

Supporting Information

Amphiphilic Block-Random Copolymer Stabilizers: Extension to Other Monomer Types

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Synthesis of Block-Random Copolymers

BRC₂: Synthesis of poly(butyl acrylate)-b-(poly(butyl acrylate-r-acrylic acid)) [PBA-b-P(BA-r-AA)]

A nitroxide-terminated PBA homopolymer was first synthesized as macroinitiator for the synthesis of the block-random copolymer poly(butyl acrylate)-b-poly(butyl acrylate-r-acrylic acid) (BRC₂). The homopolymerization of *n*-BuA was performed in dioxane ([*n*-BuA]/[dioxane], 1:1) at 110 °C in the presence of BlocBuilder™ with an 1.1:1 molar excess of SG1 to ensure a greater control of the reaction by improving the rate of deactivation. A final ratio [*n*-BuA]/[BB]/[SG1] of 66:1:0.1 with a targeted conversion of 50% was chosen to avoid side reactions that may occur at high conversions. The reaction showed linear kinetics until the desired conversion was reached (43% at 160 min), while maintaining a low dispersity ($\bar{M}_w/\bar{M}_n = 1.28$) (Fig. S1). With no further purification, *n*-BuA, AA, and dioxane were added to the mixture to reach a new ratio of [macroinitiator]/[*n*-BuA]/[AA] of 1:73:34 while keeping the same [dioxane]/[monomer] ratio for the polymerization of the random second block. This reaction was intentionally made in one pot to simplify the synthesis of the BRCs. After 140 min of reaction at 110°C, the mixture was cooled to room temperature. BRC₂ was then precipitated in hexanes and purified with three cycles of solubilisation/precipitation with THF and hexanes. GPC and NMR analyses allowed the determination of the formula of BRC₂, namely PBA₂₈-b-P(BA₃₉-r-AA₂₀), exhibiting a hydrophobic/hydrophilic molar ratio of 0.3 ($n_{\text{monomer in hydrophobic block}}/n_{\text{monomer in both blocks}}$), including 22 molar % of AA in the whole chain.

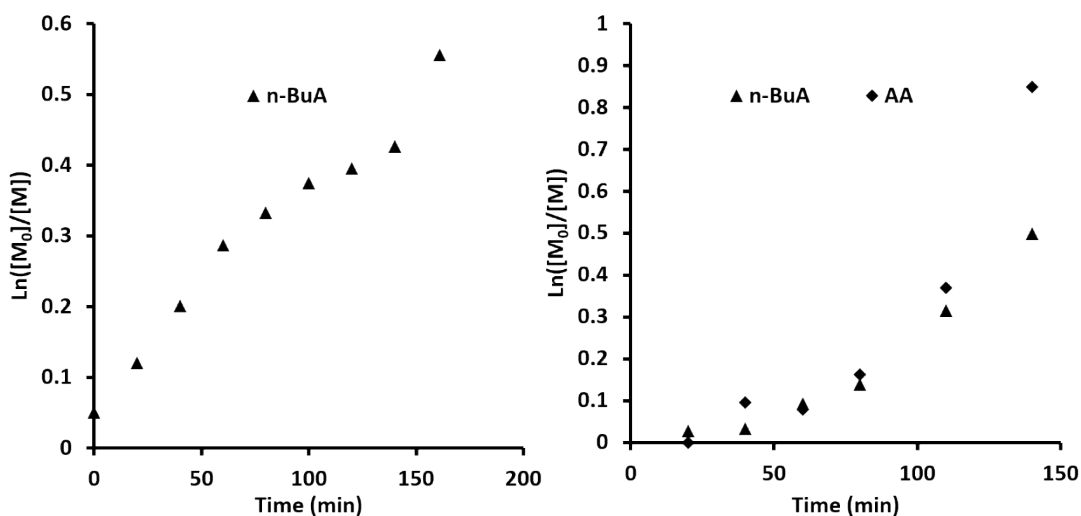


Figure S1 Conversion (determined by $^1\text{H-NMR}$) of polymerization of *n*-BuA at 110°C (left). Conversion of the polymerization of the second block; copolymer of AA and *n*-BuA at the same conditions (right).

BRC₃: Synthesis of poly(butyl acrylate-*r*-styrene)-b-(poly(butyl acrylate-*r*-styrene-*r*-acrylic acid)) [P(BA-*r*-S)-b-P(BA-*r*-S-*r*-AA)]

Following the synthesis of BRC₂, the synthesis of BRC₃ using the same initiation system was performed. The macroinitiator was synthesized in bulk with a ratio *n*-BuA:Sty:BB:SG1 of 33:33:1:0.1 at 105 °C. The presence of styrene as comonomer in the synthesis lowers the rate of polymerization by forming a more stable radical. As a result, a lower number of units is added at every cycle of activation/deactivation of the alkoxyamine and the dispersity \bar{D} is reduced. The absence of solvent for the reaction increased the rate, and the overall kinetics for the polymerization of BRC₃ were comparable to BRC₂, while reaching a similar molecular weight at a slightly lower reaction temperature (105°C vs 110°C) in 200 min (Fig. 2). The bulk system was kept for the polymerization of the second block with the addition of *n*-BuA, Sty and AA to ensure fast kinetics. The proportion of monomers relative to macroinitiator was set to 1:51:54:47 ([macroinitiator]/[Sty]/[*n*-BuA]/[AA]). The polymerization was run for 220 min at 105°C to reach an average monomer conversion of 82% with a molecular weight of 11 700 g.mol⁻¹ by $^1\text{H-NMR}$. The hydrophobic/hydrophilic molar ratio of BRC₃ is 0.25, with overall composition of P(S_{18-*r*}-BA₁₁)-*b*-P(S_{33-*r*}-BA_{29-*r*}-AA₂₁). Additional information is presented in Table 1 (main text).

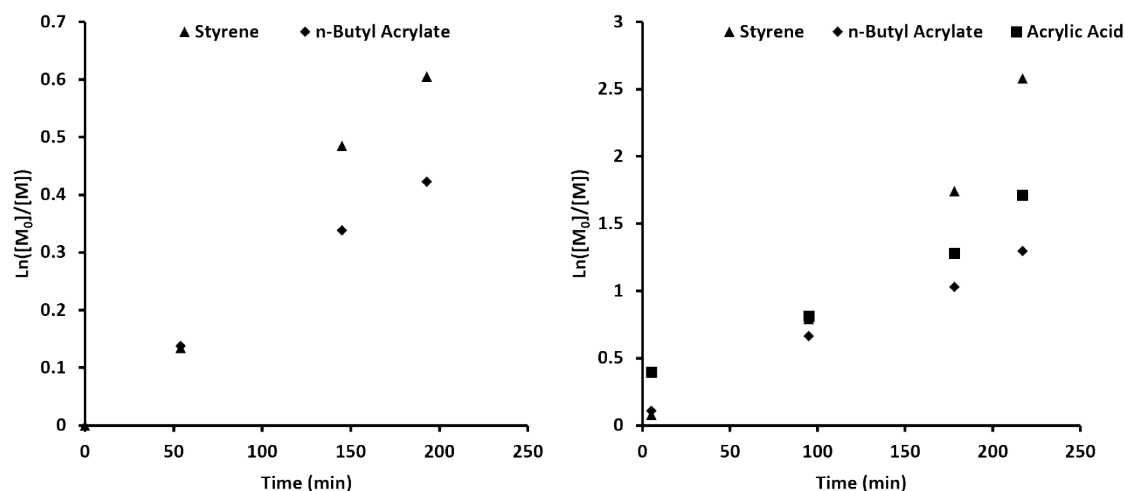


Figure S2 Conversion followed by $^1\text{H-NMR}$ of the copolymerization of *n*-BuA and styrene by NMP initiated by Blocbuilder™ at 105°C (left). Conversion followed by $^1\text{H-NMR}$ of the polymerization of the second block; copolymer of AA, *n*-BuA and styrene at the same conditions (right).

BRC₄: Synthesis of poly(methyl methacrylate-*r*-styrene)-*b*-poly(methyl methacrylate-*r*-styrene-*r*-acrylic acid) [(P(MMA-*r*-S)-*b*-P(MMA-*r*-S-*r*-AA))]

A 1:10 [styrene]/[MMA] ratio mixture was first tried in bulk as for BRC₃₋₄ but the kinetics were found to be too fast to allow a good heat dissipation, leading quickly to a gel effect. Dioxane was added for this reaction at a 1:1 ratio to the monomer, and the reactive proportions were set to 60:6:1:0.1 ([MMA]/[Sty]/[BlocBuilder™]/[SG1]). The polymerization was run for 47 min at 90 °C and the kinetics followed by $^1\text{H-NMR}$ (Fig. 3) show a first order reaction. The evolution of $\ln([M_0]/[M])$ for both monomers indicated relatively random distribution of the styrene units along the chain. The final macroinitiator exhibited a M_n of 3000 $\text{g}\cdot\text{mol}^{-1}$ by $^1\text{H-NMR}$. The second block polymerization was initiated at the same temperature with a mixture of [Macronitiator]/[MMA]/[Sty]/[AA] of 66:1:0.1:0.5. Once again, similar relative rates of monomer consumption indicated relatively random distribution of monomer units. The reaction was stopped after 90 min of reaction, resulting in an average on monomer conversion of 68% with a molecular weight of 8 600 $\text{g}\cdot\text{mol}^{-1}$ by $^1\text{H-NMR}$. The GPC traces (ESI) showed a monomodal distribution with a small fraction of low molecular chains. The hydrophobic/hydrophilic molar ratio of BRC₄ is 0.35 with a chemical denomination of P(MMA_{27-*r*}-S₃)-*b*-P(MMA_{40-*r*}-S_{4-*r*}-AA₁₈).

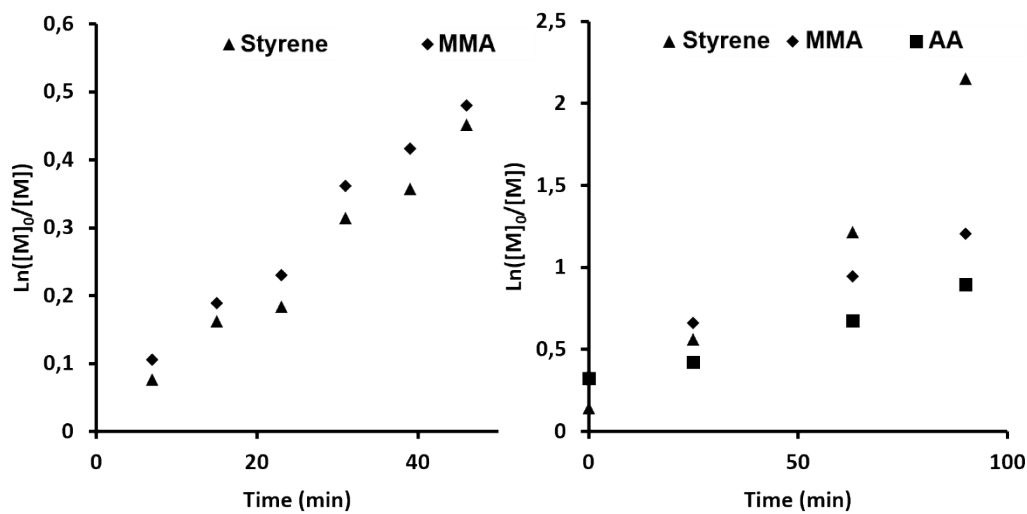


Figure S3 Conversion followed by $^1\text{H-NMR}$ of the copolymerization of MMA and styrene by NMP initiated by Blocbuilder™ at 90°C (left). Conversion followed by $^1\text{H-NMR}$ of the polymerization of the second block; copolymer of AA, MMA and styrene at the same conditions (right).

BRC₅: Synthesis of poly(methyl methacrylate-*r*-styrene-*r*-butyl acrylate)-*b*-poly(methyl methacrylate-*r*-styrene-*r*-butyl acrylate-*r*-acrylic acid) [P(MMA-*r*-S-*r*-BA)-*b*-P(MMA-*r*-S-*r*-BA-*r*-AA)]

The synthesis of BRC₅ was achieved using the same initiation and control systems as for BRC₁₋₄. The ratio between monomers was set taking into account the kinetics of the synthesis of BRC₃ and BRC₄ where styrene had a higher incorporation rate compared to the other monomers. The ratio between *n*-BuA and MMA was set to reach a higher proportion of MMA in the chains to increase the final glass transition temperature of the sample. The ratio of monomers for the polymerization of the terpolymer macroinitiator was set to 6:7:9 ($[\text{Sty}]/[n\text{-BuA}]/[\text{MMA}]$) with a global ratio of $[\text{Monomers}]/[\text{BlocBuilder}^\text{TM}]/[\text{SG1}]$ of 120:1:0.12. The synthesis was carried out in bulk at 105°C for 60 min. As with BRC₃, the concentration in styrene decreased the fastest and reached a conversion of 19% at $t = 60$ min. MMA and *n*-BuA exhibited slower kinetics and reached respectively 17 and 12% of conversion at the same time. As with the other BRCs, the Styrene, *n*-BuA and MMA are distributed fairly randomly along the chain, confirming the random nature of the macroinitiator. Without purification, acrylic acid was added to the macroinitiator for the polymerization of the second block, to reach a new ratio of 1:27:34:41:66 ($[\text{Macroinitiator}]$

[Sty]/[*n*-BuA]/[MMA]/[AA]). The excess of SG1 was still present in the media and no additional SG1 was necessary. The temperature was kept at 105°C for 400 min for the polymerization of the second block. Once again, the macroinitiator reacted preferentially with the styrene while other monomers had a lower addition rate. The absence of shoulder on the BRC GPC traces (ESI) along with the ¹H-NMR data confirmed the existence of the BRC structure with distributed monomer along the polymeric chains, exhibiting a hydrophobic/hydrophilic block ratio of 0.23, with a final chemical formula of P(S₆-*r*-BA₅-*r*-MMA₉)-*b*-P(S₁₃-*r*-MMA₉-*r*-BA₁₃-*r*-AA₂₁).

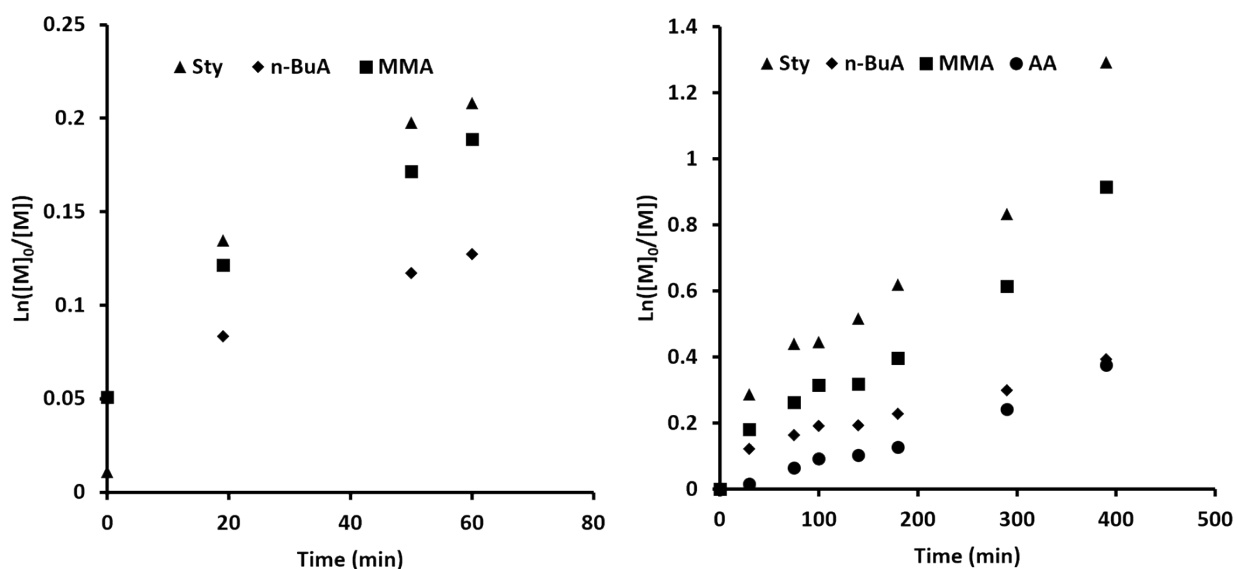
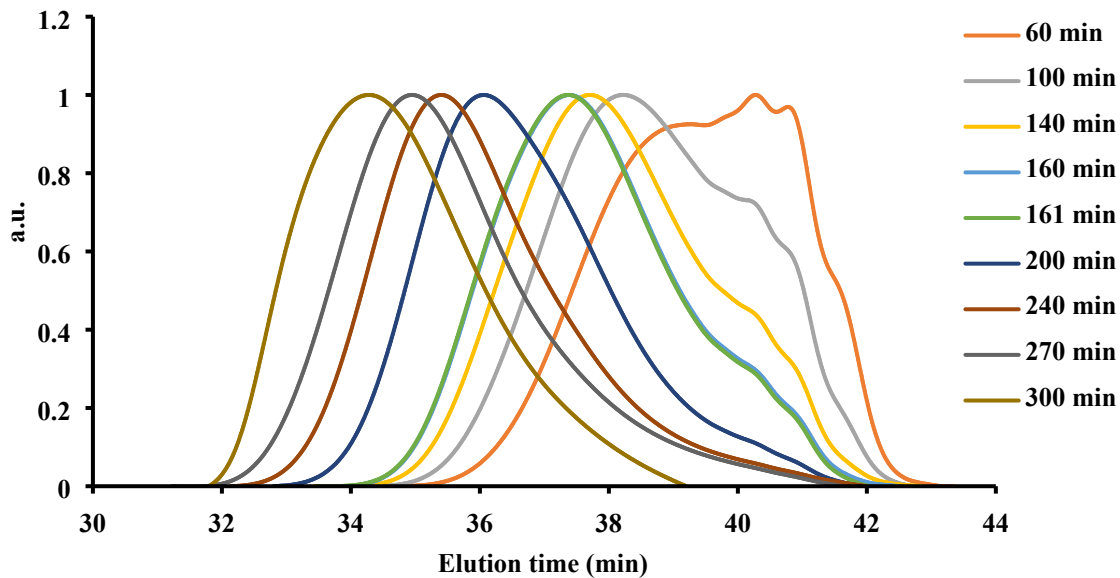


Figure S4 Conversion followed by ¹H-NMR of the copolymerization of MMA, styrene and *n*-BuA by NMP initiated by Blocbuilder™ at 105°C (left). Conversion followed by ¹H-NMR of the polymerization of the second block; copolymer of AA, MMA and styrene at the same conditions (right).

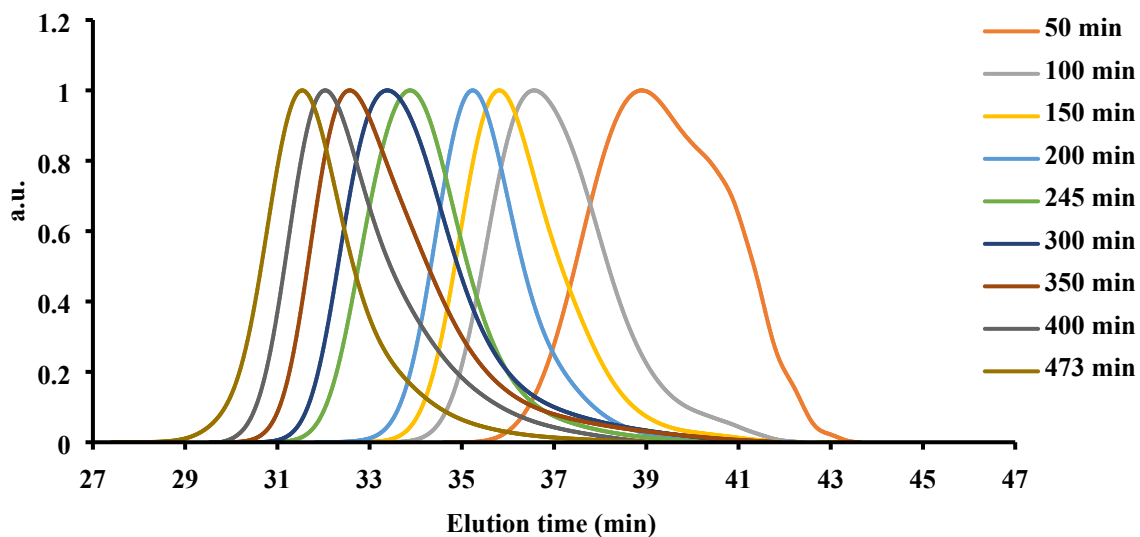
Characterisation of Block-Random Copolymers

Gel Permeation Chromatography

BRC2



BRC3



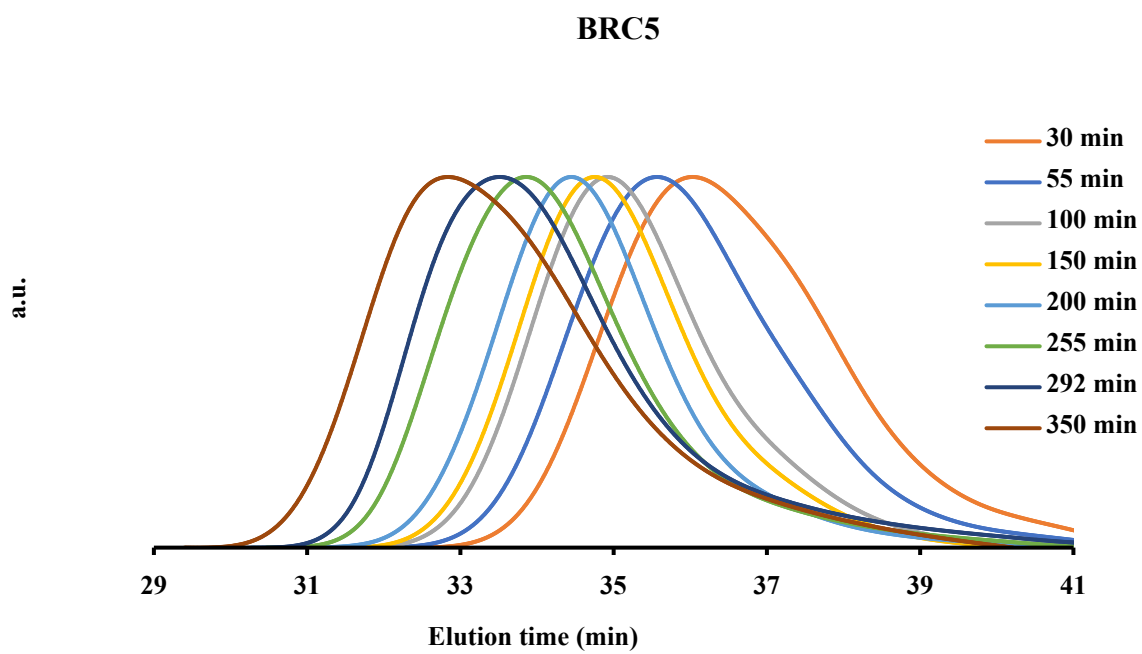
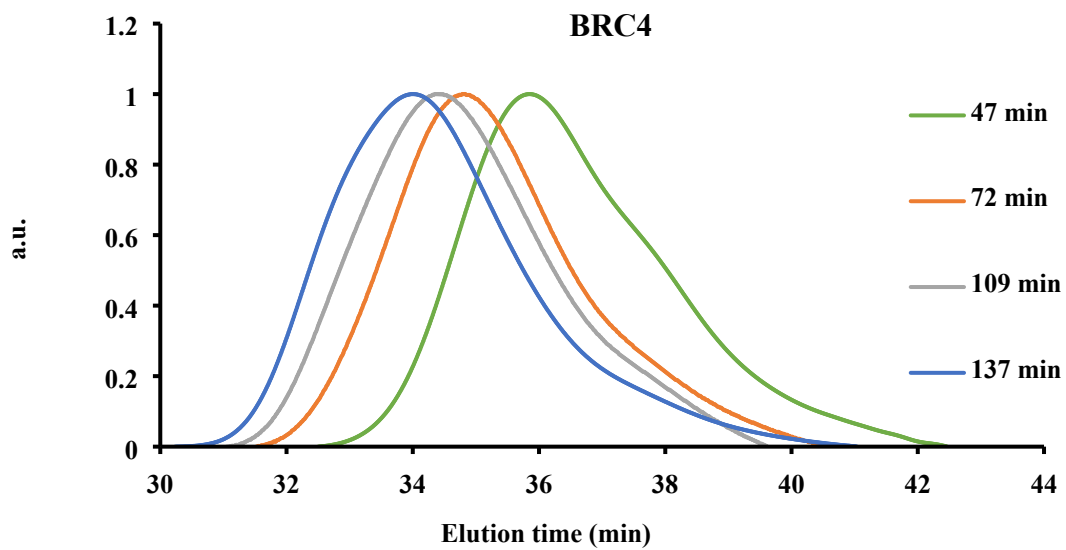


Figure S5 Evolution of the GPC traces through the polymerization of BRC_{2.5}.

Critical Aggregation Concentration Determination

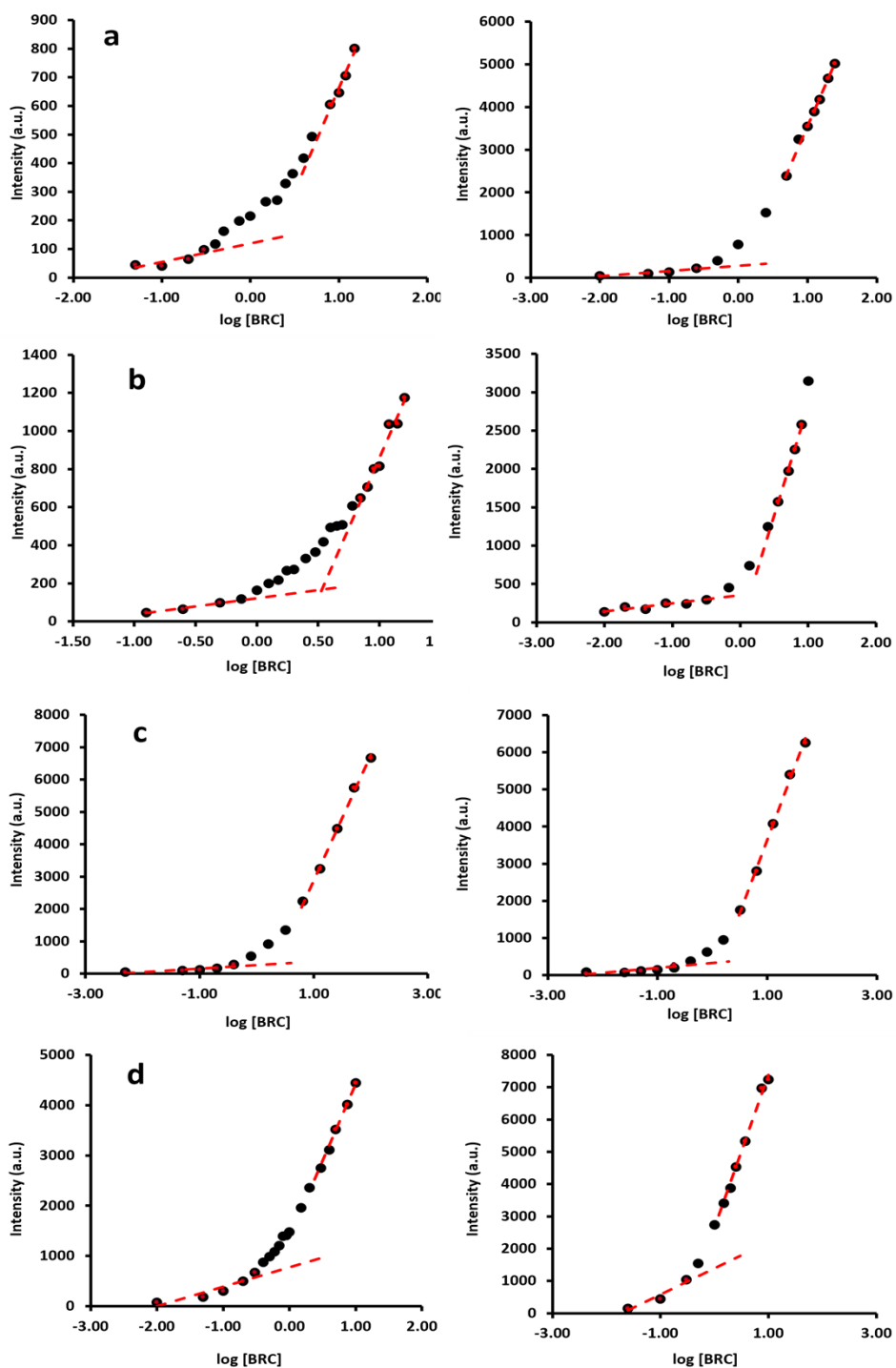


Figure S6 Dynamic light scattering result of (a) BRC₂, (b) BRC₃, (c) BRC₄, (d) BRC₅ at various concentration without salt (left) and with 100 mM NaCl (right). The extrapolated intersection of the two red dot lines represents the critical aggregation concentration (CAC) of the corresponding BRC. The values reported in the main text (Table 2) were mathematically calculated from linear regression operation while the red dash lines present in these figures represent a guide for the reader's eyes.

pH and conductivity titrations

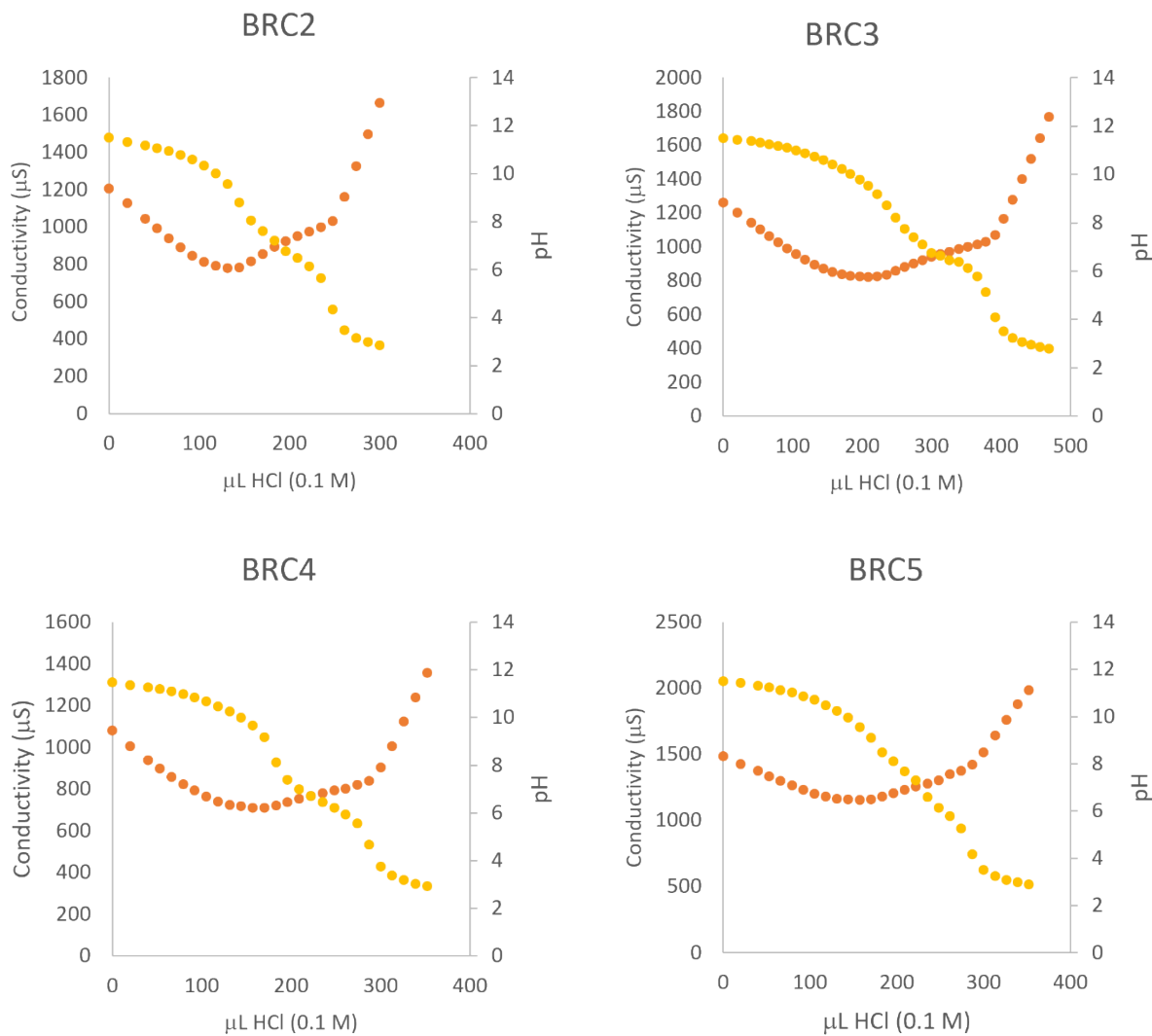


Figure S7 pH (yellow) and conductimetric (orange) titration of BRC2-5 by dropwise addition of HCl solution.