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Dynamic light scattering study of the radical copolymerization of styrene-meta divinylbenzene

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Résumé. — Nous présentons les résultats d'une étude par diffusion laser d'une copolymérisation radicalaire (styrène divinylbenzène-AIBN-benzène). Le processus conduit à une gélification irréversible. La fonction d'autocorrélation de l'intensité lumineuse diffusée par le système à l'état de sol présente deux modes de décroissance indépendants. Le temps caractéristique de la relaxation lente suit la même variation temporelle que la viscosité macroscopique du système.

Abstract. — We report a dynamic scattering study of a system undergoing irreversible gelation (styrene-divinylbenzene-AIBN-benzene). The autocorrelation function of intensity scattered from the sol exhibits two independently decaying modes. The slow-relaxation time follows the same time dependence as the macroscopic viscosity of the medium.

1. Introduction. — It is generally admitted that dynamic light scattering studies on longitudinal modes near the sol-gel transition do not provide important information on the gelation mechanism for the following reason : the collective diffusion coefficient, which characterizes the decay of the concentration fluctuations, is not very sensitive to the connectivity fluctuations occurring near the transition point [1]. In an irreversible gelation experiment, performed by radical copolymerization, the sol consists of branched polymers widely distributed in size and scattering power so that changes in the relative concentrations of different species are likely to contribute effects additional to those produced by the fluctuations in the total number density. This phenomenon has been theoretically investigated by Pusey, Fijnaut and Vrij (P.F.V.) for concentrated liquid suspensions of polydisperse hard spheres [2]. For such systems P.F.V. predicted that the light scattering correlation function consists of the sum of two independently decaying modes. The first mode is associated with the usual cooperative diffusion, while the second describes the exchange between species through self-diffusion. The existence of these two modes has been experimentally observed in microemulsions [3, 4], latex particles dispersions [5, 6] and silica spheres [7].

When a gelation is performed in the presence of a good solvent, the polymeric clusters formed near the gel point behave like hard spheres because of the excluded volume interactions, so that the gelling medium presents some similarities with the preceding systems. More specifically, we would expect a correlation function of scattered light to be composed of two independent modes with well separated decay times.

In this paper we report a dynamic light scattering study of the radical copolymerization process of styrene and *m*-divinylbenzene at 60 °C in benzenic solution. The AZO-2,2' isobutyronitrile (AIBN) was used as initiator [8].

2. Experimental. — Two experiments were performed on samples with the following compositions (in g per 100 cm³ of solution).

System A styrene : 18.44, meta DVB 1.07, AIBN 1.92

System B styrene : 19.91, meta DVB 0.061, AIBN 2.09.

The reactive elements were mixed in a glass tube, sealed after degassing under vacuum and then placed in a thermostat at 60° ± 0.1 °C, on the stage of the photon correlation spectrometer.

The polymer volume fraction, at the gel point, was not measured but from the results of previous studies, one can infer that it was about 0.1.

A Spectra-Physics argon-ion laser ($\lambda = 488$ nm) was used in conjunction with a 48 channel clipped digital autocorrelator (Precision Devices and Systems LTD Malvern) for measuring the autocorrelation function of the light scattered at an angle of 90°. We used the so-called « heterodyne » detection in which a reference beam is superimposed onto the scattered beam. This allows us to analyse unambiguously the autocorrelation function of the photocurrent which is then proportional to the autocorrelation function of scattered intensity [9]. This is an important point in a gelation study, since a swollen polymeric network scatters light from both longitudinal concentration fluctuations and quasi-static swelling inhomogeneities [10], so that the homodyne spectrum contains a mixed mode associated with the beating of these two components.

The time required for the recording of one correlation function was of the order of 30 s. The gelations considered here were rather slow (~ 15 h-25 h) and we have not investigated the very close vicinity of the gel point. Therefore the change of properties of the system during a recording time was negligible as ascertained from the comparison between repeated successive recordings.

3. Results and discussion. — The shape of the autocorrelation function was found to be strongly dependent on the stage of the reaction. The very early stage is difficult to investigate because of the time required to attain thermal stability and also because the average decay time of the correlation function is very short, owing to the small size of the diffusing scatterers.

We started our observations about 1 hour after the beginning of the copolymerization. From that time, up to the gel point (to be discussed later), the shape of the autocorrelation function is strongly non exponential and is characterized by two widely separated decays.

This is demonstrated in figure 1 which shows a typical autocorrelation function at two time scales. Figure 1a reveals the fast decay as displayed by the correlator with a sample time of 4 μs. The asymptotic behaviour of the correlation function is a straight line of non zero slope, which indicates the presence of a slow mode. The latter can be revealed by using a long sampling time ($\Delta\tau = 300$ μs) as shown in figure 1b. The corresponding decay time is obtained from a single exponential fitting procedure in which the content of the first channel is deleted as it contains most of the signal associated with the fast mode.

The determination of the fast decay times was obtained by fitting the correlation function to the sum of two exponentials using a least-squares program. As a matter of fact, the separation of the two decays was generally large enough so that the following form of the autocorrelation function could be used to fit the data when the correlator sample time was chosen to span the fast decay :

$$C_i(\tau) = A I^{-\tau/\tau_F} + B(1 - \tau/\tau_s) + C$$

Fig. 1. — Normalized autocorrelation functions for system A ; $t_c/t = 0.7$. a) $\Delta\tau = 4 \mu s$. The curve is a double exponential fit to the data. b) $\Delta\tau = 300 \mu s$. The curve is a single exponential fit to the data.

where A , B and C are constants and τ_F and τ_s are the fast and slow decay times respectively. The normalized autocorrelation function is :

$$g^{(1)}(\tau) = (C_i(\tau) - C)/(A + B).$$

The time dependences of τ_s and τ_F obtained for system A have been plotted on figure 2. The gel point t_c has been taken to be the time at which τ_s becomes too long to be measurable. As a matter of fact, t_c can be rather well detected from the observations of the speckle pattern visible at very low scattering angles on a screen placed at a remote distance from the scattering cell. This pattern fluctuates randomly when the sample is in the sol state. A net slowing down is observed when approaching t_c beyond which the pattern becomes quasi-stationary. This also corresponds roughly to the stage where the sample does not flow when the cell is tilted. The observation of stationary speckle after t_c confirms the existence of microscopic inhomogeneities inside the gel. The experimental values of t_c were 15 h 10' and 25 h 15' for systems A and B respectively. Beyond t_c the autocorrelation function consists mainly of a continuous distribution of exponential decays plus a constant background corresponding to a quasi-static scattering. An analysis based on the method of cumulants [9] with the amplitude of the background taken as an adjustable parameter leads to a variance of the order of 0.2. This variance decreases with time to reach eventually a value close to zero when the reaction is completed.

Fig. 2. — Variation of $\tau_s/\tau_{F\infty}$ and $\tau_F/\tau_{F\infty}$ versus t/t_c for system A; $\tau_{F\infty}$ represents the asymptotic value obtained for $t/t_c \rightarrow \infty$; $t_c = 15 \text{ h } 15'$.

Inspection of figure 2 reveals some characteristic features which can be summarized as follows :

a) *Fast mode*. — Obviously, the fast decay can be attributed to the collective fluctuations characterized by a relaxation time :

$$\tau_F = (D_c K^2)^{-1},$$

where D_c is the cooperative diffusion constant and the magnitude of the scattering wavevector K is given by :

$$K = \frac{4\pi n}{\lambda} \sin \theta/2,$$

where θ is the scattering angle, λ is the wavelength of the incident light in a vacuum and n is the refractive index of the scattering medium.

As expected, τ_F does not exhibit any abrupt transition at t_c . It has already been demonstrated that the cooperative diffusion constant was nearly the same in a crosslinked gel and a semi-dilute polymer solution at the same concentration [10]. Near the gel point, the sol is formed of closely packed or even slightly interpenetrated branched aggregates, and the interconnection between these aggregates should not greatly affect the collective fluctuations. Nearly constant in the sol phase, τ_F starts to decrease slowly around t_c to reach an asymptotic value $\tau_{F\infty}$ after a long period ($t/t_c > 3$). Such behaviour clearly indicates that the reaction still proceeds beyond the gel point, leading to a progressive decrease in the number of dangling chains attached by one end to the network. Also the insaturations (pendant double bonds) are slowly consumed in the later stage of the reaction [11]. As a consequence D_c increases as shown previously in a study performed on swollen model networks containing controlled amounts of pendant chains [12]. Once the asymptotic value of τ_F is reached, a further swelling of the gel up to its equilibrium value only produces a very small increase of D_c .

$D_c = 15.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for a polymer concentration $c = 0.195 \text{ g cm}^{-3}$

$D_c = 16.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for $c = 0.115 \text{ g cm}^{-3}$ (at swelling equilibrium).

This result confirms the conclusions of a previous study performed on series of gels undergoing an osmotic deswelling and which also demonstrated a very weak sensitivity of D_c to a change of concentration [13].

b) *Slow mode*. — From the considerations developed at the beginning of this paper, it seems reasonable to attribute the origin of this mode to the change in the relative concentrations of branched aggregates of different sizes. The PFV model predicts :

$$\tau_s = (D_- K^2)^{-1}$$

where D_- is an undefined average value which PFV approximate for a fairly narrow particle size distribution to the self diffusion D_s of particles with radius equal to the mean of the distribution. Several authors [3, 4] have found that D_s in microemulsions varies like the viscosity. Despite the fact that the samples investigated here exhibit a rather large polydispersity mainly near the gel point [11], it is likely that the behaviour of the slow decay time is still correlated to the viscosity of the medium. In previous studies [14-15] the time dependence of the viscosity was found to obey a power law of the form :

$$\eta \sim \left(\frac{t_c - t}{t_c} \right)^{-s}$$

where s is of the order of 1. In the close vicinity of t_c , that is at $\frac{t_c - t}{t_c} \sim 2 \times 10^{-2}$ a cross-over is observed beyond which η follows another power law with $s \sim 0.78$ [15]. Figure 3 shows a log-log plot of τ_s^{-1} versus $(t - t_c)/t_c$ for the system A. The data fit a straight line with a slope equal to -1.1 , the coefficients of correlation being of the order of 0.988. The same exponent is found for system B. As mentioned before, there is some uncertainty on the value of t_c so that the behaviour of τ_s close to the gel point cannot be characterized. However, this uncertainty does not strongly affect the exponent of the power law $\tau_s^{-1} = f\left(\frac{t - t_c}{t_c}\right)$. For instance, shifting $(t - t_c)/t_c$ from $+$ and -0.02 leads to exponents respectively equal to 1.05 and 1.2 with a coefficient of correlation 0.986.

This paper was designed to provide a description of the time dependences of the characteristic decay times of the autocorrelation function of light scattered from a system undergoing irreversible gelation. In a subsequent paper we will present a more detailed analysis which will include the behaviour of the amplitudes of the two modes and their dependences on the concentration of the styrene and of the DVB.

Fig. 3. — Log-log plot of τ_s versus reduced time $\frac{t - t_c}{t_c}$ for system A; $t_c = 15 \text{ h } 15'$. The straight line is the best linear fit to the data.

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