Theoretical Confirmation of *In Situ* Monitoring of Monomer Conversion During Acrylamide Polymerization via Pyranine Flouroprobe

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Received 23 January 2009; accepted 16 May 2009
DOI 10.1002/app.30792
Published online 15 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, a new approach for *in situ* monitoring of the monomer conversion based on the chemical interaction of a fluoroprobe, pyranine (8-hydroxypyrene-1,3,6-trisulfonic acid, trisodium salt), with polymer chains during the free radical crosslinking copolymerization of acrylamide/bisacrylamide system (AAm/Bis) has been developed. Recently, we have shown that the pyranine fluoroprobes added to the prepolymerization solution in trace amounts bind covalently to the vinyl groups of the growing polymer chains via OH group by radical addition when the free radical polymerization of acrylamide (AAm) is initiated. This covalent binding results in a considerable blue shift in the emission spectrum of the pyranine, from 515 to $\sim$ 420 nm. In this study 0.5, 0.7, and 1.0 mol L^{-1} linear and crosslinked polymers including trace amounts of pyranine were synthesized. The change in the emission spectra of pyranine during polymerization and gelation were monitored as function of time. Here, we showed that both by theoretically and by comparing the fluorescence data with gravimetric measurements, the fluorescence intensity of pyranine monitored during the polymerization process can be used for *in situ* monitoring of the monomer conversion with great sensitivity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2455–2459, 2010

Key words: copolymerization; fluorescence; gelation; hydrogels; modeling

INTRODUCTION

Monomer conversion is the key variable for polymerization studies. It has strong relationship with the progress of the reaction and the properties of the polymers. To understand the physical nature of polymerization processes, to regulate the compositions and to test the existing theories, one must follow the reaction kinetics via monomer conversion. The experimental techniques used for monitoring polymerization process must be very sensitive to the structural changes and should not disturb the system mechanically. Different methods such as gravimetry,[1] densitometry,[2] calorimetry,[3] and ultrasound velocity[4] have been used for the measurement of monomer conversion. These techniques are carried out offline, resulting in measurement delay, which is undesirable for real-time control. Some analytical techniques such as Raman,[5] dielectric,[6] and Fourier transform infrared[7] spectroscopy have been developed in the past two decades for inline or online monitoring of the compositions in polymerization processes. However, for the samples with very high conversion (especially for gels), all these methods provide a relatively poor accuracy in monomer conversion.

Fluorescence technique is based on the interpretation of the change in anisotropy, emission spectra, or intensity, and viewing the lifetimes of injected flouroprobe in trace amounts to monitor the change in their microenvironment.[8,9] This technique has been successfully used to perform the experiments on polymerization,[10,11] chemical gel formation,[12,13] testing the gelation theories at the sol–gel transition,[14,15] and examination of the volume phase transition,[16] collapsed state phases of the polymeric gels,[17] and fractal nature of the gels.[15] The steady-state fluorescence technique used to study the polymerization rate showed that for a low degree of polymerization, a linear correlation between the fluorescence intensity ratio of the monomer and pyrene excimer emissions and the degree of polymerization was observed.[18] Instead of these great sensitivities of many flouroprobe to the change in the microenvironment, the fluorescence intensity parameter is difficult to calibrate because it depends on a huge number of factors. However, the wavelength at the maximum or the average emission energy only depends on the optical device used and this can be calibrated as discussed in Ref. 19.

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For substituted pyrene compounds, the presence of constituent(s) serves to break the symmetry of the chromophore[20]; however, the extent to which the excited electronic states are coupled is still determined mostly by the chromophore local environment. It has been observed that the local environment of several substituted pyrene derivatives mediates the optical response by altering the extent of vibronic coupling between the S1 and S2 manifolds.[14,21]

Recently, it was observed that[14,15,22] a considerable blue shift, from 515 to 406 nm, in the emission spectra of the pyranine (8-hydroxypyrene-1, 3,6-trisulfonic acid, trisodium salt) occurs because of a C—O ether bond formation between the hydroxylic oxygen of pyranine and a terminal C-atom of the growing acrylamide (AAm) chain. Furthermore, ionic (electrostatic) interactions occur between the three ionized sulfonic acid groups (SO_3^-) of the pyranine and protonated amide groups on the AAm chains, and these electrostatic interactions also cause a gradual red shift in the maximum of the short-wavelength peak, from 406 to 430 nm.[22] The mechanism and kinetics of the persulfate-initiated polymerization of acrylamide was discussed in detail previously in Ref. 23.

In this work, we show that the pyranine can be used for monitoring the real-time monomer conversion during AAm polymerization or AAm/Bis crosslinking copolymerization. We proved (via the theoretical calculations and the gravimetric measurements) that the total fluorescence intensity of the bonded pyranines measured during the polymerization monitors the real-time monomer conversion with great sensitivity.

EXPERIMENTAL

Materials

The monomer (AAm), the initiator (ammonium persulfate, APS), and the multifunctional crosslinkers (methylenebisacrylamide, Bis) were supplied by Merck (Darmstadt, Germany). The fluorescence molecule (pyranine) was supplied by Sigma (St Louis, MO). All chemicals were used as received. Bidistilled water was used in the gelation and swelling studies.

Methods

Prepolymer/pregel stock solutions were prepared by using various amounts of AAm (for linear polymerization) and AAm/Bis (for gelation) by dissolving them in bidistilled water in the presence of 7.0 mmol L^{-1} APS and 10^{-4} mol L^{-1} pyranine. The concentrations of the monomer and the crosslinker used are given in Table I. The sets of identical samples were prepared from the stock solutions including 0.5, 0.7, and 1.0 mol L^{-1} AAm (Samples 2–4). Each sample including 3 mL prepolymerization/pregel solution was sealed by a Teflon stopper after deoxygenation by nitrogen for 15 min. One of the samples from each set was reserved for fluorescence measurements and inserted in the sample compartment of the spectrophotometer kept at 60°C. Then, the remaining samples in the same set were put in a heat bath at 60°C. The polymerization and the measurements for fluorescence and gravimetric samples were started at the same instant.

TABLE I
Compositions of the Samples Used in Polymerization Experiments

Sample no.	AAm (mol L^{-1})	BIS (m mol L^{-1})
1	0.3	0
2	0.5	0
3	0.7	0
4	1.0	6.4

All samples include the same amount of pyranine, 10^{-4} mol L^{-1}.

The fluorescence spectra of pyranine during the polymerization were recorded by using a charged-coupled device (CCD) array spectrophotometer (Ocean Optics USB2000) equipped with a 400W Xenon lamp, which has a spectral range 250–700 nm at 90° position where the internal slit widths were kept at 5 nm. The optical resolution of the spectrophotometer is about 10 nm. The Hellma model quartz cuvettes with 10-mm light path were used for these measurements. The sample was excited with 400 nm light, and then the variation in the fluorescence spectra/intensities were collected as a function of polymerization times.

The polymerization reaction of each sample in heat bath, prepared for gravimetric measurements, was terminated one by one at increasing reaction times: the sample was poured quickly into a vessel including 10 mL methanol and then cooled by liquid nitrogen to stop the polymerization reaction. Having the polymer parts in each sample precipitated in methanol, they were filtered and dried in the furnace at 40°C. The masses of the precipitated parts were recorded during the drying process for 2 weeks until they remained stable.

RESULTS AND DISCUSSION

Change in the fluorescence spectra of pyranine during the free radical polymerization

Typical fluorescence spectra of polymerizing samples are shown in Figures 1 and 2 for varying reaction times. No change in the emission spectra of pyranine was observed before the initiation of polymerization with APS. Upon the initiation of the polymerization, the intensity of 515 nm peak decreases and a new

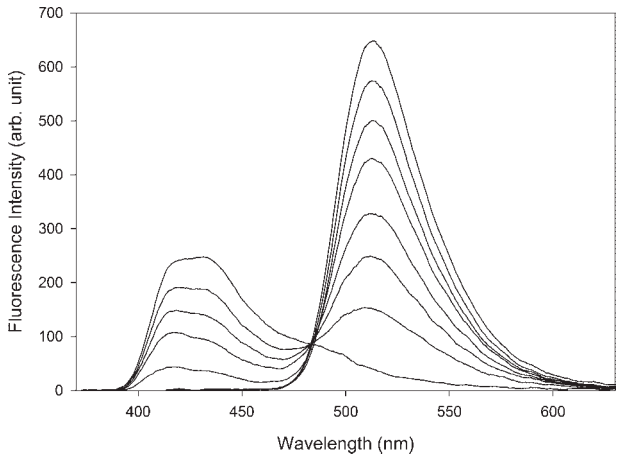

Figure 1 Typical fluorescence spectra of pyranine at different stages of the free radical crosslinking copolymerization of 0.3 mol L^{-1} AAm prepared with 10^{-4} mol L^{-1} pyranine.

peak appears around 427 nm. The intensity of the 427 nm peak increases as the intensity of 515 nm peak decreases during the course of Samples 1 (Fig. 1) and 4 (Fig. 2) polymerization, respectively.

It should be noted that the reason for this blue shift in the emission spectra (from 515 to 427 nm) is not because of the effect of pH as discussed in the literature.[21,22,24–26] The maximum of the fluorescence spectra of pyranine in pure water below pH 1 is clearly different from the 427 nm peak,[26] which appears only when the polymerization is initiated. Moreover, in our studies, the pH of the prepolymer solution was about pH 6 and did not fall down beyond pH 4 during the whole polymerization process.

The blue shift in the emission spectra of pyranine is due to the binding of pyranine to the AAm chains chemically over —*OH* groups only during the polymerization processes as discussed in a recent study.[22] This covalent binding of pyranine can be formed with the end groups of PAAm chains via the radical addition of pyranine to AAm monomers over —*OH* groups as discussed in Refs. 14, 15, and 22.

Here, we would like to note that there is a main difference in Figures 1 and 2 from the isoemissive (isostilbic) points. For the linear polymerization, only one isoemissive point located at 484 nm wavelength was observed, whereas for the gel sample, the isoemissive point first appeared at 484 nm and then shifts to 494 nm wavelength. The reason for this shift for the gel sample in the isoemissive (isostilbic) point is the change in the internal morphology of the system: at the beginning of the polymerization, the system is in the "sol" state and above a certain time it turns into the "gel" state.

Here, we would like to argue that the fluorescence intensity of the bonded pyranines is a direct measure of the monomer conversion.

Derivation of the relation between the monomer conversion and the fluorescence intensity of the bonded probes

Here, we would like to argue that the fluorescence intensity of the bonded probes, $I(t)_{\text{bonded}}$ measured during the polymerization, monitors the monomer conversion, $\chi(t)$, defined as the percentage of the monomers converted to the polymer or gel at any instant of the reaction time.

Let $n_N(t)$ be the number of polymer molecules, at time t, including N monomers (N-cluster in percolation language).[27–29] The probability, $w_N(t)$ that the macromolecule to which an arbitrary chosen monomer belongs contains exactly N monomer is given by,

$$w_N(t) = \frac{n_N(t) \cdot N}{\sum_N n_N(t) \cdot N} \tag{1}$$

as discussed in Refs. 27–29. The total number of the monomers, $M(t)$, belonging to macromolecules of any size will be given as a summation of $w_N(t) \cdot N$ over all the possible Ns[28]:

$$M(t) = \sum_N w_N(t) \cdot N = \frac{\sum_N n_N(t) \cdot N^2}{\sum_N n_N(t) \cdot N}. \tag{2}$$

Thus, the monomer conversion $\chi(t)$ can be calculated as follows:

$$\chi(t) = \frac{M(t)}{M_0} = \frac{1}{M_0} \frac{\sum_N n_N(t) \cdot N^2}{\sum_N n_N(t) \cdot N} \tag{3}$$

where M_0 is a possible total number of the monomers.

Now, let N_p be the total number of the probe molecules, N_c be the total number of polymer constitutes —AAm, Bis (if exist), APS—, and N_{water} be the total number of water molecules in the prepolymer/pregel solution. The probability, P_p, that an arbitrary

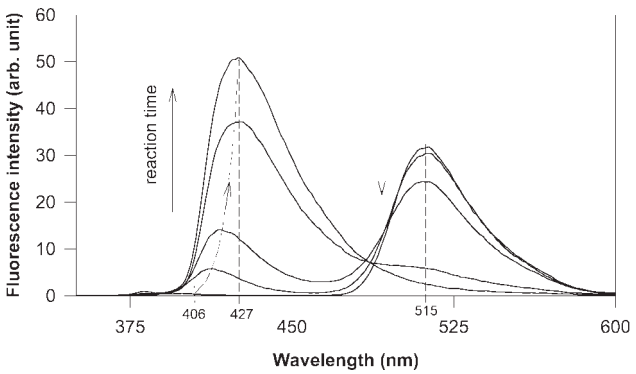

Figure 2 Fluorescence emission spectra of 1.0 mol L^{-1} AAm gel in swelling equilibrium at different pH conditions.

chosen molecule is a probe molecule, can be given simply as $N_p/(N_c + N_{water} + N_p)$. The probability, $P_m(t)$, that an arbitrary monomer is both bonded chemically to a probe and at the same time belongs to the macromolecule (or a polymer cluster) that contains exactly N monomer units, is the product of P_p and $w_N(t)$:

$$P_m(t) = P_p \cdot w_N(t) = \frac{P_p n_N(t) \cdot N}{\sum_N n_N(t) \cdot N} \quad (4)$$

Thus, $P_m(t) \cdot N$ will be the number of probes in each macromolecule including N monomers. Therefore, the total number of probes bonded to all macromolecules with different sizes, $n(t)_{bonded}$, can be calculated as a summation over all possible Ns:

$$n(t)_{bonded} = \sum_N P_m(t) \cdot N = \sum_N \frac{P_p n_N(t) \cdot N}{\sum_N n_N(t) \cdot N} \times N = \frac{\sum_N P_p n_N(t) \cdot N^2}{\sum_N n_N(t) \cdot N} \quad (5)$$

Note that the proportionality factor P_p is simply the fraction of the probe molecules in the sample, i.e., it is fixed for each sample; therefore, it can be taken out of the summation as follows:

$$n(t)_{bonded} = P_p \frac{\sum_N n_N \cdot N^2}{\sum_N n_N \cdot N} \quad (6)$$

On the other hand, $n(t)_{bonded}$ will be directly proportional to the total fluorescence intensity of the probes that are bonded to the polymer chains

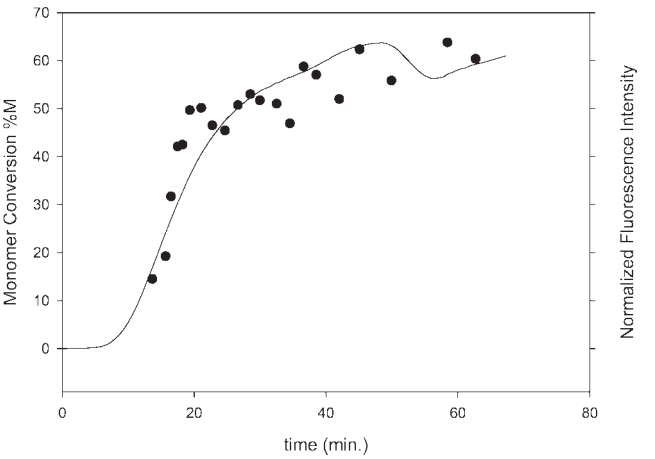

Figure 4 The fluorescence intensity of the bonded pyranines (solid line), and % monomer conversion (symbols) obtained by the gravimetric measurements for 0.7 mol L^{-1} AAm linear polymer.

$$n(t)_{bonded} \propto I(t)_{bonded} \quad (7)$$

Note that the last relation is valid only if the concentration of the probe is low enough so that the intensity would increase linearly with the concentration. Therefore, we have chosen the concentration of pyranine as 10^{-4} mol L^{-1}, which is low enough to fulfill the linearity condition. Moreover, the concentration of the bonded probes will be much lower than 10^{-4} mol L^{-1} at any instant of the reaction.

Thus, the expressions (3), (6), and (7) together give the relation between the measured fluorescence intensity of bonded pyranines, I_{bonded}, and the monomer conversion $\chi(t)$,

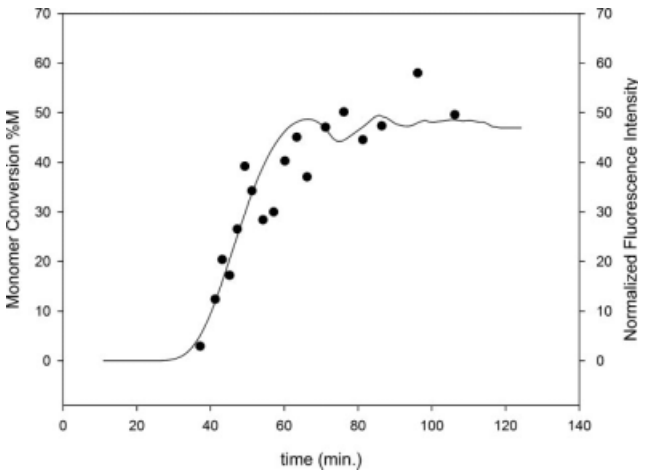

Figure 3 The fluorescence intensity of the bonded pyranines (solid line), and % monomer conversion (symbols) obtained by the gravimetric measurements for 0.5 mol L^{-1} AAm linear polymer.

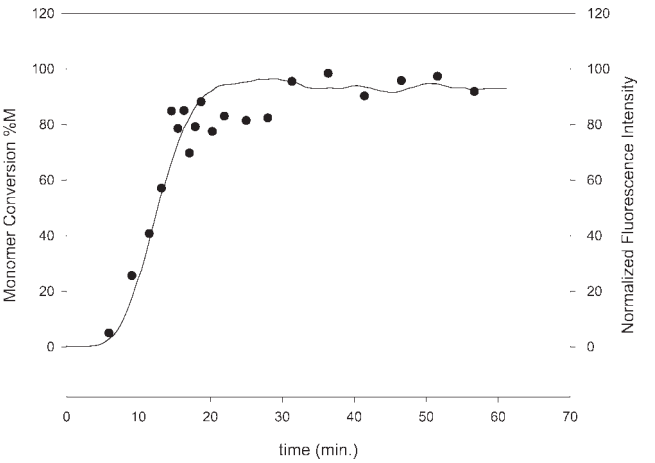

Figure 5 The fluorescence intensity of the bonded pyranines (solid line), and % monomer conversion (symbols) obtained by the gravimetric measurements for 1.0 mol L^{-1} AAm gel.

$$\chi(t) = \frac{n(t)_{\text{bonded}}}{M_0 P_p} \propto \frac{I(t)_{\text{bonded}}}{M_0 P_p} = k \cdot I(t)_{\text{bonded}} \quad (8)$$

Here, k is the proportionality constant including M_0 and P_p, which are fixed for each experiment. As seen from the last expression, the monomer conversion is directly proportional to the measured fluorescence intensity of the bonded probes. Here, it should be noted that eq. (7) needs further clarification. It is only true if nonradiative processes of the bonded species remain unaltered during the polymerization. This condition could be fulfilled in low concentrated samples. Otherwise, another contribution related with the microviscosity should be added.

Confirmation of the theory

The mass of the precipitated (and dried) parts of the samples prepared for gravimetric measurements, $m(t)_{\text{precipitated}}$, were measured and recorded as a function of the reaction time. Then, the monomer conversion was calculated as $\chi(t) = [m(t)_{\text{precipitated}}/m_{\text{total}}]$, where m_{total} is the total initial mass of the polymer constitutes, AAm, Bis for Sample 4, and APS. The percentage of measured monomer conversions and the normalized fluorescence intensities, $I(t)_{\text{bonded}}$ measured in real time, were plotted in Figures 3–5 for Samples 2–4 against the reaction time. As seen from these figures, the normalized fluorescence intensity fits, in experimentally acceptable errors, well to the monomer conversion data measured by means of the macroscopic experiments.

CONCLUSIONS

Pyranine added to the prepolymerization solution of PAAm in small amount shows a spectral shift to a shorter wavelength (from 515 to 427 nm) upon the initiation of polymerization. This spectral shift is due to the chemical binding of pyranine to the polymer chains over $-OH$ group via radical addition during the polymerization. It seems that the nonradiative processes of the bonded species remain almost unaltered, for the concentration ranges used in this work, during the polymerization, i.e., contribution related with the microviscosity becomes unimportant near the change in the spectra of pyranine because of the increasing number of bonded pyranine.

We have confirmed that the fluorescence intensity measured via parallel experiments and theoretical calculations during the polymerization process can be used for real-time monitoring of the monomer conversion with great sensitivity. We expect that this technique applied first time to the PAAm system may be used for calculating the kinetic parameters with great certainty and for testing the present theories.

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