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Determination of Individual Diffusion Coefficients in Evolving Binary Mixtures by Taylor Dispersion Analysis: Application to the Monitoring of Polymer Reaction

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This study demonstrates that it is possible to get valuable information on the individual populations of a binary mixture from the signal obtained by Taylor dispersion analysis (TDA). In the case of mixtures composed of two populations of different sizes (such as a monomer/polymer mixture), the information available from TDA is not restricted to an average diffusion coefficient or an average hydrodynamic radius calculated on the entire binary mixture. In this work, TDA was used to monitor a polymerization reaction. In this scope, it has been possible to determine the degree of conversion and the weight average hydrodynamic radius of the polymer at different reaction times. Three different methods are proposed for the data processing of taylorgrams derived from polymerization mixtures or, more generally, for taylorgrams of binary mixtures. These three methods, either based on deconvolution or on integration of the signal, were found to give similar results. TDA results obtained for a model binary mixture of acrylamide and standard polyacrylamide were consistent with DLS experiments provided that the differences in the type of average hydrodynamic radius values between the two methods are taken into account. An example of application to the monitoring of acrylamide radical polymerization is shown.

The idea of using the dispersion of a solute plug in a Poiseuille laminar flow as an alternative technique to determine diffusion coefficients was presented long time ago in the seminal work of Taylor,¹ later extended by Aris.² Because of the parabolic velocity

profile, molecules injected in a narrow band at the inlet of a capillary tube move with different velocities depending to their positions in the tube cross section. The dispersion of the solute plug depends on the molecular diffusion that redistributes the molecules over the cross section of the tube. The so-called Taylor dispersion analysis (TDA) is generally based on the measurement of the two first moments of the elution peak (elution time and temporal variance³) and does not require the assumption that the peak is Gaussian or symmetrical. Corrections to the variance arising from instrumental contributions have been studied in detail.⁴ TDA is attractive as it offers an absolute, simple and rapid method for determining average D values. TDA is applicable on (macro)molecules and particles of virtually any molar mass. Since it is an absolute measurement, no calibration is required and the knowledge of the sample concentration is not needed. It requires only minute amounts of sample (a few nanoliters are injected). It is also complementary to dynamic light scattering (DLS), probably the most popular experimental technique to determine diffusion coefficient values.⁵ Indeed, the average hydrodynamic radius $\langle R_h \rangle$ derived from TDA in the case of polydisperse sample is a weight average value in the case of a mass concentration sensitive detector,⁶ which can be very different from the harmonic z-average value obtained by DLS.⁷ As a consequence TDA is much less sensitive to aggregates or to particle impurities than DLS. The comparison between the two techniques can give valuable information on sample polydispersity. On the other hand, in the case of monodisperse samples, both techniques lead to the same R_h value.

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TDA was used to determine diffusion coefficients of analytes in gaseous⁸ or liquid phase.^{9–11} TDA was also used to measure the size of proteins,¹² nanoparticles, such as surfactant-protected platinum clusters,¹³ thiolate-protected gold clusters,¹⁴ and positively charged iron oxide maghemite nanoparticles.¹⁵ Belongia and Baygents¹⁶ extended the technique to the measurement of diffusion coefficients of colloidal particles ranging in size from 0.19 to 0.83 μm (polystyrene and polymethyl methacrylate particles, as well as tobacco mosaic virus). There are very few works dealing with the use of TDA for polymer or biopolymer analysis.^{15–21} Barooah et al. measured the diffusion coefficient of polystyrene in cyclohexane¹⁷ and in dioxane,¹⁸ at infinite dilution. Mes et al.¹⁹ reported a comparison of different methods (including DLS and TDA) for the determination of diffusion coefficients of synthetic polymers (styrene acrylonitrile copolymers). Bello et al.²⁰ demonstrated the very high reproducibility of the technique for proteins, as well as for small ions. Recently, we demonstrated the interest of TDA for the characterization of various polycations: different generations of dendrigraft polylysines²¹ and cationic polydiacetylene.²² Interestingly, it is also possible to couple online, on the same capillary, an electrophoretic separation to a TDA step, allowing an estimation of the hydrodynamic radius of each individual component constituting the injected mixture.²³ It should be noted that when TDA is implemented on a CE apparatus, UV detection is generally used, and the methodology is in that case restricted to UV absorbing polymers. Alternative detectors, for example, contactless conductimeters, must be used when the popular UV–visible detector does not operate. As for size-exclusion chromatography, in TDA, the absence of interaction between the solute and the capillary wall is required.

As discussed in detail in a previous work,⁶ the average values $\langle R_h \rangle$ obtained by TDA for a mixture of molecules or macromolecules are weight-average and number-average values for mass concentration or molar concentration sensitive detectors, respectively. These average values are obtained by integration of the entire signal (not necessarily Gaussian) and after determination of the two first moments of the peak. The main goal of this work is to demonstrate that, in the case of mixtures composed of two populations of different sizes (such as a monomer/polymer mixture), the information available from

TDA is not restricted to an average $\langle D \rangle$ or $\langle R_h \rangle$ value on the entire binary mixture. Valuable information on the two individual populations constituting the mixture can also be derived from the shape of the peak for the mixture. In the case of a monomer/polymer mixture, the main goal is to obtain the degree of conversion of the polymer reaction, as well as the average $\langle R_h \rangle$ of the formed polymer.

Of the other techniques generally used for monitoring a polymer reaction, size-exclusion chromatography (SEC),²⁴ which separates macromolecules according to their hydrodynamic volumes, is undoubtedly the most popular separation technique used for the characterization of the polymer molar mass or hydrodynamic radius distributions. Molar mass relative to a standard calibration is generally obtained by SEC when using only a mass concentration detector (such as refractive index detection or UV detection). Absolute molar mass determination by SEC requires the use of a double detection including a mass concentration detector together with a static light scattering detector. Distribution of the hydrodynamic radius can also be obtained by SEC when using an online viscosimetric detection instead of (or in addition to) the static light scattering detector. Another very popular technique for determining hydrodynamic radius is the dynamic light scattering²⁵ that generally gives access to an average hydrodynamic radius (harmonic z -average radius). This method requires great care in sample preparation as it is very sensitive to tiny amounts of aggregates or particulate materials. Regarding the monitoring of the monomer conversion, conventional analytical (HPLC, GC, CE), or spectroscopic techniques (NMR, infrared spectroscopy, UV, ...) can be used depending on the characteristics of the monomer.²⁶

THEORETICAL BACKGROUND

When performing a Taylor dispersion analysis on a mixture of two populations (e.g., a monomer m and a polymer p), a signal reflecting the Taylor dispersion is measured using a detector placed at a distance l from the capillary inlet end. Such a record of the detector signal as a function of time is called a chromatogram in chromatography, an electropherogram in electrophoresis, or a fractogram in field-flow fractionation. By analogy, we call the record of the detector signal in TDA a taylorgram. During the course of the polymerization process, monomer/polymer mixtures are sampled at different stages of the process for TDA. Let $S_i(t)$ be the signal given by the detector for the analysis of the mixture sampled at stage i . Here, t is the time elapsed since the injection of the sample in the analyzer. This signal is the superposition of the signal $S_{m,i}(t)$ of the monomer m and the signal $S_{p,i}(t)$ of the polymer p . To derive further physical data on these two species, such as the degree of conversion of the polymerization reaction or the mean hydrodynamic radius of the polymer p , each contribution to the global signal $S_i(t)$ must be separated by applying one of the following methods of

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treatment to the global signal. The degree of conversion Ψ_i of the polymerization reaction for the sample at stage i is defined as

$$\Psi_i = \frac{m_{p,i}}{m_{m,i} + m_{p,i}} \quad (1)$$

where $m_{m,i}$ and $m_{p,i}$ are the masses in sample i of the monomer m and the polymer p , respectively. The detector response coefficients, k_m and k_p , for the two species m and p are defined by

$$A_{m,i} = k_m m_{m,i} \quad (2)$$

$$A_{p,i} = k_p m_{p,i} \quad (3)$$

where $A_{m,i}$ and $A_{p,i}$ are the peak areas of the corresponding signals $S_{m,i}(t)$ and $S_{p,i}(t)$. The coefficients k_m and k_p are considered constant throughout the experiment, even if the structure of a species, for example, that of the polymer p , can evolve. This hypothesis is generally verified, as for vinylic monomers for which the coefficient k_m is generally very different from k_p because of the presence of the UV-absorbing double bond in the monomer. For vinylic homopolymer with a UV-absorbing repeating unit, k_p remains constant whatever the degree of polymerization. In Taylor dispersion analysis, the determination of the diffusion coefficient of a species is based on the measurements of the mean of its peak and its variance $\sigma_{p,i}^2$ or standard deviation, $\sigma_{p,i}$. In TDA, the peak means of the various species are identical, while their variances are different. Below we discuss three methods to obtain the variance $\sigma_{p,i}^2$ and the degree of conversion Ψ_i .

Method Based on the Analysis of the Global Signal $S_i(t)$ with No Deconvolution (Method 1). Assuming that the response factors, or at least their ratio κ , are known, it is possible to get information on the degree of conversion of the polymerization and on the hydrodynamic radius of the formed polymer directly from the global signal, $S_i(t)$, without any deconvolution.

Method Based on the Conservation of the Mass of the Injected Sample. This method relies on the assumption that the sample mass injected in the analyzer at the different stages is constant and exploits the fact that the overall peak area reflects the degree of advancement of the polymerization process provided that the response coefficients of the monomer and polymer species are different. The mass of sample i can be expressed as the sum of the mass of the monomer and that of the polymer

$$m_i = m_{m,i} + m_{p,i} \quad (4)$$

where m_i can be considered as the mass introduced in the capillary for the experiment at stage i . Let assume here that the sample mass, m_i , is kept constant from one sample to the other $m_i = m$ for all i . The total area A_i of the signal $S_i(t)$ is

$$A_i = k_m m_{m,i} + k_p m_{p,i} \quad (5)$$

At the beginning of the polymerization process ($i = 0$), the sample contains only a mass m of the monomer, so

$$A_0 = k_m m_{m,0} = k_m m \quad (6)$$

Then, by combining eqs 5 and 6, eq 1 can be written as

$$\Psi_i = \frac{1}{1 - \kappa} \frac{A_0 - A_i}{A_0} \quad (7)$$

$$\kappa = \frac{k_p}{k_m} \quad (8)$$

Thus, the degree of conversion Ψ_i can be directly calculated from the total area A_0 and A_i of the signal before polymerization ($i = 0$) and at the current stage i . This is possible when the mass of the sample is constant and if k_p is different from k_m so that the peak areas of the initial sample ($i = 0$) and of the sample at stage i differ and, hence, that the numerator and the denominator of eq 7 do not vanish.

Method Not Requiring the Conservation of the Mass of the Injected Sample. When the requirement of constant injected mass over several samples is too restrictive or difficult to fulfill, the method described below can be used. This method exploits the fact that the change observed in the variance of the sample peak is related to the advancement of the polymerization process. Assuming that the mean time $t_{d,m}$ and $t_{d,p}$ of the two signals $S_{m,i}(t)$ and $S_{p,i}(t)$ are the same and that these two signals are symmetrical around this common mean time $t_{d,i}$, the maximum h_i of the global signal $S_i(t)$ arises at $t_{d,i}$ and is given by

$$h_i = h_{m,i} + h_{p,i} \quad (9)$$

where $h_{m,i}$ and $h_{p,i}$ are the heights of the peaks of the signals $S_{m,i}(t)$ and $S_{p,i}(t)$, respectively. Similarly, it was shown⁶ that the variance, σ_i^2 , of the global signal $S_i(t)$ can be expressed by

$$\sigma_i^2 = \frac{A_{p,i}}{A_{m,i} + A_{p,i}} \sigma_{p,i}^2 + \frac{A_{m,i}}{A_{m,i} + A_{p,i}} \sigma_{m,i}^2 \quad (10)$$

where $\sigma_{m,i}^2$ and $\sigma_{p,i}^2$ are the variances of $S_{m,i}(t)$ and $S_{p,i}(t)$, respectively. We introduce the parameter y_i defined as the fractional peak area of the polymer component

$$y_i = \frac{A_{p,i}}{A_{m,i} + A_{p,i}} \quad (11)$$

By combining eqs 1–3, 8, and 11 to eliminate $m_{m,i}$ and $m_{p,i}$, it is easy to show that eq 11 can be written as

$$y_i = \frac{\kappa \Psi_i}{1 - \Psi_i + \kappa \Psi_i} \quad (12)$$

or, equivalently

$$\Psi_i = \frac{y_i}{y_i + \kappa(1 - y_i)} \quad (13)$$

The two parameters of interest are $\sigma_{p,i}^2$ and Ψ_i . The latter is connected to the areas $A_{m,i}$ and $A_{p,i}$ via eqs 11 and 13. The method involves the introduction of two new variables, α_i and β_i ,

whose values are experimentally accessible from the signals of the peak obtained before the start of the polymerization process and that of the peak at stage i

$$\alpha_i = \frac{h_i A_0}{h_0 A_i} \quad (14)$$

$$\beta_i = \frac{\sigma_i^2}{\sigma_{m,i}^2} = \frac{\sigma_i^2}{\sigma_{m,0}^2} \quad (15)$$

Introducing the parameter x_i as

$$x_i = \frac{\sigma_{p,i}}{\sigma_{m,i}} \quad (16)$$

and noting that, for each species and at all stages, the ratio of the peak area to the product of the peak height times the standard deviation is constant, it can be shown that

$$\alpha_i = 1 - y_i + \frac{y_i}{x_i} \quad (17)$$

$$\beta_i = 1 - y_i + y_i x_i^2 \quad (18)$$

Equations 17 and 18 lead to a system of two equations with two unknown variables (x_i and y_i) for which the physically acceptable solutions are

$$x_i = \frac{1}{2} \left(\sqrt{\frac{4\beta_i - 3 - \alpha_i}{1 - \alpha_i}} - 1 \right) \quad (19)$$

$$y_i = (\beta_i - \alpha_i) \frac{x_i}{x_i^3 - 1} \quad (20)$$

Finally, the value Ψ_i can be derived from y_i using eq 13. $\sigma_{p,i}$ is obtained using eq 16, assuming that $\sigma_{m,i} = \sigma_{m,0}$ (the variance of the monomer contribution remains unchanged, as stated in eq 15).

Thus, according to this method, the measurements of the area A_0 and A_i , of the heights h_0 and h_i , and of the standard deviation $\sigma_{m,0}$ of the signal $S_{m,0}(t)$ of the monomer before the polymerization reaction, allow the determination of the degree of conversion Ψ_i and of the standard deviation $\sigma_{p,i}$ of the polymer contribution. It is worth noting that the knowledge of the response factor is only required for the calculation of the degree of conversion (eq 13) but not for the measurement of the polymer size.

Deconvolution of the Global Signal $S_i(t)$. Deconvolution Using Gaussian Curves (Method 2). Assuming that the signals $S_{m,i}(t)$ and $S_{p,i}(t)$ can be described using a Gaussian distribution, one has

$$S_{m,i}(t) = \frac{A_{m,i}}{\sigma_{m,i} \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{t - t_{d,m}}{\sigma_{m,i}} \right)^2 \right] \quad (21)$$

$$S_{p,i}(t) = \frac{A_{p,i}}{\sigma_{p,i} \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{t - t_{d,p}}{\sigma_{p,i}} \right)^2 \right] \quad (22)$$

where $\sigma_{m,i}$ and $\sigma_{p,i}$ are the standard deviations, $t_{d,m}$ and $t_{d,p}$ the mean values, and $A_{m,i}$ and $A_{p,i}$ the areas of the signals $S_{m,i}(t)$ and $S_{p,i}(t)$. It is then possible to fit the global signal $S_i(t)$ by the sum of the two Gaussian curves. This fit involves six parameters, namely, $\sigma_{m,i}$, $\sigma_{p,i}$, $t_{d,m}$, $t_{d,p}$, $A_{m,i}$, and $A_{p,i}$. It is possible to reduce the number of unknown parameters to four since $\sigma_{m,i} = \sigma_{m,0}$ and $t_{d,m} = t_{d,p}$. $\sigma_{m,0}$ can be measured through an initial Taylor experiment with a solution containing only the monomer ($i = 0$). It is worth noting that, in Taylor dispersion, the peak variance only depends on the solute diffusion coefficient (or solute size), and not on the concentration, at least when the sample has been adequately diluted in the carrier liquid. Therefore, the variance relative to the monomer peak should not depend on the monomer concentration (and thus on the degree of conversion of the reaction).

Deconvolution by Subtracting the Monomer Contribution (Method 3). When the molar mass distribution of the polymer p is too broad, it is no longer possible to fit the polymer contribution using a single Gaussian distribution. In this case, the method consists in subtracting the Gaussian contribution of the monomer $S_{m,i}(t)$ to the global signal $S_i(t)$ to obtain a reduced signal $S'_i(t)$. The fitting is obtained by adjusting the $A_{m,i}$ parameter ($\sigma_{m,i} = \sigma_{m,0}$ being known from the preliminary analysis of the peak for the monomer alone). Then, the variance of the reduced signal $S'_i(t)$ is taken as an approximation of $\sigma_{p,i}^2$

$$\sigma_{p,i}^2 = \frac{\int_{t_{d,i}-b}^{t_{d,i}+b} S'_i(t) \cdot (t - t_{d,i})^2 \cdot dt}{\int_{t_{d,i}-b}^{t_{d,i}+b} S'_i(t) \cdot dt} \quad (23)$$

where b is a time interval large enough to ensure that the integrations in eq 23 are performed for the whole duration when $S'_i(t)$ deviates from its baseline value. This method works well when the characteristic parameters of the signal of the monomer $S_{m,i}(t)$ are significantly different from those of the signal of the polymer, that is, when the signal of the monomer $S_{m,i}(t)$ can be "visually" separated from the signal of the polymer $S_{p,i}(t)$. This is verified when the size of the polymer is much larger than that of the monomer, which occurs rapidly during the polymerization process as far as very small oligomers are not concerned.

One criterion for the curve fitting is to test the shape of the reduced signal $S'_i(t)$ by adjusting the $A_{m,i}$ parameter. This test may consist in calculating the number of zeros of the derivative of the reduced signal $S'_i(t)$: if the derivative has three zeros, it means that the area of the fitted Gaussian distribution is too large ($A_{m,i}$ parameter too high) and that a part of the polymer signal has been considered as belonging to the monomer signal. Thus, in the iteration process of the fitting, the area of the Gaussian monomer contribution is decreased. On the contrary, if the derivative has only one zero, it may mean that the area of the fitted Gaussian distribution is too small ($A_{m,i}$ parameter too low) and that a part of the monomer signal has not been taken into account in the monomer signal. The

convergence of such an iteration process results in a limit by excess of the area of the monomer signal.

Determination of the Degree of Conversion of the Reaction (Methods 2 and 3). It is to be noticed that $A_{m,i}$ can be derived from the results of the fitting using the Gaussian distribution. From the deconvolution of the contributions of the monomer and the polymer, it is thus possible to obtain the degree of conversion Ψ_i for a sample at stage i

$$\Psi_i = \frac{A_{m,0} - A_{m,i}}{A_{m,0}} \quad (24)$$

Determination of the Hydrodynamic Radius of the Polymer. The data on the elution profiles of the monomer/polymer mixture can be used to determine the hydrodynamic radius $R_{h,p,i}$ of the polymer that is connected to the diffusion coefficient $D_{p,i}$. The polymer diffusion coefficient is obtained using the classical relationship in TDA

$$D_{p,i} = \frac{R_c^2 t_{d,i}}{24\sigma_{p,i}^2} \quad (25)$$

where R_c is the capillary internal diameter. This equation is verified as long as the two following conditions are fulfilled.^{15,27} First, the dimensionless residence time, $\tau = (D_{p,i} t_{d,i}) / (R_c^2)$, which is the ratio of the mean analyte residence time to the time required for an analyte to diffuse a distance equal to the radius of the capillary, should be higher than 1.4 to ensure that the analyte sufficiently samples all flow streamlines for the dispersion to reach its long-time limit leading to eq 25. Second, the Peclet number, which describes the relative rates of mass transfer along the axis of the capillary because of convection and diffusion, should be higher than 69 for the axial diffusion contribution to the peak variance to be neglected in eq 25. The Peclet number is given by $Pe = (uR_c) / (D_{p,i})$, with u the mean linear velocity. Finally, the hydrodynamic radius of the polymer is obtained using the Stokes–Einstein equation

$$R_{h,p,i} = \frac{k_B T}{6\pi\eta_0 D_{p,i}} \quad (26)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η_0 the viscosity of the carrier liquid.

MATERIALS AND METHODS

Chemicals. Sodium chloride (NaCl) was purchased from Acros Organics (Geel, Belgium). Acrylamide (AM, 99+% electrophoresis grade), potassium persulfate, and tetramethylethylenediamine (TMEDA) were obtained from Sigma-Aldrich (Steinheim, Germany) and were used as received. The water used to prepare all solutions was purified with a Milli-Q system from Millipore (Molsheim, France).

Acrylamide should be manipulated with great caution. Direct exposure to pure acrylamide by inhalation, skin absorption, or eye contact irritates the exposed mucous membranes and can also cause sweating, urinary incontinence, nausea, myalgia, numbness,

paresthesia, and weakened legs and hands. In addition, the acrylamide monomer is a potent neurotoxin.

Polyacrylamide Standards. Standards of polyacrylamide (PAM 3.5k, PAM 20k, and PAM 350k with weight average molar masses determined by size exclusion chromatography (SEC) $M_w = 3500$, 21 900, and 367 000 g/mol, respectively) were purchased from Polymer Standards Service (PSS, Mainz, Germany). The polydispersity indexes of the PAM standards are 1.2 for PAM 3.5k, 1.6 for PAM 20k, and 2.6 for PAM 350k. The absolute molar masses given by the manufacturer (PSS) were determined by SEC coupled to a double detection (light scattering and refractive index detection). To avoid any monomer residues in the PAM standards, each standard was dialyzed against water for 3 days and lyophilized.

Polymerization of Acrylamide by Radical Polymerization. In a flamed and vacuum-dried two-neck flask, 2.662 g (3.74×10^{-2} mol) of acrylamide were dissolved in 35 mL of deionized water. After addition of 10 mL of absolute ethanol, the reaction medium was purged with nitrogen for 40 min. Then, a solution of 97 mg (3.6×10^{-4} mol) of potassium persulfate $K_2S_2O_8$ in 2.5 mL of water was added. Three minutes later, a solution of 83.5 mg (7.18×10^{-4} mol) of tetramethylethylenediamine (TMEDA) in 2.5 mL of water was also added to the reaction medium. The polymerization was allowed to proceed for 1 h at room temperature. To study the kinetics of the polymerization by TDA, aliquots (10 μ L) were taken at different reaction times and diluted with 990 μ L of 0.1 M NaCl aqueous solution directly in CE vials. The final acrylamide concentration in the CE vials is 0.53 g/L (7.5 mM). All the polymerization samples were kept at 4 °C on the CE carousel. It is worth noting that the sample was not only cooled after the sampling from the reactor but also diluted 100 times with the NaCl solution. This dilution considerably decreased the reaction rate (as the dilution factor, by a factor 100). This insures that the polymer reaction does not progress during the TDA run.

Protocol for Taylor Dispersion Analysis. Taylor dispersion analysis (TDA) experiments were performed on a PACE MDQ Beckman Coulter (Fullerton, CA) apparatus equipped with a monochromatic UV detector or on an Agilent 3D-CE system (Walbronn, Germany) with a diode array detector. Neutrally coated capillary tubing (polydimethylsiloxane, DB-1) was purchased from CIL Cluzeau (Sainte-Foy-la-Grande, France). Capillary dimensions were 30 cm (20 cm to the detector) \times 50 μ m i.d. on PACE MDQ and 30.7 cm (22.2 cm to the detector) \times 50 μ m i.d. on Agilent. The electrolyte used for pressure mobilization during the TDA step was a 0.1 M NaCl solution (viscosity $\eta_0 = 0.89 \times 10^{-3}$ Pa s at 25 °C). New capillaries were conditioned with the following flushes: water for 10 min and NaCl 0.1 M for 15 min. AM and PAM samples were dissolved in the electrolyte at 0.7 g/L. Sample injection was performed hydrodynamically: 0.3 psi (21 mbar), 5 s on PACE MDQ and 17 mbar, 5 s on Agilent. Mobilization pressure was applied with 0.1 M NaCl electrolyte vials at both ends of the capillary. Between two TDA analyses, the capillary was flushed with 0.1 M NaCl for 1 min. Solutes were monitored by UV absorbance at 200 nm on the PACE MDQ and both 190 and 240 nm wavelengths on Agilent. The temperature of the capillary cartridge was set at 25 °C.

(27) Taylor, G. *Proc. R. Soc. London, Ser. A* **1954**, 225, 473–477.

Table 1. Diffusion Coefficients and Hydrodynamic Radii Obtained by TDA and DLS for Four PAM Standards and for AM

technique	AM		PAM 3.5k		PAM 20k		PAM 350k	
	D (m ² /s)	R_h (nm)	D (m ² /s)	R_h (nm)	D (m ² /s)	R_h (nm)	D (m ² /s)	R_h (nm)
TDA ^a	1.06×10^{-9}	0.23	2.21×10^{-10}	1.11	6.58×10^{-11}	3.73	1.89×10^{-11}	13.00
DLS, intensity average ^b	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	9.78×10^{-12}	25.0	7.93×10^{-12}	30.9
DLS, weight average (using Mark–Houwink coefficient) ^d	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	4.79×10^{-11}	5.10	1.48×10^{-11}	16.5

^a Diffusion coefficients were obtained by Gaussian curve fitting using eq 25. The average diffusion coefficients derived from TDA for a mass concentration-sensitive detector⁶ are given by $\langle D_{TDA} \rangle = (\sum_i N_i M_i) / (\sum_i N_i M_i / D_i)$. The hydrodynamic radii were determined using the Stokes–Einstein relationship, with $\eta = 0.89 \times 10^{-3}$ Pa s. The average hydrodynamic radii obtained by TDA for a mass concentration-sensitive detector⁶ are given by $\langle R_{h,TDA} \rangle = (\sum_i N_i M_i R_{h,i}) / (\sum_i N_i M_i)$. In these expressions, N_i , D_i , and $R_{h,i}$ are the mole number, diffusion coefficient, and hydrodynamic radius of the polymer of molar mass M_i . ^b Diffusion coefficients obtained by DLS are a *z*-average value (i.e., an intensity-averaged value): $\langle D_z \rangle = (\sum_i N_i M_i^2 D_i) / (\sum_i N_i M_i^2)$. ^c Not determined (scattered intensity is too low). ^d The weight average R_h values were derived from DLS data using the Mark–Houwink scaling law $[\eta]_i = 5.31 \times 10^{-3} M_i^{0.79}$, where $[\eta]_i$ is in mL/g and M_i in g/mol, as explained in the text.

The elution time was corrected from the delay in the application of the pressure using the following equation (in min):⁴

$$t_{r,i} = t_{r,i,obs} - 0.125 \quad (27)$$

where $t_{r,i,obs}$ is the observed elution time. Corrections for injected volume on the average detection times and on the observed variances were considered as demonstrated elsewhere²¹ using the following equations:

$$t_{d,i,corr} = \frac{t_{d,i}}{1 - \frac{V_i}{2V_c}} \quad (28)$$

$$\sigma_{i,corr}^2 = \frac{1}{1 - \frac{V_i}{V_c}} \left[\sigma_i^2 - \frac{t_{d,i}^2}{12} \left(\frac{\frac{V_i}{V_c}}{1 - \frac{V_i}{2V_c}} \right)^2 \right] \quad (29)$$

where V_i is the injected volume, V_c the capillary volume from inlet to detector, equal to $\pi d_c^2 l_d / 4$. Correction on the average detection time ($t_{d,i}$) is about 0.5% independently of the mobilizing pressure. Correction on the temporal variance (σ_i^2) was always lower than 4% for the monomer and 1% for the polymer as calculated using eq 29.

Dynamic Light Scattering. Dynamic light scattering (DLS) experiments were performed using a standard setup by Brookhaven Instruments Co. (BI-900AT). All measurements were performed at a scattering angle $\theta = 90^\circ$, using a 100 mW Argon ion laser with in vacuo wavelength $\lambda = 514$ nm. The sample was thermostated at 24.6 ± 0.1 °C. In DLS, information on the size distribution of the sample are obtained from the shape of $f(\tau)$, the autocorrelation function of the temporal fluctuations of the scattered intensity.⁵ For relatively small polymers undergoing Brownian motion, size polydispersity results in a nonexponential decay of $f(\tau)$ with time delay τ . We used the CONTIN algorithm^{28,29} provided in the Brookhaven software package to calculate the size distribution from $f(\tau)$. We recall that DLS provides a *z*-harmonic size distribution (i.e., an intensity-weighted size distribution) of the scatterers.⁷ Special care should thus be taken when comparing

DLS data to size distribution data obtained by TDA, as discussed in the next section. PAM and AM samples were at the same monomer concentration (~ 0.5 g/L) as for the TDA experiment.

RESULTS AND DISCUSSION

Before applying the Taylor dispersion analysis to the monitoring of polymerization reactions, we first investigated the application of the three aforementioned methods for characterizing binary AM/PAM mixtures of well-known composition. Three standards of poly(acrylamide) with weight average molar masses of 3500 (PAM 3.5 k), 21 900 (PAM 20 k), and 36 7000 g/mol (PAM 350 k) were used as model compounds. For a better characterization of the PAM standards, TDA and DLS experiments were performed in the same conditions (concentration, temperature, ionic strength) for the three PAM samples, as well as for the AM (all samples were injected as pure compounds, taylorgrams are not shown). We report in Table 1 the diffusion coefficients and hydrodynamic radii obtained by TDA and DLS. For AM and PAM 3.5k, the scattered intensity was too low, and only the TDA results are reported. As shown in Table 1, large discrepancies were obtained on the average hydrodynamic radii given by the two methods, but this can be explained by the polydispersity of the standards, since TDA leads to the weight average R_h value, while DLS gives a *z*-harmonic average value (see Table 1 for the equations). It is worth noting that the PAM standards should be considered as secondary standards since the polydispersity indexes are relatively large (from 1.2 for PAM 3.5k to 2.6 for PAM 350k). The differences between the two methods are considerably reduced after recalculation of the weight average R_h value from the R_h distribution obtained by means of the CONTIN algorithm in DLS. This calculation requires knowledge of the weighing terms $N_j M_j$ for each bin corresponding to an interval of radii centered around $R_{h,j}$ (N_j and M_j are the mole number and molar mass of polymers belonging to the *j*th bin, respectively. See caption of Table 1 for more details). However, the CONTIN algorithm only provides $B_j = N_j M_j^2$ because the DLS signal is proportional to the intensity of the scattered light, that is, to mass squared. We note that the molecular hydrodynamic volume, $V_{h,j}$ ($= 4\pi R_{h,j}^3 / 3$), of the polymer is related to its intrinsic viscosity, $[\eta]_j$, according to Einstein's law for viscosity, as

$$[\eta]_j = \frac{5 N_A V_{h,j}}{2 M_j} \quad (30)$$

(28) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213–217.

(29) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229–242.

where N_A is the Avogadro number, and that the dependence of the intrinsic viscosity on molar mass is expressed by the Mark–Houwink relationship as

$$[\eta_j] = KM_j^a \quad (31)$$

where K and a are constants for a given polymer–solvent–temperature system. Then, the molar mass is related to the hydrodynamic radius by

$$M_j = \left(\frac{10\pi N_A R_{h,j}^3}{3K} \right)^{1/(1+a)} \quad (32)$$

with $a = 0.79$ for the PAM solutions.³⁰ Note that Mark–Houwink relationship from ref 30 is given for a temperature of 30 °C in a 0.12 M NaCl aqueous solution. We consider that the a coefficient is not different at the temperature of the experiment (25 °C) and for similar ionic strength (0.1 M). To convert the CONTIN data to a weight distribution of sizes, we thus use $N_j M_j \sim B_j / R_j^{3/(1+a)}$.

Taylor Dispersion Analysis of Known AM/PAM Mixtures.

To mimic a polymerization medium, AM/PAM (10/90 v/v) mixtures were prepared for each PAM standards, and TDA was performed on each mixture. TDA was carried out on DB-1 coated capillaries with 50 μm internal diameter at 0.7 psi mobilization pressure using 0.1 M NaCl as the mobile phase. Such polydimethylsiloxane coating considerably reduced the PAM adsorption onto the capillary wall, as compared to fused silica capillary. The presence of NaCl was also found to limit the interaction between the polymer and the capillary wall. Figure 1 (solid lines) displays the UV traces obtained for the three mixtures. The profile of the taylorgrams is basically the sum of two distinct contributions, as typically observed for binary mixtures with compounds of largely different sizes.⁶ Using these experimental conditions, the average migration times of the monomer and the polymer contributions were found to be identical as assumed in the theoretical part. The larger the PAM, the broader the polymer contribution to the TDA signal, as shown in Figure 1A–C on the same time-scale.

The three aforementioned methods were next used for extracting information on the polymer size from the taylorgrams. Table 2 recapitulates the diffusion coefficients and the corresponding hydrodynamic radii obtained for the three model mixtures using the three described methods. It is worth noting that the $\tau > 1.4$ condition was verified since the elution time to the detector (close to 2.65 min) was much higher than the characteristic diffusion time in the capillary cross section. τ values were 285 for AM, 53 for PAM 3.5k, 17 for PAM 20k, and 4.5 for PAM 350k. The condition on the Peclet number ($Pe \gg 6.9$) was also verified since $Pe = 28$ for AM, 150 for PAM 3.5k, 448 for PAM 20k, and 1796 for PAM 350k. Method 1 is only based on the global signals of the mixture and the pure monomer without any deconvolution. This method only requires the global peak heights (h_0 and h_i), signal areas (A_0 and A_i) and signal variances ($\sigma_{m,0}$ and σ_i). Intermediate parameters α_i , β_i and x_i were first determined according to eqs 14, 15, and 19. $\sigma_{p,i}$ was next derived from x_i using eq 18 assuming that $\sigma_{m,i} = \sigma_{m,0}$. Average R_h values obtained by

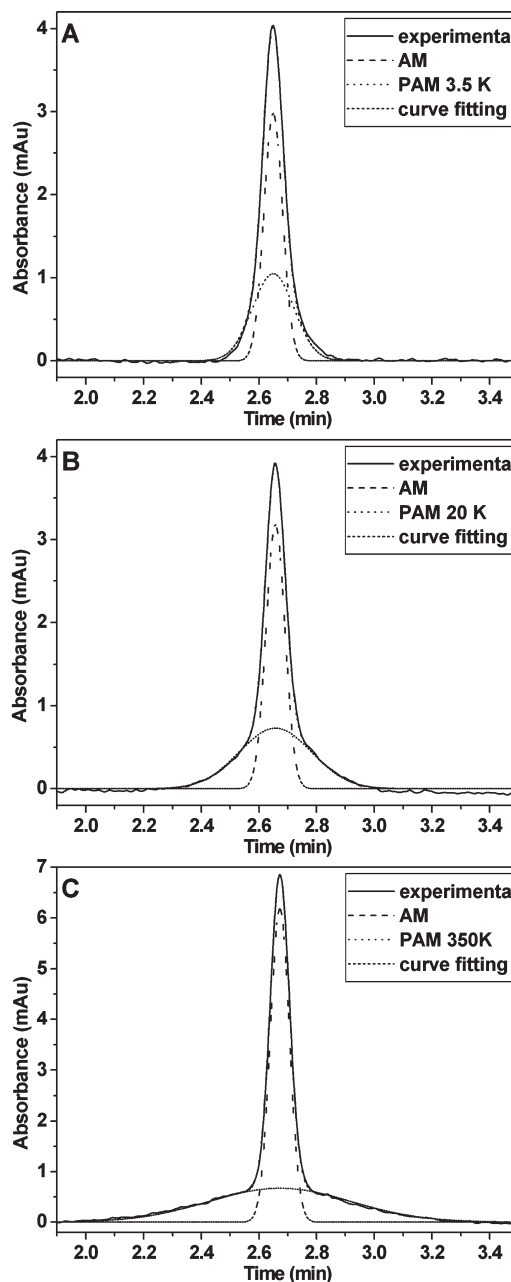


Figure 1. TDA (UV traces) of AM/PAM standard mixtures. PAM 3.5k (A), PAM 20k (B), and PAM 350k (C). Polydimethylsiloxane (DB-1) capillary, 30 cm (20 cm to the detector) \times 50 μm i.d. 0.1 M NaCl mobile phase. Mobilization pressure: 0.7 psi (50 mbar). AM (0.07 g/L) and PAM (0.63 g/L) in 0.1 M NaCl. Hydrodynamic injection: 0.3 psi (21 mbar), 5s. Flushes between analysis: 0.1 M NaCl (20 psi, 1 min). UV absorbance at 200 nm. Temperature: 25 °C.

method 1 are given in Table 2 and are in good agreement with the values obtained by TDA of the pure PAM (Table 1). Method 2, based on the deconvolution of the global signal by two Gaussian curves, is well adapted to this example (monomer/polymer mixture) as shown by the excellent fitting of the experimental taylorgrams (Figure 1). Method 2 gives also access to the characteristics of the monomer population (monomer peak area and average R_h value) from which the calculation of the degree of conversion can be easily obtained for monitoring the polymerization reaction (see eq 24). Method 3 consists in subtracting the monomer contribution

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Table 2. Determination of the Diffusion Coefficients and Hydrodynamic Radii from Three AM/PAM (10/90 v/v) Mixtures Using Methods 1, 2, and 3

TDA method	AM		PAM 3.5k		PAM 20k		PAM 350k	
	D (m ² /s)	R_h (nm)	D (m ² /s)	R_h (nm)	D (m ² /s)	R_h (nm)	D (m ² /s)	R_h (nm)
1			2.09×10^{-10}	1.17	7.01×10^{-11}	3.50	1.75×10^{-11}	14.0
2	1.16×10^{-9}	0.22	2.13×10^{-10}	1.15				
2	1.12×10^{-9}	0.22			6.95×10^{-11}	3.53		
2	1.14×10^{-9}	0.22					1.78×10^{-11}	13.8
3			2.28×10^{-10}	1.08	7.34×10^{-11}	3.34	1.85×10^{-11}	13.3

Table 3. Determination of the Molar Masses (in 10³ g/mol) of PAM Standards from the (10/90 v/v) AM/PAM Mixtures Using Methods 1, 2, and 3 and eq 32

$\langle M_{TDA} \rangle^a$	PAM 3.5k		PAM 20k		PAM 350k	
	3.4		19.9		303	
	SEC	TDA ^b	SEC	TDA ^b	SEC	TDA ^b
1	3.5	3.2	21.9	20.2	367	207
2	3.5	3.1	21.9	20.5	367	200
3	3.5	2.8	21.9	18.7	367	189

^a Expected values derived from eq 35 as described in the text.

^b Calculated from the weight average R_h obtained by TDA of AM/PAM mixture.

to the global signal to extract the polymer contribution. The fitting is obtained by adjusting the $A_{m,i}$ parameter corresponding to the peak area of the monomer contribution taking the monomer variance $\sigma_{m,i} = \sigma_{m,0}$ derived from the taylor-gram of a pure monomer solution. The variance of the polymer contribution is then obtained by integration of the resulting signal. All three methods lead to similar results in terms of polymer R_h for the three PAM standards.

The molar mass $M_{p,i}$ of the polymer is obtained from the hydrodynamic radius by means of eq 32, with $a = 0.79$ and $K = 5.31 \times 10^{-3}$ with $[\eta]$ in mL/g and M in g/mol.³⁰ Table 3 shows the PAM molar masses obtained from PAM weight average hydrodynamic radii given in Table 2 by means of eq 32, as well as PAM weight average molar masses, M_w , obtained by SEC. A fairly good agreement with the M_w molar masses was obtained for PAM 3.5k and 20k, while a much lower value was obtained by TDA and the Mark–Houwink equation for PAM 350k.

However, because the PAM standards are somehow polydisperse, one does not expect a perfect agreement between the

average molar mass. Indeed, for a polydisperse sample, TDA performed with a mass concentration detector provides a weight average hydrodynamic radius, $\langle R_{h,TDA} \rangle$, defined as

$$\langle R_{h,TDA} \rangle = \frac{\sum_j N_j M_j R_{h,j}}{\sum_j N_j M_j} \quad (33)$$

The average molar mass derived from TDA, $\langle M_{TDA} \rangle$ is then, according to eq 32

$$\langle M_{TDA} \rangle = \left(\frac{10\pi N_A}{3K} \right)^{1/(1+a)} \langle R_{h,TDA} \rangle^{3/(1+a)} \quad (34)$$

that is, when combining eqs 33 and 34 and using the relationship between $R_{h,j}$ and M_j given by eq 32

$$\langle M_{TDA} \rangle = \left(\frac{\sum_j N_j M_j^{(4+a)/3}}{\sum_j N_j M_j} \right)^{3/(1+a)} \quad (35)$$

As the weight distributions of molar masses provided by SEC with double detection of the three PAM samples are reasonably well described by a log-normal function, we computed, by means of eq 35 with $a = 0.79$, the $\langle M_{TDA} \rangle$ values for weight log-normal distributions having the same number-average and weight-average molar masses³¹ as those provided by the supplier for each PAM sample. Since a is smaller than 2, $\langle M_{TDA} \rangle$ is slightly lower than M_w . These expected $\langle M_{TDA} \rangle$ values, reported in Table

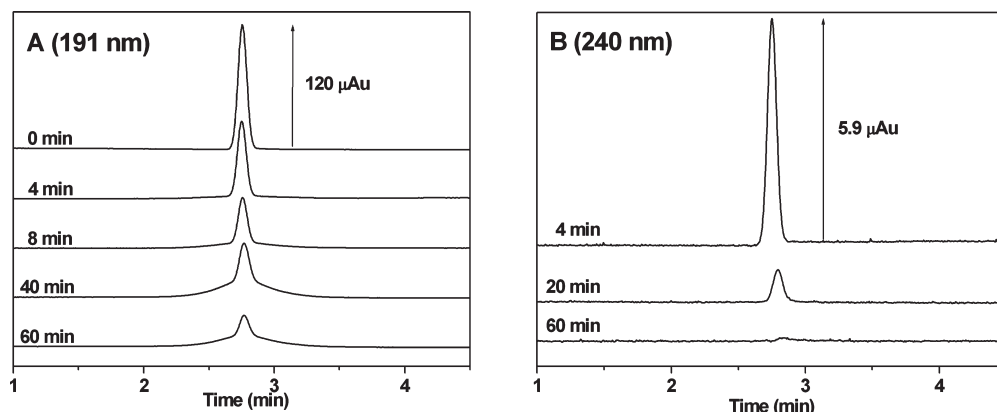


Figure 2. TDA signals at different stages of the polymerization of acrylamide for two different wavelengths 191 nm (A) or 240 nm (B). Polydimethylsiloxane (DB-1) capillary, 30.7 cm (22.2 cm to the detector) \times 50 μ m i.d.. Mobilization pressure: 50 mbar. Hydrodynamic injection: 17 mbar, 5s. Flushes between analysis: 0.1 M NaCl (930 mbar, 2 min). Temperature: 25 °C.

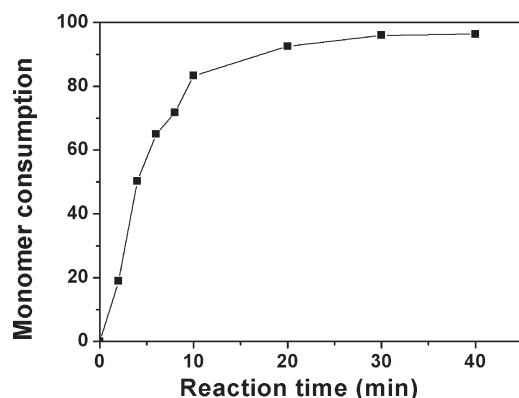


Figure 3. Variation of monomer consumption with time during radical polymerization of acrylamide obtained by Taylor dispersion analysis at 240 nm using eq 24. See the Experimental Section for the experimental conditions of polymerization.

3, are in fairly good agreement with values obtained by either of the three methods of treatment of experimental data described in the Theoretical Background section as concerns PAM 3.5k and PAM 20k. This is not the case for PAM 350k. The discrepancy between expected and observed values in this case might be explained by the fact that the hydrodynamic radius is lower than expected on the basis of the Mark–Houwink relationship as a result of the increasing degree of branching with increasing M_w , according to the information provided by the supplier.

Monitoring the Polymerization Reaction by TDA. Acrylamide polymerization was carried out by radical polymerization at room temperature in a water/ethanol (80/20 w/w) mixture under N_2 atmosphere using potassium persulfate and tetramethyldiethylenediamine as redox initiators (see Experimental Section for more details). The initial acrylamide concentration was 0.75 M (53 g/L). After the initiation of the polymerization, aliquots of 10 μ L of the reaction medium were regularly taken and immediately diluted with 990 μ L of 0.1 M NaCl aqueous solution. The diluted sample vial was then introduced in liquid nitrogen to completely stop the polymerization reaction and was further maintained at 4 °C in the capillary electrophoresis apparatus prior to TDA analysis.

The taylorgrams obtained at different reaction times (up to one hour) are reported in Figure 2 for two wavelengths. Both polymer and monomer absorb UV light at 191 nm (k_m being much higher than k_p), while at 240 nm, only the monomer absorbs.

In this example, without any deconvolution, it is possible to monitor the degree of conversion of the reaction (as depicted in Figure 3) by following the monomer peak area at 240 nm and by using eq 24. A degree of advancement of the reaction of 90% was reached after 20 min of polymerization.

The three aforementioned methods were applied to obtain the weight average R_h value of the PAM. Within 4% differences, the three methods lead to similar R_h values as shown in Figure 4, either in time scale (A) or in degree of conversion scale (B). As shown in Figure 4, the hydrodynamic radius of the formed PAM tends to decrease slightly with the degree of polymer conversion from 13 to 8 nm. It may appear surprising that the mean hydrodynamic radius decreases with elapsing reaction time. It should be noted that R_h , in Figure 4, is not the mean hydrodynamic radius of the entire reaction mixture (which is expected to increase as the polymerization progresses) but that of its sole polymeric part. This part is small at the beginning of the reaction and increases with time. In fact, conventional free radical polymerization is a non-living-chain polymerization. This means that all the polymer chains do not grow at the same time, contrary to what is obtained in controlled polymerization such as ATRP (atom transfer radical polymerization). In conventional radical polymerization, the degree of polymerization is given by the ratio of the kinetic propagation rate to the kinetic rate of radical transfer to the monomer. Ideally, this ratio should be constant with conversion. Nevertheless, with termination reactions occurring during the polymerization, the DP decreases slightly since the polymerization ends prematurely. As a consequence, for conventional radical polymerization, the polymer R_h (or molar mass) should be ideally constant with reaction time (or conversion)³² or slightly decreasing in case of termination reactions.

Method 1 has the advantage of not requiring any deconvolution of the signal; nevertheless it requires the definition of lower and upper limits in time for the integration of the global signal (calculation of A_0 and A_i). The final results can be sensitive to the definition of these limits, especially if the baseline is noisy or if it includes a drift in time. Although the response coefficients were not determined, method 1 could be applied to determine the hydrodynamic radius of the formed polymer since it only requires the determination of the heights of the signal peaks (h_0 and h_i), of the peak areas (A_0 and A_i) and of the peak variances ($\sigma_{m,0}^2$ and σ_i^2) of the global Taylor signal before polymerization and for each polymerization time. Even

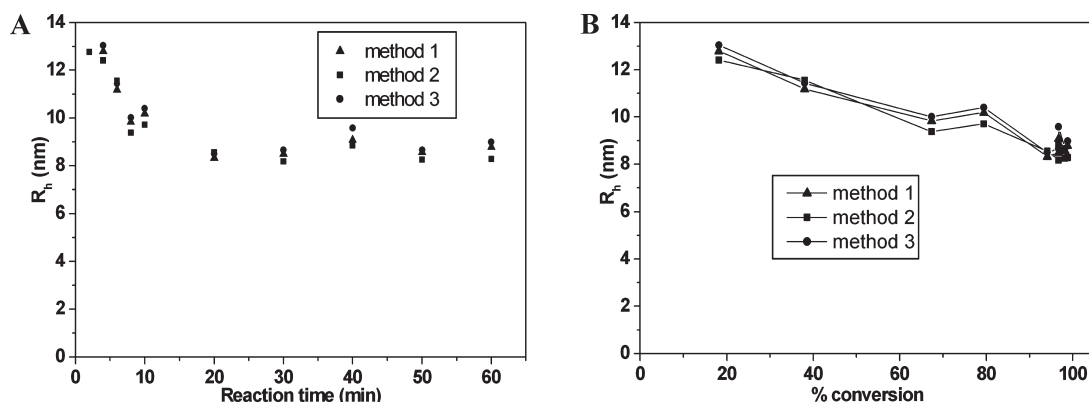


Figure 4. Variation of the PAM hydrodynamic radius as a function of the reaction time (A) or the monomer consumption (B). Experimental conditions as in Figure 2. See Theoretical Background section for the definition of the different methods for the TDA data processing.

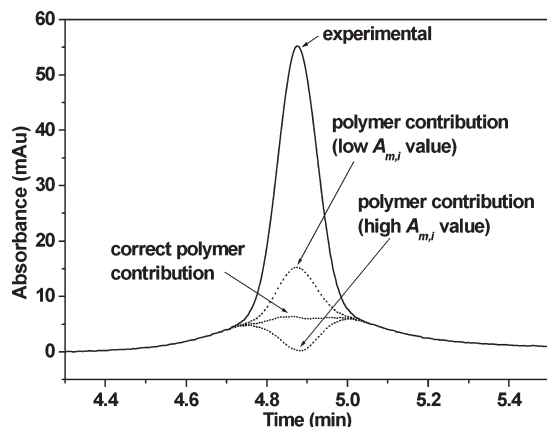


Figure 5. Example of curve fitting according to method 3 by adjustment of $A_{m,i}$ parameter for reaction time of 120 min. Mobilization pressure: 30 mbar. Other experimental conditions as in Figure 2.

if the response coefficients were not determined, this did not prevent us from determining the reaction conversion using eq 24 and the TDA signal at 240 nm. Methods 2 and 3 are rather similar since they both require the adjustment of parameters for the curve fitting. Method 3, which is based on subtracting the monomer contribution, is more general because it does not require that the polymer contribution is Gaussian. An example of curve fitting using method 3 by adjusting the $A_{m,i}$ parameter is given in Figure 5 with different traces showing how the modification

of the $A_{m,i}$ parameter (by excess or by default) changes the resulting polymer contribution. Nevertheless, it is worth noting that, in this example of acrylamide polymerization, method 2 is well adapted since both monomer and polymer contributions could be well fitted by Gaussian curves.

CONCLUSION

TDA analysis was found to be an appropriate technique for a rapid determination of the polymer hydrodynamic radius R_h and for the monitoring of the monomer consumption during a polymerization reaction. Three different methods can be used for processing taylorgrams derived from polymerization mixtures, or more generally, taylorgrams of binary mixtures. These three methods, either based on deconvolution or on integration of the signal, were found to give similar results. Two of these methods (methods 1 and 3) require the taylorgram of one the components of the mixture as a pure compound (e.g., a monomer), while the second method can be applied to any binary mixture without any prerequisite except the knowledge of the monomer peak variance. TDA results obtained on model binary mixtures of monomer and standard PAM were consistent with DLS experiments provided that the differences in the kind of average on R_h inherent to the two techniques are properly taken into account. The methodology proposed in this study can be also applied to other evolving binary mixtures, such as polymer degradation, or polymer (protein) aggregation.

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