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Amphiphilic Diblock Copolymers with a Moderately Hydrophobic Block: Toward Dynamic Micelles

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Amphiphilic diblock copolymers consist of two antagonistic blocks connected by a covalent bond. When dispersed in aqueous solution, a selective solvent for the hydrophilic block, the polymers self-assemble into nanoscale aggregates in order to protect their hydrophobic blocks from water.[1−3] Because of their similarity with low molecular weight surfactants,[3] amphiphilic diblock copolymers were initially expected to form micelles in thermodynamic equilibrium with free polymer chains (unimers) as their low-molecular-weight counterparts do. However, most amphiphilic diblock copolymers form "frozen" aggregates[4−6] in aqueous solution, that is, out-of-equilibrium structures unable to exchange "unimers" within the experimental time window. It follows that amphiphilic block copolymers are difficult to disperse in aqueous medium, leading to aggregates whose shape and size are kinetically controlled, that is, depending on the way they were dispersed.[6−10] This behavior is generally admitted for block copolymers possessing a glassy hydrophobic block such as poly(styrene).[2,11,12] But, it must be highlighted that a low T_g of the hydrophobic block, with the exception of a few examples where the aggregates seem to be dynamic,[13] mostly leads to frozen systems in aqueous solution, too.[4,8,10,14−16] As an example, three groups studied in parallel amphiphilic block copolymers based on a common poly(*n*-butyl acrylate) (P*n*BA) hydrophobic block whose T_g is as low as −55 °C. Jacquin et al.[16,17] as well as Colombani et al.[10,18] agreed, using different characterization methods, that poly(*n*-butyl acrylate)-*block*-poly(acrylic acid) (P*n*BA-*b*-PAA) diblock copolymers form kinetically frozen aggregates which are not able to reorganize over months. Garnier et al.[19] reached the conclusion that diblock copolymers consisting of a P*n*BA hydrophobic block and various hydrophilic blocks were able to hybridize to some extent upon mixing in aqueous solution. It however takes days and requires the use of an organic cosolvent in the first step of the polymer dispersion, thus showing that the system is not as dynamic as the authors argue. These three groups agree on the fact that P*n*BA-based amphiphilic block copolymers do not reorganize at all, or only very slowly, in spite of the liquidlike behavior of their hydrophobic block.

Recent results indicate that the key to controlling the dynamics of self-assembly of amphiphilic (di)block copolymers in a selective solvent is not the T_g of the core-forming block, but its length[4,20,21] as well as its interfacial tension with the solvent.[4,14,16,21−23] Reducing the size of the hydrophobic block may indeed promote unimer exchange,[4,24,25] but this can be difficult to achieve from a synthetic point of view. Changing the hydrophobic block/solvent interfacial tension seems easier. Accordingly, addition of a nonselective cosolvent to the aqueous solution reduces the hydrophobic block/aqueous solution interfacial tension and may thus promote unimer exchange.[4,12,22,26] Addition of low-molecular-weight surfactants may have a similar effect, although the mechanism is more complex.[12] Despite their efficiency in many cases, these two strategies present the drawback that the dynamic behavior of the system is not an intrinsic property coming from the polymer itself, but the result of the addition of other species which could limit potential applications. Moreover, the success of these strategies depends very strongly on the polymer/surfactant pair[12,27] and to some extent on the polymer/solvent one.[28]

Here, we propose a way to transform a frozen system into a dynamic one by only acting on the chemical structure of the amphiphilic block copolymer. Our approach consists in introducing some hydrophilic units in the hydrophobic block in order to reduce the interfacial tension between the "moderately hydrophobic" block and both the hydrophilic block and the aqueous medium, thus promoting unimer exchange. Bendejacq et al.[29,30] as well as Laruelle et al.[31] showed that the addition of acrylic acid (AA) units in the poly(styrene) (PS) hydrophobic block of PS-*b*-PAA diblock copolymers allows pH-induced reorganizations of the aggregates of P(S-*co*-AA)-*b*-PAA in aqueous solution, whereas such reorganizations are not observed for pure PS-*b*-PAA diblock copolymers. However, the reversibility of the reorganization for such systems upon pH changes has never been reported to the best of our knowledge. The present work focuses on a P(*n*BA-*stat*-AA)-*b*-PAA block copolymer, that is, a pure PAA hydrophilic block connected to a statistical copolymer of *n*BA and AA units forming the "moderately hydrophobic" block. We have already mentioned that a pure P*n*BA-*b*-PAA forms frozen aggregates.[10,16] In our efforts to tune the hydrophobicity of the hydrophobic block, we first targeted a polymer containing 50 mol % of acrylic acid units in the P(*n*BA-*stat*-AA) "hydrophobic" block and 100 monomer units in each block. The polymer synthesized will be noted P(*n*BA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$, where the subscripts 99 and 98 correspond to the degrees of polymerization actually achieved for each block, whereas the percentages correspond to the molar ratios of *n*BA and AA in the "hydrophobic" block. This Communication discusses first the controlled synthesis of the P(*n*BA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ block copolymer using atom transfer radical polymerization (ATRP),[32] stressing the statistical distribution of the hydrophobic (*n*BA) and hydrophilic (AA) units in the P(*n*BA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$ first block. Cryogenic transmission electron microscopy (cryo-TEM) and small-angle neutron scattering (SANS) measurements in aqueous solution reveal that the polymer forms aggregates whose aggregation number depends on the ionization degree of the AA units, α. Moreover, pH cycles clearly prove the reversibility of these aggregation changes, thus hinting at a system able to reach thermodynamic equilibrium, at least at the tested α.

The synthesis of the P(*n*BA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ block copolymer by ATRP was achieved using a macroinitiator technique as already performed for pure P*n*BA-*b*-PAA diblocks.[18] First, a P(*n*BA$_{50\%}$-*stat*-*t*BA$_{50\%}$)$_{99}$-Br precursor was prepared by copolymerizing *n*BA with *tert*-butyl acrylate (*t*BA), the latter monomer being a precursor of AA units.[33] Figure 1 reveals that the reaction proceeded without significant termination or transfer reactions: the first-order plot of the monomer conversion as well as the evolution of the molecular weight with conversion are

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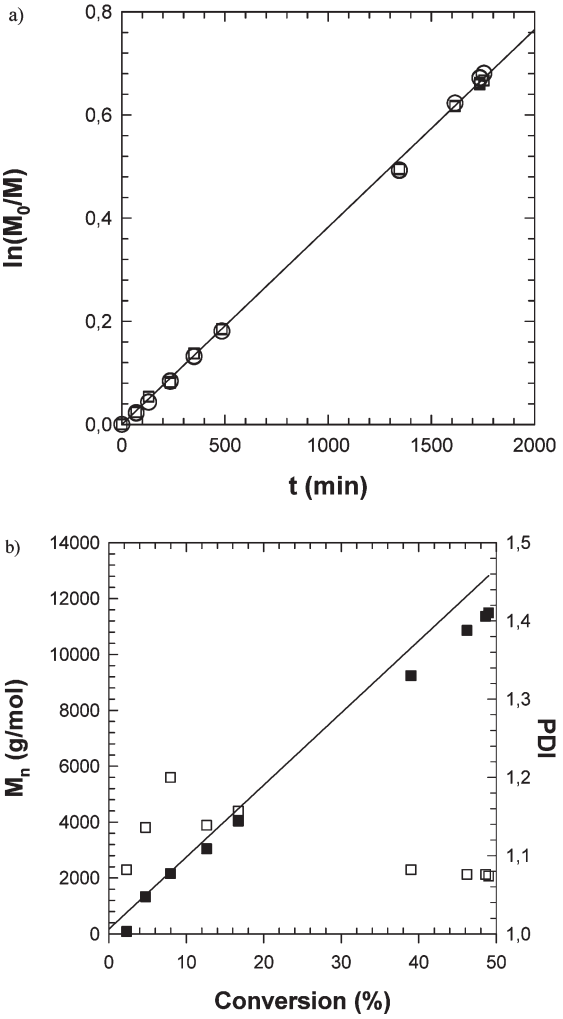

Figure 1. Kinetics of the polymerization of the P(nBA$_{50\%}$-*stat*-tBA$_{50\%}$)$_{99}$-Br block. (a) First-order plot of the nBA (□) and tBA (○) conversions followed by gas chromatography using n-decane as internal standard and fitted linearly (—). (b) M_n (■) and PDI (□), determined by SEC with polystyrene standards, vs conversion. The straight line corresponds to the theoretical molecular weight calculated from the initial monomer to initiator ratio and the conversion.

linear, while the polydispersity index (PDI) remains low and decreases with increasing conversion to PDI ~ 1.1. Moreover, nBA and tBA polymerize exactly at the same rate (Figure 1a), indicating that the first block is fully statistical. This result was expected since nBA and tBA have a very similar chemical structure. Still it is worth mentioning because the self-assembling behavior of the final amphiphilic block copolymers will probably depend on the distribution of the hydrophilic units in the "moderated hydrophobic" block. Charleux et al.[34] indeed reported that gradient and statistical copolymers of styrene and acrylic acid behave differently. The first block (DP = 99, M_n = 12.8 × 10^3 g/mol, PDI = 1.1)[35] was then purified and used to initiate the polymerization of a pure PtBA block. Here again, the polymerization proceeded in a controlled manner (see Supporting Information). Importantly, the P(nBA$_{50\%}$-*stat*-tBA$_{50\%}$)$_{99}$-*b*-PtBA$_{98}$ diblock copolymer (M_n = 25.4 × 10^3 g/mol, PDI = 1.1) contains no significant trace of residual first block (Figure 2), indicating an efficiency of the P(nBA$_{50\%}$-*stat*-tBA$_{50\%}$)$_{99}$-Br macroinitiator close to 100%. Finally, the targeted P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ was obtained by trifluoroacetic acid-catalyzed elimination of isobutylene from the tBA units of the P(nBA$_{50\%}$-*stat*-tBA$_{50\%}$)$_{99}$-*b*-PtBA$_{98}$. This last step was already shown to be quantitative and selective, meaning that it transforms all tBA

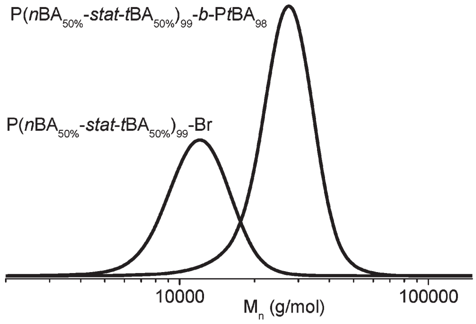

Figure 2. Size exclusion chromatograms of the first block P(nBA$_{50\%}$-*stat*-tBA$_{50\%}$)$_{99}$-Br and of the diblock copolymer P(nBA$_{50\%}$-*stat*-tBA$_{50\%}$)$_{99}$-*b*-PtBA$_{98}$. The molecular weights are calculated using polystyrene standards calibration.

units into AA ones without affecting the nBA units.[18] On the whole, a three-step synthesis based on ATRP yielded a narrowly distributed copolymer (M_n = 17.1 × 10^3 g/mol, PDI ~ 1.1), containing no significant traces of the first block, and whose block lengths and molar ratio of AA units in the "hydrophobic" block (50 mol %) almost reached the targeted values (targeted DP = 100 for each block) through a fine-tuning of the reaction conditions.

The P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ copolymer was first directly dispersed in water at 10 g/L without addition of sodium chloride and in the presence of the amount of sodium hydroxide (NaOH) required to reach a degree of ionization of the AA units, α = 10% (pH = 4.6). Here, it must be highlighted that Bendejacq et al. reported that when NaOH was added to an aqueous solution of P(S-*co*-AA)-*b*-PAA, the AA units of the hydrophilic block were ionized first, followed by those of the "hydrophobic" block.[29] At the moment, we do not know whether our system behaves similarly or not. Consequently, the value of α given in this paper corresponds to the ratio of ionized AA units among all AA units in the polymer, including those of the "hydrophobic" block. The amount of NaOH necessary to reach the target value of α was calculated based on the chemical structure of the polymer. Concentrated NaOH (1 mol/L) was further added to the solution at α = 10% to reach α = 30% (pH = 5.4) and then α = 50% (pH = 6.1) without significant dilution. Although rather spherical aggregates are obtained in all cases according to cryo-TEM experiments (Figure 3), their size strongly decreases upon ionization of the AA units. On the basis of previous results obtained on pure PnBA-*b*-PAA diblocks,[18] it can be assumed that the denser part of the aggregates revealed by cryo-TEM corresponds to their "hydrophobic" core. The size of the core thus decreases with increasing α, indicating a lowering of the aggregation number of the aggregates.

The same qualitative trend is observed with small-angle neutron scattering (SANS) experiments performed on solutions in D_2O at α ranging from 10 to 90% and containing 0.3 M NaCl. Here, the solutions were prepared by first dispersing the polymer at 20 g/L and α = 10% without added salt and then adjusting α gradually to higher values (i.e., to 30, 50, and finally 90%) by addition of concentrated NaOD solutions ([NaOD] = 10 mol/L, polymer dilution can be neglected). The NaCl concentration was finally adjusted to 0.3 M. The scattered intensity in the SANS data (Figure 4, see Supporting Information for α = 30%) measures the product of the structure factor $S(q)$, illustrating the interactions between the scattering objects, with the form factor $P(q)$ of the objects. The structure factor dominates the scattering intensity in the low q region and gives various behaviors as a function of α: a flat plateau for α = 10%, indicating a screening of the interactions; a nice maximum at $q \sim 0.02$ Å^{-1} for α = 50%, indicating repulsive interactions between the objects.

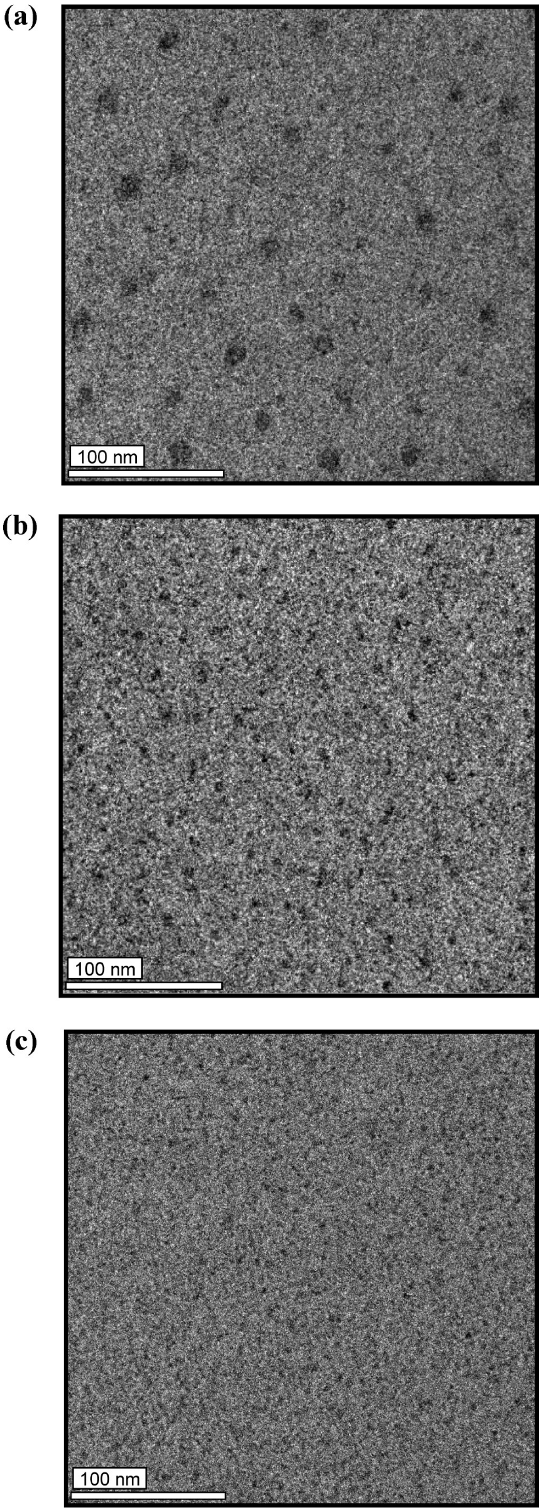

Figure 3. Cryo-TEM of the P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ diblock copolymer dispersed at 10 g/L in water at α = 10% (top), 30% (middle), and 50% (bottom) ionization of the AA units into AA^{-},Na^{+} units.

Finally, a power law decrease of the intensity for $\alpha = 90\%$ indicates some large-scale aggregation.[37] As α increases, the curves clearly shift toward higher q values, which means that the size of the scattering objects decreases. Simultaneously, the scattered intensity in the intermediate q region strongly decreases as α increases. Qualitatively, this indicates that the molecular weight of the aggregates decreases with increasing α.[38] The SANS experiments thus confirm the cryo-TEM results.

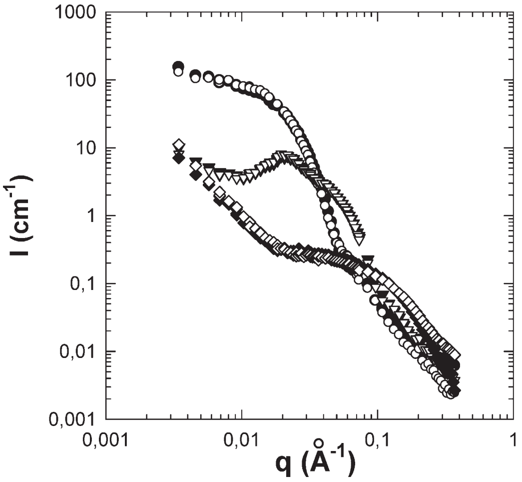

Figure 4. Small-angle neutron scattering curves for the P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ diblock copolymer at 20 g/L in the presence of 0.3 M NaCl and at 10% ionization (polymer powder directly dispersed ●, from α = 50% ○), 50% ionization (from α = 30% ▼, from α = 90% ▽), 90% ionization (from a solution prepared at α = 10% brought to 90% in 3 steps ◇, from another solution prepared at α = 10% brought to 90% in 2 steps ◆). The SANS experiments were performed at Laboratoire Léon Brillouin (LLB, Saclay, France) on the PACE spectrometer. Data were treated according to ref 36 with the software PASINET.

Table 1. Core Radius of the Aggregates of P(nBA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ Determined by Cryo-TEM and SANS

α	10%	30%	50%	90%
R_{SANS} (nm)[a]	8.6 ± 2.2[b]	3.8 ± 1.0[b]	3.4 ± 1.0[b]	1.7[c]
$R_{\mathrm{cryo\text{-}TEM}}$ (nm)[d]	7	3	2.5	

[a] SANS solutions: 20 g/L of polymer in D_2O, 0.3 M NaCl. [b] Data obtained by applying a form factor for polydisperse spheres. The error represents the polydispersity of the spheres. [c] Data obtained from a Guinier fit. The scattering objects corresponding to a Gaussian coil here rather than to spheres. [d] Cryo-TEM solutions: 10 g/L of polymer in H_2O solutions without added salt. No error is given here because the values are only rough estimates.

Both cryo-TEM and SANS results were analyzed more quantitatively (Table 1). For cryo-TEM, data given in Table 1 should be considered as rough estimates only. The aggregates indeed exhibit a very poor contrast versus the solvent compared to aggregates of their PnBA-*b*-PAA homologues observed with the same TEM microscope,[10] making the size analysis difficult. This might be an indication that the "hydrophobic" core is partly swollen with water as was already observed for other amphiphilic block copolymers with a mildly "hydrophobic" block.[24,29] This is why at this stage no aggregation number was extracted from the size of the aggregates determined by cryo-TEM or SANS. For the SANS data, the form factor of the objects $P(q)$, which weighs at larger q, has been fitted using a model of polydisperse spheres displaying a log−normal distribution of their radii. Such an approximation is possible as the distortion of the signal due to interparticles interactions ($S(q)$) does not influence the particle sizes extracted from the presented analysis as illustrated with the Porod representation on Figure 5. Sizes measured from SANS and cryo-TEM agree rather well within experimental error (Table 1), which means that SANS mainly probes the denser hydrophobic core of the aggregates as already reported for pure diblock homologues: PnBA-*b*-PAA.[10] The estimated sizes (Table 1) are of the same order of magnitude than the core size of frozen aggregates based on the pure diblock homologue PnBA$_{90}$-*b*-PAA$_{100}$ (R_{core} = 11 nm).[10] However, the latter remains constant with α, whereas the "moderately hydrophobic" diblock copolymer displays a high sensitivity to α.

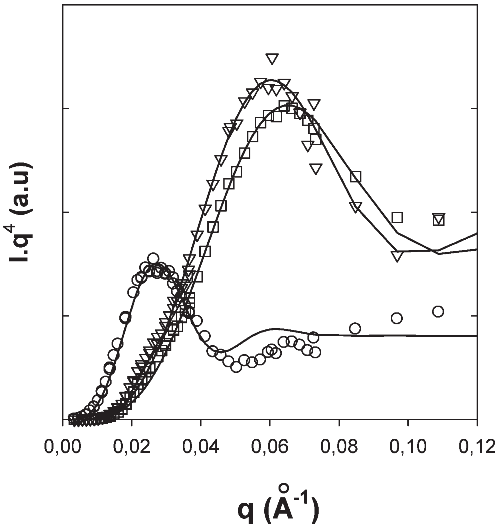

Figure 5. Porod representation of the small-angle neutron scattering data for the P(*n*BA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ diblock copolymer in the presence of 0.3 M NaCl and at 10% ionization (polymer powder directly dispersed ○), 30% ionization (from α = 10% ▽), 50% ionization (from α = 30% □). For α = 90%, the SANS data correspond to a Gaussian coil, illustrated by a q^{-2} dependence of the intensity (plot not represented here) and do not present a plateau at larger q in a Porod representation.

Since the volume of the core is proportional to the aggregation number, the cryo-TEM and SANS experiments indicate qualitatively that the system is able to decrease its aggregation number upon increasing of α. Let us now focus on the reversibility of this behavior. For that purpose, the previous SANS solution prepared at α = 50% was brought back to α = 10%, whereas the solution at α = 90% was brought back to α = 50%. In both cases, concentrated DCl (1 mol/L) in the required amounts was used to decrease α without diluting too much the solutions. Moreover, all changes of α were done before addition of any NaCl to the solutions. Consequently, the salt generated by the addition of DCl has been taken into account, and the final NaCl concentration was adjusted to 0.3 M. Finally, a new polymer solution was prepared at α = 10% and brought up to 90% passing through α = 50%. For each α value, this provided us with two solutions obtained via different pathways. The SANS curves at α = 50% are the same no matter the initial α (respectively 30 or 90%; Figure 4), showing that the size, shape, and organization of the aggregates is the same no matter the preparation pathway. This trend, i.e., a reversibility of the organization of the system no matter the preparation pathway, is also observed at α = 10 or 90% (Figure 4) and when α = 50% was reached starting from a solution at α = 10% (data not shown).

As a conclusion, we demonstrated that whereas pure P*n*BA-*b*-PAA diblock copolymers form frozen aggregates whose organization is preparation dependent and not sensitive to external stimuli,[10,16] controlled statistical incorporation of acrylic acid units in the hydrophobic block leads to a P(*n*BA$_{50\%}$-*stat*-AA$_{50\%}$)$_{99}$-*b*-PAA$_{98}$ copolymer undergoing dramatic and reversible reorganization upon changes of the ionization degree of the AA units, α. These preliminary results, and in particular the reversibility of the system, are strongly hinting at dynamic aggregates able to exchange unimers to reach thermodynamic equilibrium no matter the preparation conditions (at least for the investigated α values). Indeed, on one hand, an increase of the ionization degree α leads to smaller objects, but this can be achieved by splitting bigger aggregates.[9] On the other hand, the growth in size observed during the reverse path (that is upon the decrease of α) involves fusion of smaller aggregates and/or incorporation of unimers, which requires the system to be dynamic at some point. We believe this chemical approach to be highly relevant to tune the dynamics of self-association of amphiphilic block copolymers. First, it is universal, as it is always possible to add hydrophilic units in the hydrophobic block in order to moderate its hydrophobicity. Moreover, it leads to systems that are intrinsically dynamic and do not require further use of organic cosolvents or molecular surfactants.

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Supporting Information Available: Experimental details for the synthesis, kinetic study of the polymerization of the second block, reference for the experimental details for the cryo-TEM, $I = f(q)$ SANS curves including α = 30%. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) It must be highlighted here that the contrast of the objects slightly changes upon variation of the ionization degree and contributes to some extent to the variation of the scattered intensity. However, the contrast variation alone is far too small to explain the observed changes because protonated and ionized AA units have a similar contrast. The molecular weight thus undoubtedly varies upon pH change.