

Supporting Information on the paper

Synthesis of Poly(*n*-butyl acrylate)-*block*-Poly(acrylic acid) Diblock Copolymers by ATRP and Their Micellization in Water

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Synthesis of PnBA₁₀₀-PAA₁₅₀

PnBA₁₀₀-PAA₁₅₀ was prepared following the same approach than the other block copolymers that is polymerization of PnBA first, then use of this first block for the polymerization of *t*BA, and finally selective acidolysis of the PtBA block into PAA to yield PnBA-PAA. However, slightly different conditions were used for the polymerization of the first block PnBA₁₀₀: the polymerization was performed in 71%wt of ethyl acetate and 3% of decane at 77°C, the monomer:initiator:CuBr:ligand ratio was 140:1:2:2, and a final conversion of 70% was reached. Polymerization of the second block was performed in conditions comparable to that described for the other copolymers except that the final conversion was 60%.

In spite of that, the polymerization of the first block proceeded with a good control and with minimal transfer and termination reactions as hinted by the final low polydispersity index, the linear evolution of $\ln([M_0]/[M])$ versus time and of M_n versus conversion, and the agreement between the theoretical molecular weight and the expected one (Figures S1-S2). The second block was also well controlled according to figures S3 and S4. However, the polydispersity index of the PnBA-PtBA diblock is not that

small and size exclusion chromatography (Figure S5) reveals a bimodal distribution. This latter result indicates that the *Pn*BA block was not able to fully reinitiate the polymerization of the second block because of loss of some bromine end groups, either because of transfer or termination reactions, or during the purification of this block. Transfer reactions are most probable, although they are not revealed by the kinetics of the polymerization of the first block (Figure S2), taking into account the high PMDETA ratio (this ligand is indeed known to act as a transfer agent) and the final conversion above 50%. Thus, *Pn*BA-*Pt*BA contained residual homo*Pn*BA and the degree of polymerization of its *Pt*BA block was not 120 as expected from the *t*BA to *Pn*BA ratio and the conversion. The efficiency of the reinitiation was estimated to be 80% and corresponds to a theoretical degree of polymerization of the *Pt*BA block of 150, which fits with the molecular weight determined by size exclusion chromatography ($M_{n\text{-theoretical}} = 32\,000\text{ g/mol}$, $M_{n\text{-SEC}} = 33\,700\text{ g/mol}$ when taking into account only the diblock peak and using poly(styrene) calibration).

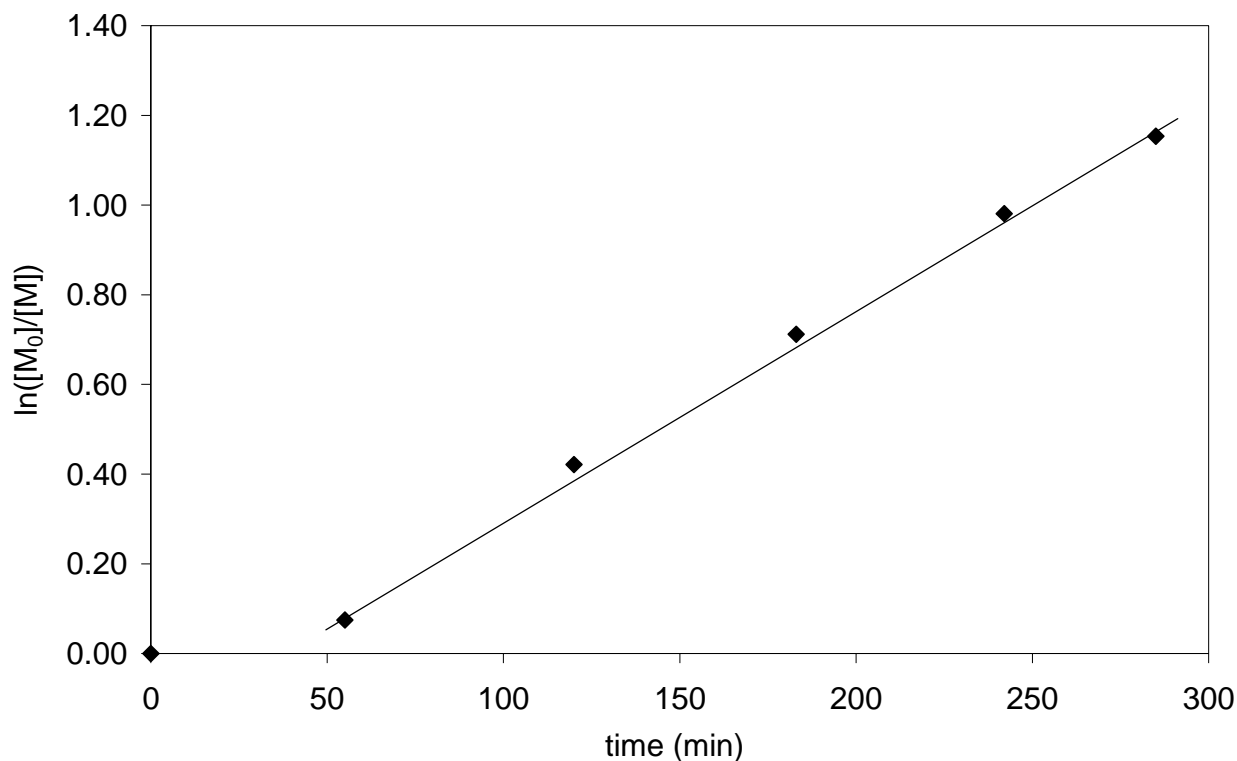


Figure S1. Evolution of $\ln([M]_0/[M])$ with time during the synthesis of PnBA_{100} (followed by gas chromatography). Since the ligand is added at room temperature (t_0) and the temperature raised to 77°C only afterwards, the plot of $\ln(M_0/M)$ becomes linear only after the second point (i.e. when the temperature becomes constant).

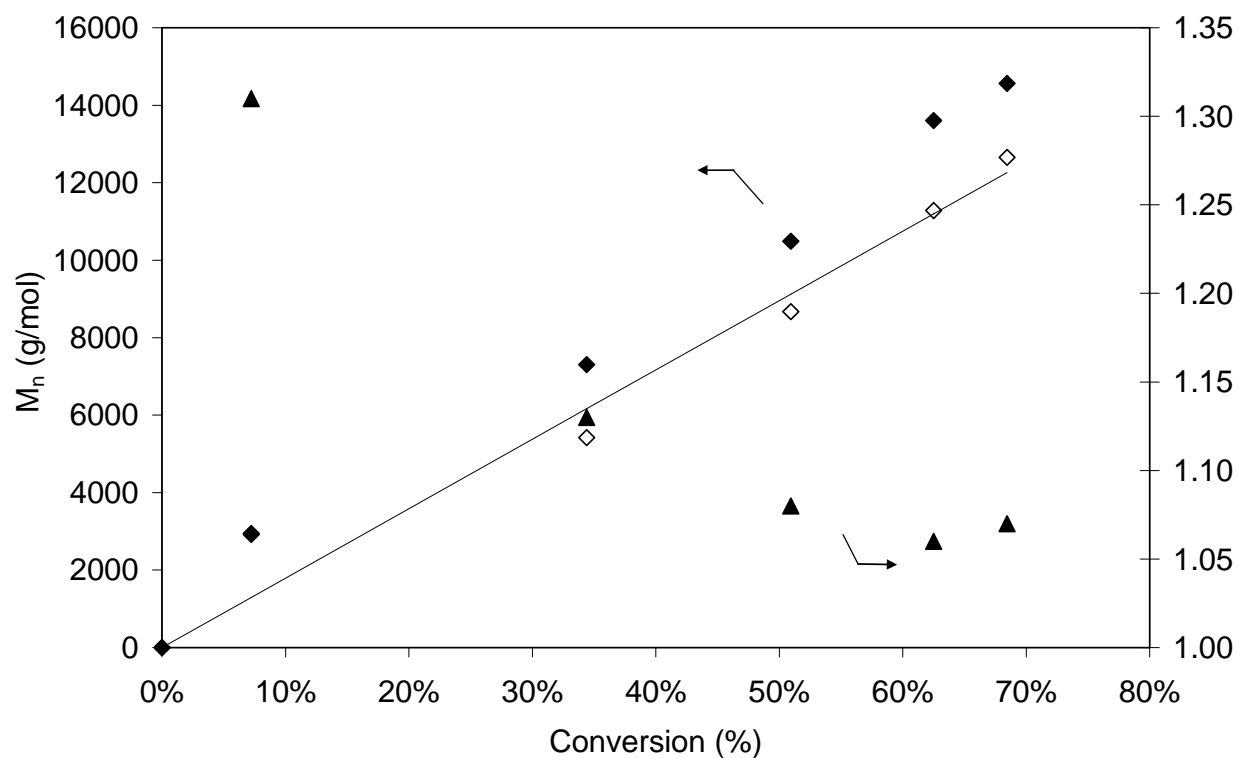


Figure S2. Evolution of the molecular weight, M_n , followed either by MALDI-TOF MS (◇), or size exclusion chromatography (◆), and of the polydispersity index (▲) followed by size exclusion chromatography, for the synthesis of PnBA_{100} .

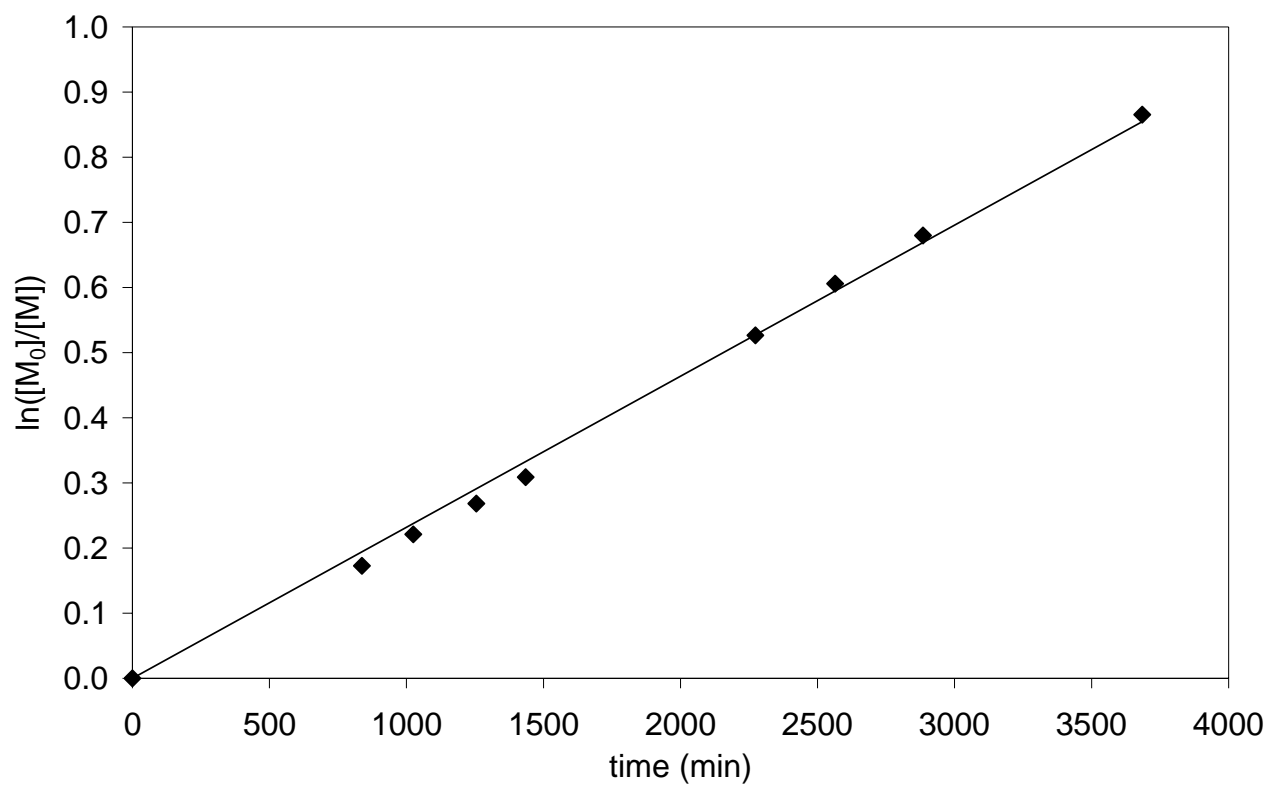


Figure S3. Evolution of $\ln([M]_0/[M])$ with time during the synthesis of $PnBA_{100}$ - $PtBA_{150}$ (followed by gas chromatography).

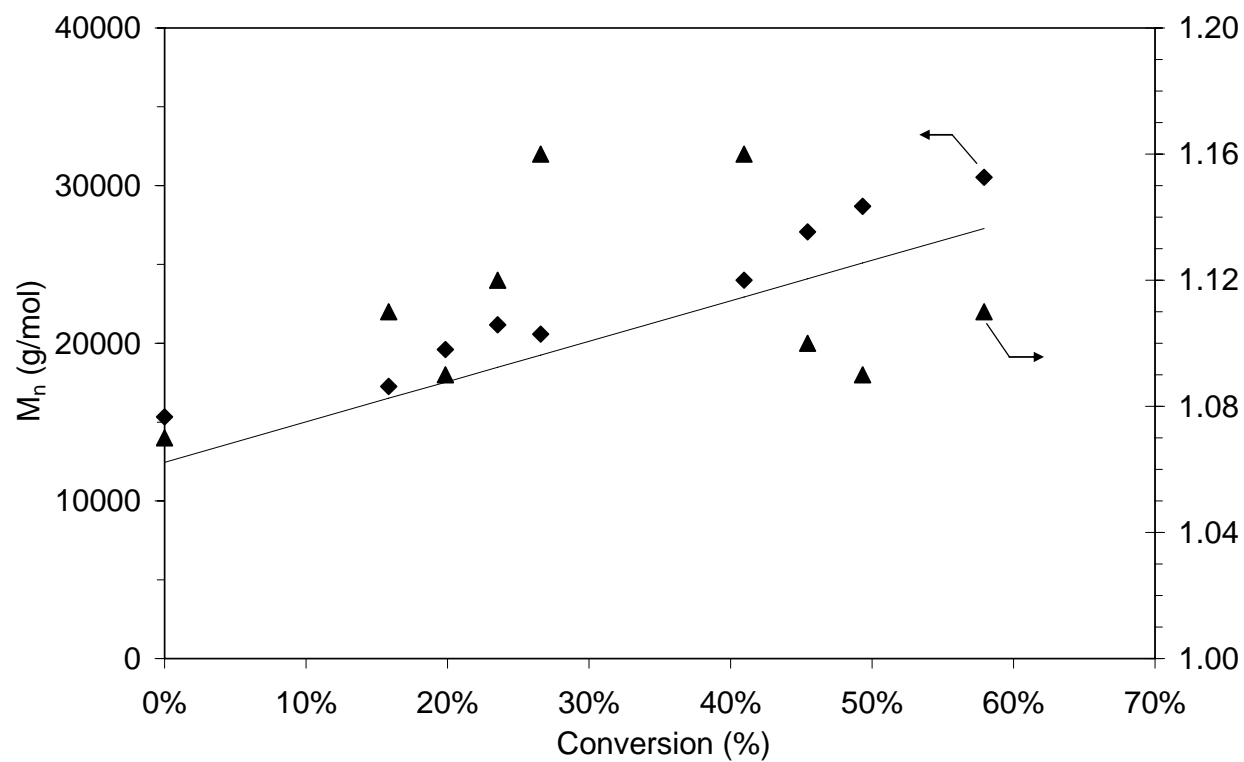


Figure S4. Evolution of the molecular weight, M_n (◆), and of the polydispersity index (▲) followed by size exclusion chromatography, for the synthesis of $PnBA_{100}$ - $PtBA_{150}$.

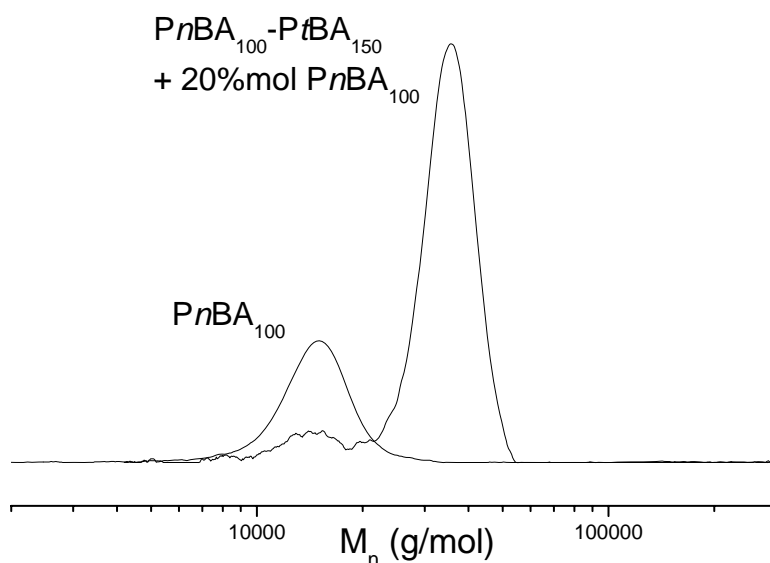


Figure S5. Size exclusion chromatography eluograms of $PnBA_{100}$ and $PnBA_{100}$ - PAA_{150} before purification.

Elimination of the residual homo $PnBA$ from the $PnBA$ - $PtBA$ diblock was not an easy task because of the comparable solubility of both blocks. Thus, the diblock copolymer was first acidolyzed with trifluoroacetic acid. Afterwards, soxhlet extraction with cyclohexane removed the residual homo $PnBA$ from the $PnBA$ - PAA diblock obtained.

Since the acidolyzed $PnBA$ - PAA cannot be analyzed easily by SEC in THF because PAA adsorbs on the columns, the purity of this polymer was checked by SEC using a method developed by Eisenberg et al.¹ The polymer was first dissolved in THF. When the dissolution was complete, 1 to 1.1 equivalents (compared to the content of AA units) of aqueous NaOH (1M) was added. This first triggered the precipitation of the polymer. However, after a few hours of vigorous stirring, inverse micelles were formed and the solution was clear again. This solution was analyzed by SEC and complete separation between the inverse micelles and the homo $PnBA$ was achieved thanks to their huge difference of hydrodynamic radius (Figure S6). Whereas the purified block copolymer does not contain any residual homo $PnBA$ (Figure S6b), the unpurified polymer contained about 20% by mol (Figure S6a). The final

polymer is thus pure $PnBA_{100}$ -PAA₁₅₀, whose composition is in agreement with ¹H NMR and potentiometric titration.

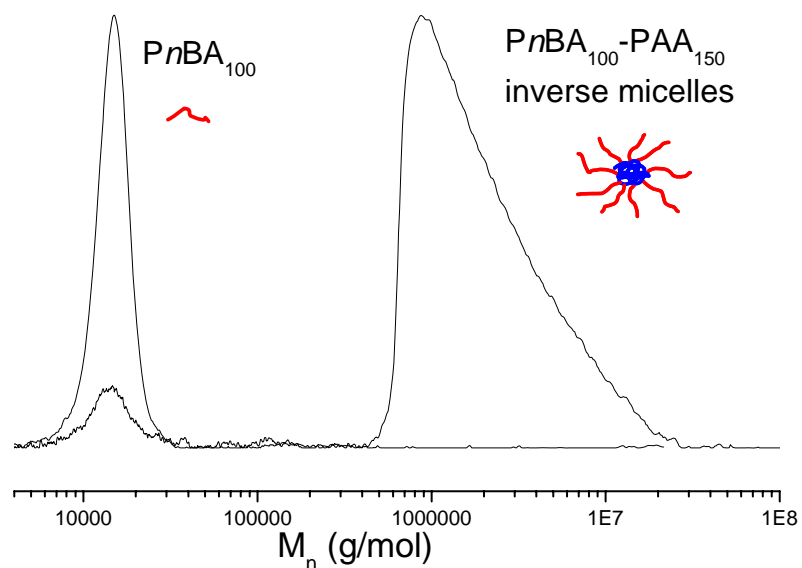


Figure S6a. Size exclusion chromatography traces of $PnBA_{100}$ and $PnBA_{100}$ -PAA₁₅₀ before purification. $PnBA_{100}$ -PAA₁₅₀ is injected in a THF/aqueous NaOH mixture (0.9/0.1 vol/vol, 1 equivalent of NaOH) in order to trigger the formation of inverse micelles and increase the difference of hydrodynamic radius between the homo and the block copolymer. The residual homo $PnBA$ is clearly seen before purification.

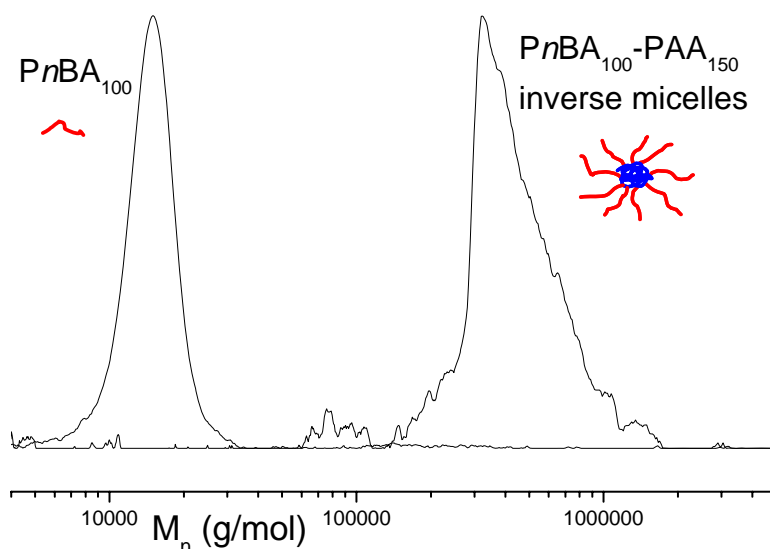


Figure S6b. Size exclusion chromatography traces of $PnBA_{100}$ and $PnBA_{100}$ - PAA_{150} after purification by soxhlet extraction in cyclohexane. $PnBA_{100}$ - PAA_{150} is injected in a THF/aqueous NaOH mixture (0.9/0.1 vol/vol, 1 equivalent of NaOH) in order to trigger the formation of inverse micelles and increase the difference of hydrodynamic radius between the homo and the block copolymer. No residual homo $PnBA$ is seen after purification.

Fitting procedure of the fluorescence correlation spectroscopy (FCS) data

When the polymer concentration was sufficiently high, the FCS data were successfully fitted by a single component model yielding slow diffusion times corresponding to micelles. Similarly, a single component model yielding the diffusion time of free dye molecules was applied to treat the data at the lowest polymer concentrations. In the intermediate concentration regime, a one component model did not accurately fit the data and a two-component model had to be applied. This model leads to a successful fitting of all experimental correlation functions within the intermediate concentration regime. Whereas the fast diffusion mode could be easily assigned to the free dye, the diffusion times for the slow modes are increasing as polymer concentration decreases.

To exclude a fitting artifact due to an alleged fraction of the free dye, the experimental autocorrelation data were also treated by applying a two-component model, where both diffusion times had been fixed to constant values, corresponding to those of the free dye molecules and the micelles at the highest polymer concentration, respectively. (related to hydrodynamic radii of 26 nm and 55 nm for PnBA90-PAA100 and PnBA90-PAA300, respectively). Figure S7 clearly shows that this fitting model does not grant for a reasonable description of the experimental data. Moreover, a three component model in order to account for the presence of free dye, free dye–single chain conjugates, and micelles did not yield reasonable fitting parameters either.

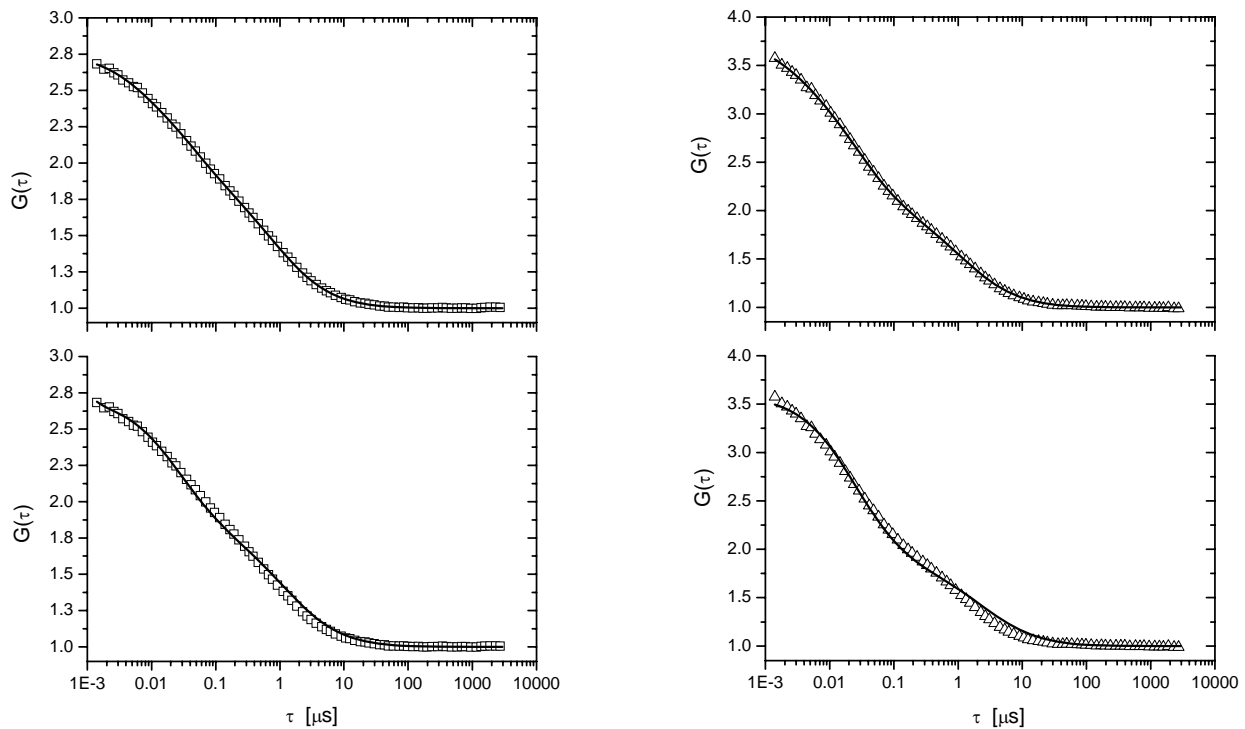


Figure S7. Experimental autocorrelation function of PnBA₉₀-PAA₁₀₀ (□, left) and PnBA₉₀-PAA₃₀₀ (△, right) at 9 mg/L (pH ~ 9.5, $\alpha = 1$). Experimental data were fitted to the FCS autocorrelation function by applying a constant value for the structure factor *S*. Top: best fits (—) with no restrictions on diffusion times and fractions (PnBA₉₀-PAA₁₀₀: $\chi^2 = 2.65 \times 10^{-3}$; PnBA₉₀-PAA₃₀₀: $\chi^2 = 7.17 \times 10^{-3}$). Bottom: best fits applying fixed diffusion times for both the free dye and the micelles (2700 μ s (PnBA₉₀-PAA₃₀₀) and

1400 μ s (PnBA₉₀-PAA₁₀₀), respectively; PnBA₉₀-PAA₁₀₀: $\chi^2 = 6.65 \times 10^{-2}$, probability (F-Test): 0.40 %;
PnBA₉₀-PAA₃₀₀: $\chi^2 = 2.88 \times 10^{-1}$, probability (F-Test): 0.17 %).

REFERENCES

- (1) Eisenberg, A. *Journal of Polymer Science: Part B: Polymer Physics* **1999**, 37, 1469-1484.