. 5. Fluorescence emission intensity at 425 nm ($\lambda_{\text{ex}} = 337 \text{ nm}$) vs. reaction time for microemulsions containing 0.1% MMA and three different initiator (KPS) concentrations with (a) SDS and (b) Brij98 as surfactant. The compositions of all reaction solutions are shown.

MMA (g)	H ₂ O (g)	KPS (mg)	SDS (g)	Brij98 (g)	Hexylalcohol (g)	Hexadecane (g)	KPS/MMA (wt %)
0.01	10	5	0.3	0	0.03	0	50
0.01	10	1	0.3	0	0.03	0	10
0.01	10	0.2	0.3	0	0.03	0	2
0.01	10	5	0	0.3	0	0.03	50
0.01	10	1	0	0.3	0	0.03	10
0.01	10	0.2	0	0.3	0	0.03	2



after 90 min, indicating the great difficulty in starting the polymerization when both monomer and initiator concentrations are small. While with Brij98 as surfactant, the decrease in the initiator concentration mainly resulted in a decrease in the polymerization rate and, on a closer inspection, a slight

increase of the induction period (the polymerization rate profiles are not shown for the sake of clarity). The effect of surfactant in this regime of very low monomer contents is evident for all initiator concentrations, but most strikingly at the lowest initiator concentration (2% with respect to mono-

Fig. 6. Fluorescence emission intensity at 425 nm ($\lambda_{\text{ex}} = 337$ nm) vs. reaction time for microemulsions containing 0.1% MMA with three successive additions of the monomer: (a) with SDS and (b) with Brij98 as surfactant.

MMA (g)	H ₂ O (g)	KPS (mg)	SDS (g)	Brij98 (g)	Hexylalcohol (g)	Hexadecane (g)	MMA/H ₂ O (wt %)
0.01	10	5	0.3	0	0.03	0	0.1
0.01	10	5	0	0.3	0	0.03	0.1

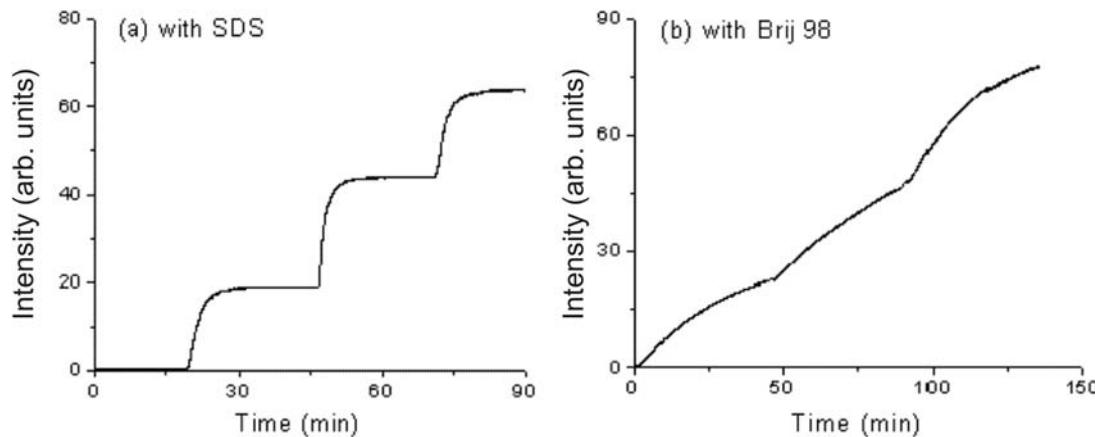
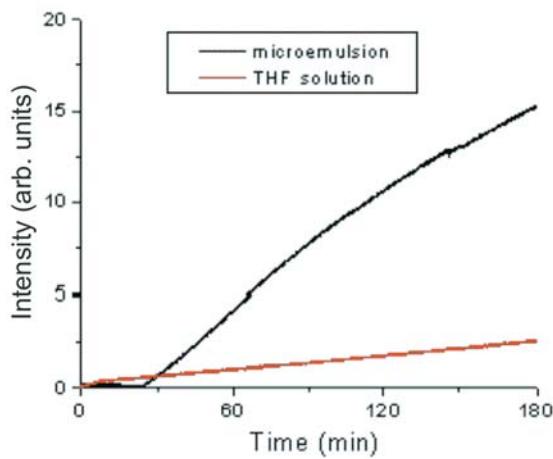


Fig. 7. Plots of fluorescence emission intensity at 425 nm ($\lambda_{\text{ex}} = 337$ nm) vs. reaction time for a microemulsion containing 0.1% MMA with AIBN as initiator and for a THF solution containing 0.1% MMA with AIBN as initiator (the compositions of the two reaction solutions are indicated).

MMA (g)	H ₂ O (g)	AIBN (mg)	THF (g)	Brij98 (g)	Hexadecane (g)	MMA/H ₂ O (wt %)
0.01	10	1	0	0.3	0.03	0.1
0.01	0	1	10	0	0	0.1



mer). We emphasize that all the experiments reported in Figs. 4 and 5 were carried out under the same experimental conditions, so that the induction period cannot be caused by the residual oxygen presented in the reaction solutions.

A microemulsion features an excess of surfactant molecules, and as the polymerization progresses, more empty micelles of the surfactant coexist with polymer latex particles.⁹

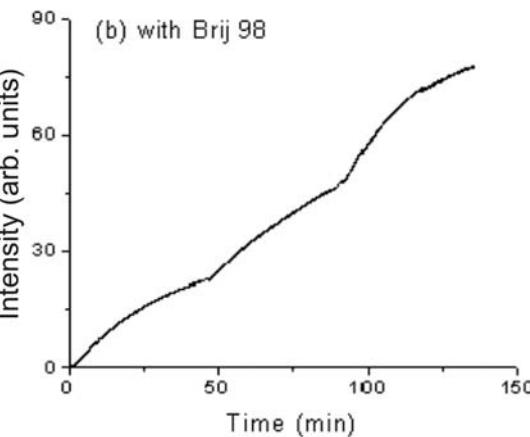
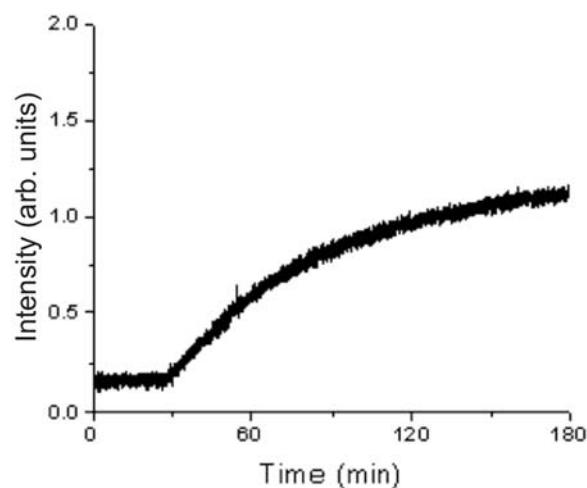


Fig. 8. Fluorescence emission intensity at 425 nm ($\lambda_{\text{ex}} = 337$ nm) vs. reaction time for a microemulsion containing 0.0035% MMA (water-to-monomer ratio: 28 000) (the composition of the reaction solution is shown).

MMA (g)	H ₂ O (g)	KPS (mg)	SDS (g)	Hexylalcohol (g)	MMA/H ₂ O (wt %)
0.00035	10	5	0.3	0.03	0.0035



It is known that when more monomers are added into the solution at the end of a microemulsion polymerization, the reaction could resume, resulting in more polymer particles. We found that this could also happen with very low monomer contents. Figure 6 shows the result obtained with a solution containing 0.1% of MMA, with both SDS and Brij98 as the surfactant. In the case of SDS, after the fluorescence intensity reached the plateau level for some time, the same

amount of MMA was injected into the solution using a syringe through a parafilm covering the cuvette containing the solution; it took about 1 min before resuming the fluorescence intensity measurement (in other words, there was a 1 min delay between the cycles of polymerization). The result shows that within experimental error, at the end of the initial microemulsion polymerization, the two successive additions of more monomers proceeded with the same kinetics and a similar conversion degree, but with no induction period. This observation suggests that at the end of the first polymerization cycle, free radicals could be in empty micelles of the surfactant, so that once more monomers were added in the solution and solubilized by the micelles, new polymerization could take place immediately. Basically, the same conclusion can be drawn with Brij98 even though the kinetic process is different (slower polymerization rate with almost no induction period).

With an extremely low monomer content and in the presence of an excess amount of surfactant molecules, can the microemulsion polymerization get close to a homogeneous (single-phase) polymerization? An experiment was conducted with 0.1% MMA to get an answer to the question. Figure 7 compares the apparent kinetics of the polymerization of 0.1% MMA in a microemulsion with Brij98 as surfactant and in THF, with AIBN as initiator in both cases. The polymerization in THF solution started quickly but proceeded very slowly due to the low monomer concentration, while the microemulsion polymerization was much faster but started only after an induction period. These results indicate that at this low monomer content, the microemulsion polymerization is still a heterophase polymerization. The reaction inside monomer droplets is faster than the reaction in a homogeneous solution in which monomer molecules are much diluted. This result also gives a hint on the different kinetics by using SDS and Brij98 (Figs. 4 and 5). It would be possible that with very low monomer content, the reaction solution with Brij98 was closer to a homogeneous system than the solution with SDS, which accounts for the different induction periods. Finally, to highlight the unprecedented sensitivity of this fluorescence method in monitoring the kinetics of microemulsion polymerization, Fig. 8 shows the result obtained with 0.0035% of MMA, i.e., at a water-to-monomer ratio $> 28\,000$! Even with this extremely low content of monomer, the typical kinetic process of the microemulsion polymerization of MMA with SDS as surfactant could still be detected, with of course a weak fluorescence signal. In principle, the sensitivity can further be improved by increasing the concentration of AnMA in the monomer.

Conclusions

We presented a fluorescence method that made it possible to monitor the kinetics of microemulsion polymerization with very (or even extremely) low monomer contents. Using AnMA as the fluorescent probe, kinetic data of polymerization of MMA in a microemulsion with a water-to-monomer ratio as high as 28 000 could be obtained. The results show that with low monomer content, such as 0.1% of MMA with respect to water, the surfactant had a more profound effect on the kinetics than with a relatively high monomer content,

such as 3%. Using the anionic surfactant of SDS, the polymerization rate was fast, but there was an induction period, while with the non-ionic surfactant of Brij98, the polymerization started much earlier, but the reaction rate was slower. A decrease in the concentration of the water-soluble initiator KPS either further lengthened the induction period or slowed down the polymerization. With the unprecedented sensitivity, this fluorescence method is well-suited for kinetic study in the regime of low monomer contents. It can also be explored for monitoring polymerization systems, for which other methods are inaccessible or can be utilized with difficulties.

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