Polymer Bulletin 40, 195–202 (1998)

Polymer Bulletin
© Springer-Verlag 1998

Analysis of the microemulsion-polymerization of acrylamide by time resolved fluorescence

Myung-Ae Chung, Jörg Adams, Jürgen Fuhrmann*

Institut für Physikalische Chemie, TU Clausthal, Arnold-Sommerfeld-Strasse 4, D-38678 Clausthal-Zellerfeld, Germany

Received: 3 November 1997/Accepted: 20 November 1997

Summary

The polymerization of acrylamide in an inverse microemulsion has been studied by time resolved fluorescence measurements. The reaction was initiated by thermal and by photochemical decomposition of the initiator AIBN. A decrease of the fluorescence lifetime of the probe molecule pyrenetetrasulfonic acid sodium salt was observed. In case of the photochemically initiated reaction two distinct lifetimes could be separated. The corresponding pre-exponential factors showed a good correlation with the gravimetrically obtained conversion. During the thermally initiated polymerization the fluorescence decays as well as the intensity of the scattered light were measured on-line and analyzed by a mono-exponential decay law.

Introduction

Even though emulsion- and microemulsion-polymerizations (1,2) are widely used to prepare stable and well-defined polymer dispersions of a variety of polymers, not much is known about the numerous kinetical and structural aspects important for this type of reactions. Questions on how the monomer is transferred from individual microemulsion particles to the growing polymer chain and how the structure of the growing particles influences this dynamic process are still of interest.

In this paper we want to present some of our fluorescence based investigations on the polymerization of acrylamide (3-6) in an inverse aqueous microemulsion. The investigations were carried out by means of a fluorescence spectroscopic analysis of an ionic fluorescence probe embedded into the aqueous, monomer bearing phase. A fluorescence probe technique (7-9) was used, because it is easily possible to delegate the signal giving species into the region of interest. Such probes can give information about the local viscosity (10,11), polarity (12), concentration of the reactant or monomer exchange during the polymerization reaction (9). Here we want to present the results of an analysis of the time resolved fluorescence of the probe molecule pyrenetetrasulfonic acid sodium salt (PTA) during a free radical polymerization. The reaction mixture consists of toluene as continuous phase, aqueous acrylamide solution as dispersed polar phase and the anionic emulsifier AOT (sodium sulfonic-bis(2-ethylhexyl)ester).

* Corresponding author

The nonpolar initiator AIBN (azobisisobutyronitrile) was used to start the reaction. The initiator was either decomposed thermally or by irradiation with UV-light.

Experimental

Materials and preparation of the microemulsion

The monomer acrylamide (Aldrich), the fluorescence probe pyrenetetrasulfonic acid sodium salt (PTA, Kodak Co.) and the anionic surfactant AOT (Fluka) were used as received. AIBN (Aldrich) was twice recrystallized from ethanol. As continuous phase anhydrous toluene (Aldrich, spectrophotometric grade) was used. Demineralized water was used for all solution.

To prepare the inverse microemulsion the surfactant AOT was dissolved in toluene and the aqueous acrylamide solution was added in the desired proportions. An aqueous solution ($1 \cdot 10^{-3}$ mol/l) of the fluorescence probe was added to all solutions to give a total concentration of $1 \cdot 10^{-5}$ mol/l PTA. The initiator was added as a toluene solution. To obtain a homogenous microemulsion the mixtures were stirred at 10°C in the dark until they became clear.

To eliminate molecular oxygen from the polymerization mixtures they were degassed five times by pump and freeze cycles under high-vacuum ($1 \cdot 10^{-7}$ mbar) in sealable quartz fluorescence cells. After this procedure the cells were refilled with Argon up to a pressure of 1 bar to avoid boiling of the toluene. Prior to polymerization the solutions were stored at -10°C in the dark.

Polymerization

The UV-initiated polymerization was carried out at 20°C in the sealable fluorescence cells without mechanical stirring. The temperature was controlled by using a thermostated sample holder. To start the polymerization the initiator was decomposed by irradiation with UV light from a mercury lamp (Philips). Heating of the solution by IR-radiation was reduced by a water filter. The irradiation wavelength of 320 nm was selected by an interference filter (LOT Oriel). The duration of the irradiation was usually 10 min. After a polymerization period the time resolved fluorescence decay was accumulated until 10000 photons were collected at the maximum. After that, another irradiation step was performed. To obtain the degree of conversion the reaction mixture was precipitated into methanol, washed, filtered and dried.

For the thermally initiated polymerization the same experimental setup was used, beside the mercury lamp. The polymerizations were carried out at 40°C and fluorescence decays were accumulated continuously with a sampling time of 60 s.

Fluorescence measurements

Fluorescence decay curves were obtained by using the time-correlated single photon counting technique. The excitation source was a PRA ns-flash lamp with H_2 as discharge medium. The excitation wavelength was set to 360 nm by using an interference filter (LOT Oriel). The emission wavelength was also selected by an interference filter (380 nm). Some of the thermally initiated polymerizations were carried out without an emission filter. In this way, not only the fluorescence light was detected but also the scattered excitation light at an angle of 90° with respect to the incident beam could be collected.

The fluorescence decay curves recorded during the intermittent photopolymerization experiment were analyzed by assuming a bi-exponential decay law (eq. 1) using a weighted

non-linear least-squares procedure (13) with an implemented *Levenberg-Marquardt* algorithm to find the fit parameters τ_i and a_i.

$$I(t) = a_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + a_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) \qquad (1)$$

I(t) is the observed intensity at time *t* after excitation, τ_i are the lifetimes of the two exponential decays and a_i the corresponding pre-exponential factors. These two factors are proportional to the number of emitting molecules being excited at $t = 0$.

The decay data during thermal polymerization were analyzed assuming a mono-exponential decay law. The scattering intensity was obtained by addition of the weighted instrumental response function to the convoluted fluorescence test function prior to calculation of the χ^2-parameter of the weighted non-linear least-squares procedure.

Results and Discussion

The main reason for using the fluorophore PTA was the possibility to analyze the change of rotational mobility during the polymerization of acrylamide inside the microemulsion droplets. The results of these investigations will be presented in a subsequent paper.

To calculate the rotational mobility the lifetime of the fluorescence probe has to be measured by time resolved fluorescence measurements. It was known from literature that the monomer acrylamide is a fluorescence quencher for many fluorophores (9,14). Therefore we investigated the quenching ability of AAM in the inverse microemulsions under variation of the AAM-concentration. Fig. 1 shows the resulted data in a so-called *Stern-Volmer*-plot (15).

According to the *Stern-Volmer* equation (eq. 2) the dynamic quenching rate constant was calculated to $k_q = 4 \cdot 10^7$ l·mol^{-1}·s^{-1}.

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q C_{AAM} \qquad (2)$$

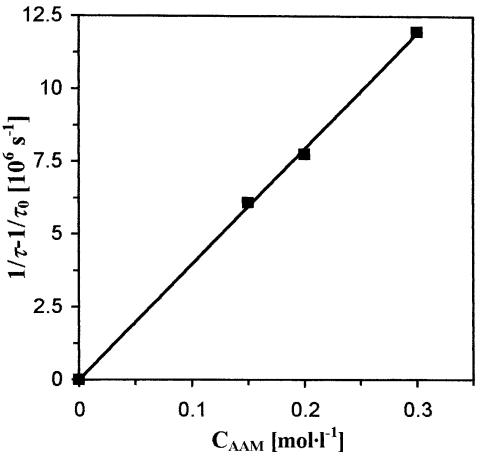

Figure 1: *Stern-Volmer* plot of the mono-exponential determined lifetime of PTA versus AAM-concentration. $\tau_0 = 8.1$ ns. Continuous phase toluene.
$T = 25$°C, $C_{AOT} = 0.4$ mol/l, $C_{H2O} = 4$ mol/l, $C_{AIBN} = 1.5 \cdot 10^{-3}$ mol/l. $\lambda_{Ex} = 360$ nm, $\lambda_{Em} = 390$ nm.

Due to quenching properties of the monomer and its consumption during the thermally initiated polymerization, we expected a lifetime increase. To our surprise, as shown in fig. 2, this was not the case. Depicted are the fluorescence decay curves at three different polymerization times. The fluorescence lifetime decreases from 7.8 ns at the start of the reaction down to 5.1 ns at the end.

By the photochemically initiated polymerization in the inverse microemulsion at 20°C it was possible to extend the time of observation and hence to analyze the fluorescence of the PTA in more detail. Again we observed a decrease of the lifetime. Due to the higher number of photons being accumulated, the fluorescence decays could be analyzed bi-exponentially according to eq. 1.

The analysis of the obtained parameters showed that each lifetime (τ_1, τ_2) changes only insignificantly over the course of the reaction.

Hence, the changes in the decay curves are attributed to changes of the pre-exponential factors a_1 and a_2. Therefore, for a given polymerization time the data evaluation was carried out by first fitting all parameters to determine the average values of each of the two lifetimes. The average value of τ_1 for several experiments varied between 9.2 ± 0.2 ns and the value of the shorter lifetime τ_2 between 5.5 ± 0.2 ns. With the two averaged lifetimes the data were fitted again by only adjusting the pre-exponential factors.

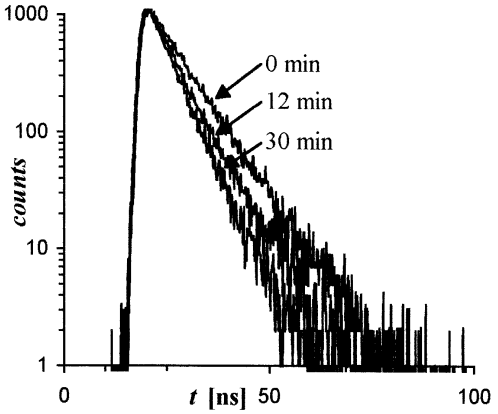

Figure 2: Semi-logarithmic Fluorescence decay of PTA at different times during a thermally initiated polymerization of acrylamide.
T= 40°C, C_{AOT} = 0.4 mol/l, C_{H2O} = 4 mol/l, C_{AAM} = 0.3 mol/l, C_{AIBN} = $1.5 \cdot 10^{-3}$ mol/l.
λ_{Ex} = 360 nm, λ_{Em} = 380 nm. Sampling time 60 s.

Because a_1 and a_2 depend on the intensity of the pulse lamp and the quantum yield of the probe, it is not useful to discuss these parameters directly. Therefore, the fractions $f_i = a_i / (a_1 + a_2)$ were calculated and their changes over the course of the polymerization are depicted in fig. 3. The values of f_1 and f_2 are the fractions of PTA fluorophors in a certain photophysical situation emitting with the lifetime τ_i and τ_2 respectively.

As can be seen from fig. 3, the fraction of PTA molecules f_1 associated with the longer lifetime decreases with polymerization time whereas consequently the fraction f_2 of the shorter lifetime increases. The same data are also presented as a function of the conversion in figure 4. From the linear relationship of f_i versus conversion it can be concluded that the analysis of the fluorescence lifetime leads to a direct measure of the conversion.

It has to be noted that neither at the beginning nor at the end of the polymerization f_1 or f_2 becomes either 0 or 1 as one would expected for 0 and 100% conversion.

The details causing the two distinguished photophysical situations are not fully understood yet. Therefore we propose to concentrate on the distinctive features of the two lifetimes, which enable spectroscopic measurements of conversion due to the linear dependence between fraction f_i and conversion.

Beside the possibility to determine the conversion spectroscopically, the existence of two distinguished photophysical situations supports the continuous nucleation model (6): the probe seems to be either in one or the other situation and there is no gradual change from monomer containing particle to a polymer bearing particle as it would be expected in case of a particle formation only in the early stages.

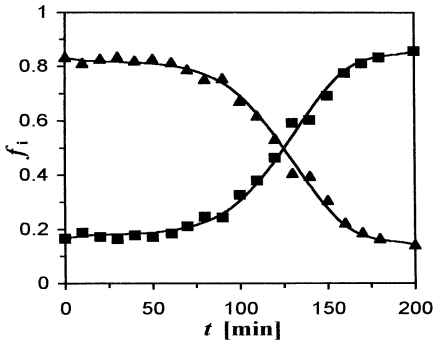

Figure 3: Fraction f_i of dyes associated with lifetime τ_i at different polymerization times t.
▲:f_1 (τ_1 = 9.10 ns), ■: f_2 = 5.47 ns)
T= 20°C, continuous phase toluene, C_{AOT} = 0.4 mol/l, C_{H2O} = 4 mol/l, C_{AAM}= 0.1 mol/l, C_{AIBN} = $1.5 \cdot 10^{-3}$ mol/l.

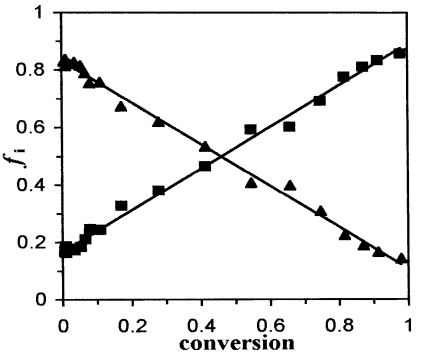

Figure 4: Fraction f_i of dyes associated with lifetime τ_i as a function of the conversion.
▲: f_1 (τ_1 = 9.10 ns), ■: f_2 (τ_2 = 5.47 ns)
Same reaction conditions as for fig. 3.

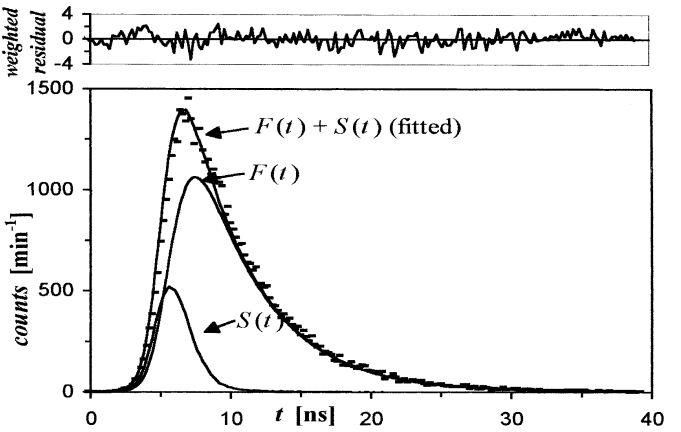

Figure 5: Fluorescence decay of PTA together with the weighted residuals of the fit after 60 min. conversion time. Reaction conditions see fig. 2. λ_{Ex} = 360 nm, measured without wavelength selection on the emission side. – : signal; $F(t)$: fitted fluorescence decay; $S(t)$: fitted instrumental response function, i.e. scattering intensity.

For the thermally initiated microemulsion polymerization the signal to noise ratio was to low to analyze the fluorescence decays according to eq. 1. Because at least 10 min. sampling time are needed to measure an evaluable bi-exponential character of the fluorescence decay, we performed mono-exponential decay fits within a time period up to complete conversion to get reasonable results. Most of the thermal polymerizations were measured without an interference filter on the emission side to collect the scattering intensity. Figure 5 shows such a fluorescence decay together with the corresponding fit and the instrumental response function, i.e. scattering intensity according to a lamp pulse width of 3.2 ns.

It has to be noted that the scattering intensities obtained from these fits are not calibrated to a standard with a known *Rayleigh*-ratio and that they should therefore only be discussed regarding changes during the polymerization reaction.

Figure 6 shows the lifetime τ and the scattering intensity I_{scatt} of a thermally initiated polymerization as a function of the polymerization time. The dotted line indicates the heating period in which the thermostated sample holder was heated from room temperature to the polymerization temperature of 40°C.

During the heating period (0 - 14 min.) the lifetime decreases due to an increasing quenching rate caused probably by an increased diffusional mobility of the probe molecules. In this period the scattering intensity remains zero. After this initial phase the lifetime shows a further decrease whereas I_{scatt} increases only slightly. A strong increase in I_{scatt} can be detected near the end of the lifetime plateau. The polymerization is completed after 60 min.

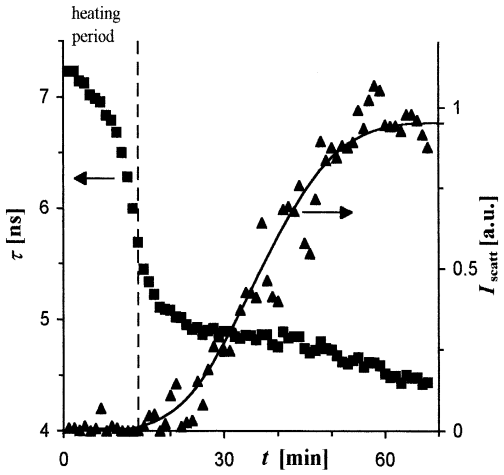

Figure 6: Lifetime (■) of PTA during the thermally initiated polymerization of acrylamide and scattering intensity (▲).
Same conditions as in fig. 5.

Because the thermally initiated and the photoinitiated reactions exhibit both a decrease in lifetime, we assume the same photophysical origin for both. A calculation of the conversion from the fluorescence data should therefore be possible under the following consideration: the mono-exponentially calculated lifetime τ of the thermal polymerization is the mean value of two lifetimes, weighted by the fluorescence intensity of the individual species (eq. 3).

$$\tau = <\tau> = \frac{\sum_i I_i \tau_i}{\sum_i I_i} = \frac{\sum_i f_i \tau_i^2}{\sum_i f_i \tau_i} \qquad (i = 1,2) \qquad (3)$$

The validity of eq. 3 was confirmed by analyzing the decays of the photochemical reaction mono-exponentially and by comparing the obtained τ with $<\tau>$ from eq. 3.

To determine τ_1 and τ_2 for the thermally initiated polymerization through bi-exponential fitting, the fluorescence was measured with a longer sampling time after the polymerization had finished. τ_1 and τ_2 were determined to 6.0 ns and. 3.8 ns for the polymerization shown in fig. 6. These values are lower than the ones obtained for the photoinitiated polymerization due to the higher temperature and also due to the higher AAM concentration.

With these two lifetimes and the τ values obtained by mono-exponential fitting it was possible to calculate f_2, the fraction which represents the conversion linearly. These f_2 values and the scattering intensity are plotted versus the polymerization time in fig. 7. Only the positive values of f_2 are depicted. Not shown are the physically meaningless negative values between 0 and 14 min. polymerization time. They are a result of the high mono-exponential lifetimes τ during the heating period ($\tau > \tau_1$).

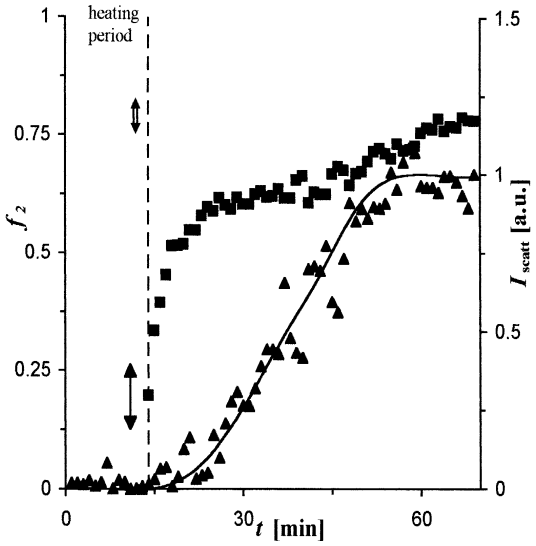

Figure 7: Fraction f_2 (■) of PTA molecules in the polymer particles and scattering intensity (▲) during thermal polymerization. (↕resp. ⇳) are error bars characterizing the range of possible f_2 values at 0% resp. at 100% conversion. Reaction conditions see fig. 2.

It can be seen from fig. 7 that f_2 just becomes positive when the scattering intensity starts to rise. We see this coincidence as an indication for the correctness of our calculations. The fast increase of f_2 at the beginning can be seen as an evidence for a polymerization in the microemulsion particles prior to a significant increase of the particle size. Due to the non-isothermal conditions at the beginning, i.e. changing sign of f_2, there is an f_2-error estimated to ±0.07. At 100% the calculated f_2-error is ±0.03.

Both time dependent quantities shown in fig. 7 give information about changes of the properties in the reaction mixture during the polymerization. However, their courses are not identical because different types of information are gathered by fluorescence and light scattering. While the scattering intensity allows to observe the formation, growth and aggregation of larger particles, the fluorescence data give an insight into the molecular changes in the interior of the particles.

How these observation fit into the kinetic schemes described in literature(6,16) and are able to give an insight into kinetical and structural aspects of heterogeneous polymerization reaction are the issues of future investigations.

Acknowledgement

The Authors gratefully acknowledge the support by the *Deutsche Forschungs Gemeinschaft* (DFG).

Literature

1. Barton J, Capek I (1994) Radical Polymerization in Disperse Systems, Ellis Horwood, New York
2. Barrett KEJ (1975) Dispersion Polymerization in Organic Media. John Wiley & Sons, London
3. Candau F (1992) Polymerization in Microemulsion. In: Paleos CM (ed) Polymerisation in Organized Media. Gordon and Breach Science Publishers, Philadelphia
4. Candau F, Leong YS, Fitch RM (1985) J Polym Sci Polym Chem Ed 23:193
5. Carver MT, Candau F, Fitch RM (1989) J Polym Sci A: Polym Chem 27:2179
6. Candau F (1990) Polymerization in inverse emulsion and microemulsion. In: Candau F, Ottewill RH (ed) An introduction to polymer colloids. Kluwer Academic Dortrecht (NATO ASI Ser C, vol 303)
7. Kalyanasundaram K (1987) Photochemistry in Microheterogeneous Systems. Academic Press, New York
8. Tamura K, Nii N (1989) J Phys Chem 93:4825
9. Lacík I, Barton J, Warr GG (1995) Macromol Chem Phys 196:2223
10. Valeur B, Keh E (1979) J Phys Chem 83:3305
11. Zinsli PE (1979) J Phys Chem 83:3223
12. Dong DC, Winnik MA (1984) Can J Chem 62:2560
13. Grinwald A, Steinberg IZ (1974) Anal Biochem 59:583
14. Lissi EA, Encinas MV, Bertolotti SG, Cosa JJ, Previtalli CM (1990) Photochem Photobiol 51:53
15. Lakowicz JR (1983) Principles of Fluorescence Spectroscopy. Plenum Press, New York
16. Antonietti M, Basten R, Lohmann S (1995) Macromol Chem Phys 196:441