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O'Reilly, Rachel; Keogh, Rob; Blackman, Lewis D.; Foster, Jeff; Varlas, Spyridon

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Communication

The Importance of Cooperativity in Polymer Blending: Toward Controlling the Thermoresponsive Behavior of Blended Block Copolymer Micelles

Robert Keogh, Lewis D. Blackman, Jeffrey C. Foster, Spyridon Varlas, and Rachel K. O'Reilly*

Dr. R. Keogh, Dr. J. C. Foster, Mr. S. Varlas, and Prof. R. K. O'Reilly

School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, Birmingham, UK

Email: R.OReilly@bham.ac.uk

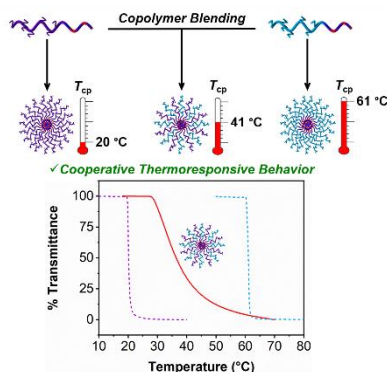
Dr. R. Keogh, Dr. L. D. Blackman

Department of Chemistry, University of Warwick, Gibbet Hill Road, CV4 7AL, Coventry, UK

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Understanding, predicting and controlling the self-assembly behavior of stimuli-responsive block copolymers remains a pertinent challenge. As such, the copolymer blending protocol provides an accessible methodology for obtaining a range of intermediate polymeric nanostructures simply by blending two or more diblock copolymers with similar block lengths in the desired molar ratio to target specific stimuli-response. Herein, a range of thermoresponsive diblock copolymers were blended in various combinations to investigate whether the resultant cloud point temperature could be modulated by simple manipulation of the molar ratio. Amphiphilic thermoresponsive diblock copolymers composed of statistical

poly(*n*-butyl acrylate-*co*-*N,N*-dimethylacrylamide) (p(*n*BA-*co*-DMA)) core-forming blocks and four different thermoresponsive corona-forming blocks, namely poly(diethylene glycol monomethyl ether methacrylate) (p(DEGMA)), poly(*N*-isopropylacrylamide) (p(NIPAM)), poly(*N,N*-diethylacrylamide) (p(DEAm)) and poly(oligo(ethylene glycol) monomethyl ether methacrylate) (p(OEGMA)) were selected for evaluation. Using variable temperature turbidimetry, the thermoresponsive behavior of blended diblock copolymer self-assemblies was assessed and compared to the thermoresponsive behavior of the constituent pure diblock copolymer micelles to determine whether comicellization was achieved and more significantly, whether the two blended corona-forming thermoresponsive blocks exhibited cooperative behavior. Interestingly, blended diblock copolymer micelles composed of p(DEGMA)/p(OEGMA) mixed coronae displayed cooperative behavior, highlighting the potential of copolymer blending for the preparation of stimuli-responsive nanomaterials in applications such as oil recovery, drug delivery, biosensing, and catalysis.



Stimuli-responsive polymers that undergo phase transitions in response to externally applied stimuli such as pH, light, temperature, enzymes, or redox potential, have been of great interest in recent years.^[1-4] In particular, thermoresponsive polymers have been extensively studied as

they can respond to subtle environmental changes and thus are attractive candidates for biological applications.^[5-7] Thermoresponsive polymers can exhibit a distinct change in solubility upon heating due to the disruption of intermolecular interactions between the polymer chains and the solvent, resulting in chain collapse and aggregation.^[8] The temperature at which this change in solubility occurs is defined as a critical solution temperature (CST) or in some instances, the cloud point temperature (T_{cp}).^[8] Importantly, the true lower critical solution temperature (LCST) of a thermoresponsive polymeric system is defined as the lowest critical point of a CST *versus* volume fraction phase diagram.^[8] Considering that a full phase diagram is required in order to characterize a true LCST, the T_{cp} or CST is often referred to instead, and represents the temperature at which macroscopic precipitation occurs at a given concentration and under the chosen experimental conditions.^[8] Tuning the CST of thermoresponsive polymers is key with regards to their applications, and has been found to depend on chemical composition, molecular weight, architecture, block length, concentration, solution state morphology, pH, amongst other factors.^[9-15]

In addition to these variables, the CST can be precisely modulated *via* the copolymerization of thermoresponsive monomers with either differently responsive or non-responsive monomers, which has distinct advantages over systems composed of homopolymeric blocks.^[7, 16-23] However, this technique is somewhat limited for controlling and predicting self-assembly behavior and thermoresponse, with a trial-and-error approach often required to target specific polymer properties. Moreover, statistical copolymerization is not always possible and thus the resultant microstructure could adversely alter self-assembly behavior and polymer properties.^[24-26] In light of these limitations, an alternative strategy has been developed involving copolymer blending, whereby two or more block copolymers that vary in functionality or stimuli-response are mixed to obtain polymer nanostructures with a range of

compositions and properties that are intermediate of the constituent polymers.^[27-30] The inherent advantages of this copolymer blending methodology are that it precludes exhaustive synthesis as well as offering a scalable and facile route for targeting a wide array of polymer nanostructures.^[31]

Gibson and co-workers have explored copolymer blending to modulate phase behavior, demonstrating that a single cooperative transition could be achieved upon blending thermoresponsive homopolymers with varying molecular weights formed from the same monomer.^[32, 33] In addition, Iván and co-workers have demonstrated that blending different thermoresponsive homopolymers resulted in the reversible formation of interpolymer complexes, for which the CST could be tuned in either aqueous or organic media upon varying the molar mixing ratio, pH and/or polymer molecular weight.^[34, 35] Furthermore, Burel and co-workers discovered that the cloud point temperature of thermoresponsive micellar solutions could be modulated *via* blending two amphiphilic block copolymers comprised of a lipid core and two different thermoresponsive corona-forming blocks.^[36] Despite the advantages of using copolymer blending to prepare thermoresponsive nanostructures over alternative methods, there exists a limited number of reports focused upon blending thermoresponsive amphiphilic block copolymers in self-assembled systems.^[36, 37] Herein, we explored whether this methodology could be utilized to predictively modulate the cloud point temperatures of thermoresponsive polymer nanostructures with the aim to better understand and expand its potential for future applications.

In previous studies, our group explored the main factors that influence the degree of thermal hysteresis for block copolymer micelles through the synthesis of thermoresponsive amphiphilic diblock copolymers composed of statistical $p(nBA-co-DMA)$ core-forming blocks with varying degrees of hydrophobicity and four different thermoresponsive corona-forming blocks:

p(DEAm), p(NIPAM), p(DEGMA) or p(OEGMA).^[38, 39] Based upon these findings, we hypothesized that the cloud point of a micellar solution could be tuned by blending thermoresponsive amphiphilic diblock copolymers. The copolymer blending protocol is largely dependent upon whether polymeric micelles can reach thermodynamic equilibrium within the experimental timeframe whilst possessing compatible core-forming blocks.^[40] As such, we envisaged that selecting amphiphilic diblock copolymers composed of short core-forming blocks with relatively low hydrophobic character coupled with a relatively high degree of chain mobility, would drive the formation of blended micelles. Moreover, if the two corona-forming thermoresponsive blocks displayed cooperative behavior, then blended diblock copolymer micelles may exhibit a cloud point at an intermediate temperature with respect to the two constituent pure diblock copolymer micelles. Considering this, amphiphilic diblock copolymers (**P1-P4**) with the lowest percentage incorporation of *n*BA in the respective core-forming blocks for each of the four distinct thermoresponsive corona-forming blocks analyzed in our previous study were selected for further evaluation herein (**Figure 1A**).

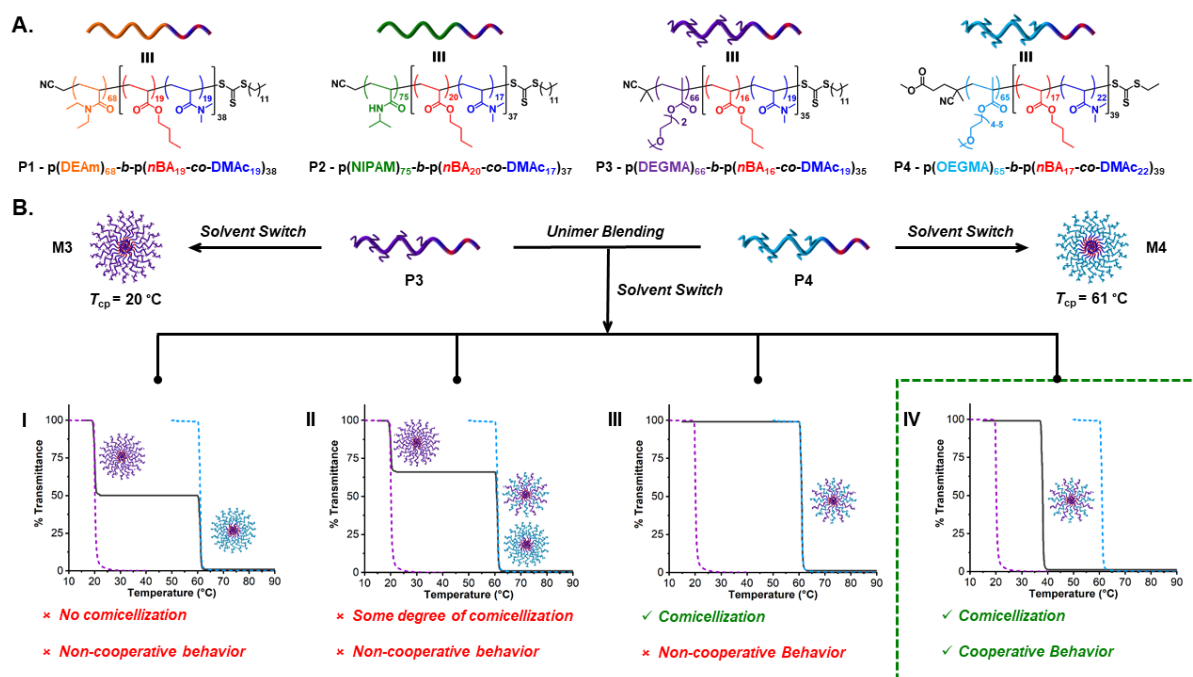


Figure 1. A) Chemical structures of amphiphilic thermoresponsive diblock copolymers **P1-P4** (characterization data for which is provided in Table S3).^[38] B) Top: Schematic depicting the separate self-assembly of diblock copolymers **P3** and **P4** into spherical micelles (**M3** and **M4**, respectively),^[38] and the preparation of a blended diblock copolymer micellar solution *via* unimer blending. Bottom: Representative variable temperature turbidimetry analyses (black line) of diblock copolymer mixtures that could form from the self-assembly of thermoresponsive diblock copolymers **P3** and **P4** *via* unimer blending. Dashed lines correspond to the variable temperature turbidimetry analyses obtained previously for pure diblock copolymer micelles **M3** (purple) and **M4** (light blue).^[38]

Amphiphilic thermoresponsive diblock copolymers **P1-P4** (Figure 1A) were synthesized *via* reversible addition-fragmentation chain transfer (RAFT) polymerization (Tables S3 and S4).^[38] Comparison of the light scattering data for the corresponding diblock copolymer micelles **M1-M4** (Table S4) revealed negligible differences in their hydrodynamic radii (R_h), micellar core radii (R_{core}) and aggregation numbers (N_{agg}). Considering that amphiphilic diblock copolymers **P1-P4** principally differ in their corona block chemistry, it was proposed that transmission electron microscopy (TEM) and light scattering analysis would not allow sufficient evaluation of the successful formation of blended diblock copolymer micelles. As such, we supposed that variable temperature turbidimetry analysis of blended diblock copolymer mixtures could be used to confirm copolymer blending, and to determine whether the two corona-forming thermoresponsive blocks exhibited cooperative behavior upon comicellization (Figure 1B). For instance, self-assembly of thermoresponsive diblock copolymers **P3** and **P4** *via* unimer blending could rationally result in four different potential outcomes (Figure 1B-I-IV). Firstly, the unsuccessful formation of blended diblock copolymer

micelles, with the formation of two separate populations of pure diblock copolymer micelles instead (Figure 1B-I). A second outcome could be the formation of blended diblock copolymer micelles as well as pure diblock copolymer micelles in solution (Figure 1B-II). Alternatively, copolymer blending could lead to the successful formation of blended diblock copolymer micelles for which the two thermoresponsive corona-forming blocks exhibit non-cooperative behavior upon comicellization (Figure 1B-III). Finally, self-assembly of thermoresponsive diblock copolymers *via* unimer blending may lead to the successful formation of blended diblock copolymer micelles that exhibit cooperative behavior as desired (Figure 1B-IV).

Initially, two blended diblock copolymer micellar solutions, **UB-A** and **UB-B**, were prepared by blending **P3** ($T_{cp, M3} = 20\text{ }^{\circ}\text{C}$) with either **P1** ($T_{cp, M1} = 32\text{ }^{\circ}\text{C}$) or **P2** ($T_{cp, M2} = 32\text{ }^{\circ}\text{C}$) respectively, in a 1:1 molar ratio to target an intermediate cloud point of $26\text{ }^{\circ}\text{C}$ (Figure 2A and Table S1). Turbidimetry analysis of **UB-A** revealed a single broad phase transition with a measured $T_{cp} = 33\text{ }^{\circ}\text{C}$ (Figure 2B). Comparison of the turbidimetry data obtained for **UB-A** with respect to pure p(DEGMA)-based diblock copolymer micelles (**M3**) and pure p(DEAm)-based diblock copolymer micelles (**M1**) indicated that blended diblock copolymer micelles in solution had indeed formed. Critically, no significant change in percentage transmittance was observed at $20\text{ }^{\circ}\text{C}$ for **UB-A**, which would correspond to the macroscopic precipitation of pure **M3** (Figure 2B). Moreover, the absence of a thermal hysteresis for **UB-A** suggested that the formation of blended diblock copolymer micelles was relatively favored. However, no change in percentage transmittance was observed at $26\text{ }^{\circ}\text{C}$ for **UB-A** as originally targeted (Figure 2B), and thus the two thermoresponsive corona-forming blocks exhibited non-cooperative behavior. Non-cooperative behavior was also observed for **UB-B** (Figure 2A-II). Again, no change in percentage transmittance was observed at $26\text{ }^{\circ}\text{C}$, with a broad phase transition detected instead at a $T_{cp} = 32\text{ }^{\circ}\text{C}$ which closely matched the respective cloud point temperature of pure

p(NIPAM)-based diblock copolymer micelles (**M2**) (Figure 2C). Interestingly, a small degree of broadening coupled with a slight shift towards higher temperatures was observed for the phase transitions for **UB-A** and **UB-B**. We rationalized this phenomenon in terms of a random distribution of coronal compositions and their respective collapse state within blended diblock copolymer micelles. Ultimately, whilst comicellization was achieved for both **UB-A** and **UB-B**, the collapse of brush-like p(DEGMA) chains did not directly affect the collapse of either linear p(DEAm) or p(NIPAM) chains in solution. Considering this, we proposed that blended diblock copolymer micelles consisted of partially phase separated coronae due to significant differences in both corona-forming block chemistry and architecture, which lead to the observed phase transition behavior.

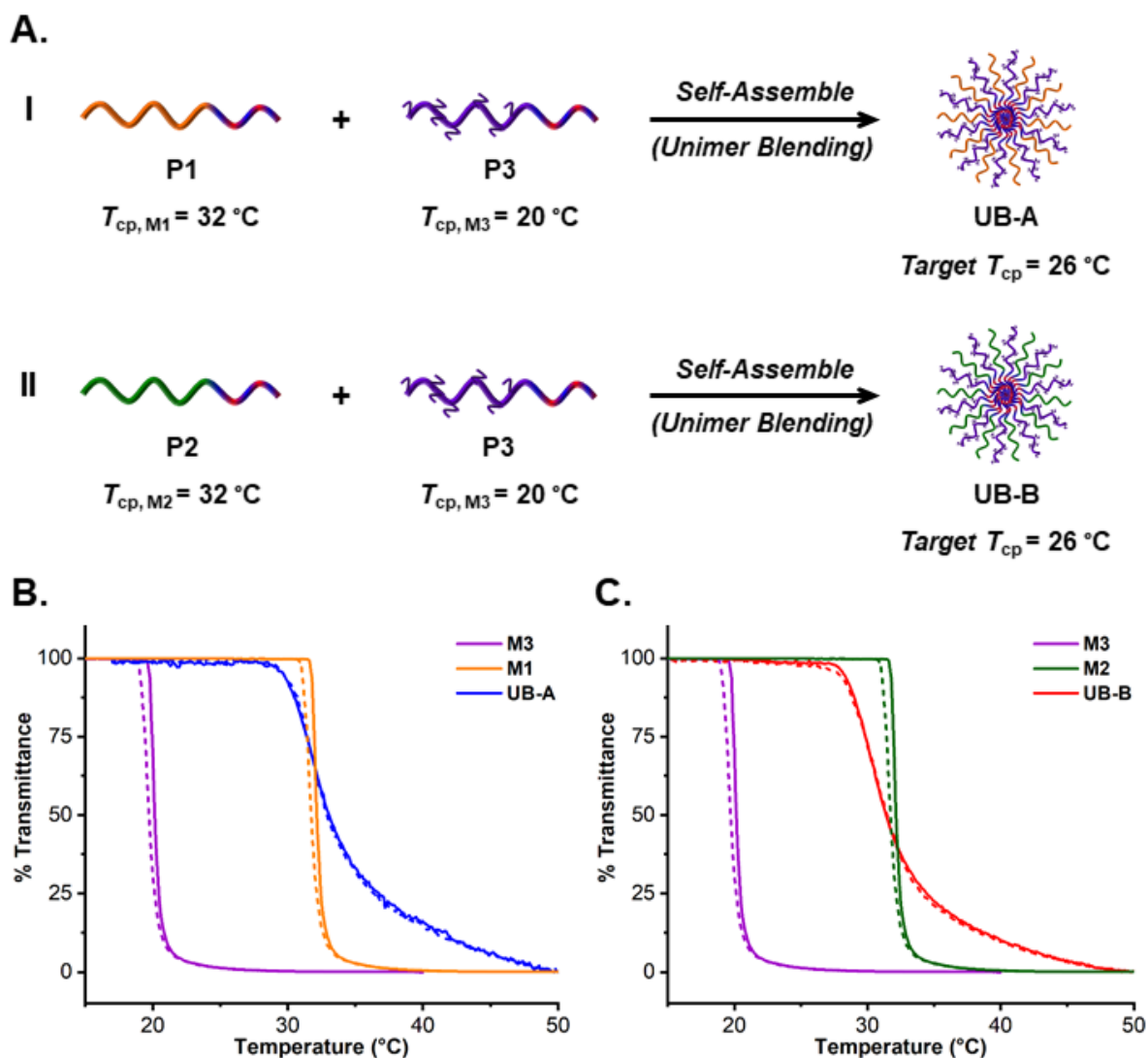


Figure 2. A) I) Preparation of blended diblock copolymer micellar solution **UB-A** *via* unimer blending of **P1** and **P3** (1:1 molar ratio). II) Preparation of blended diblock copolymer micellar solution **UB-B** *via* unimer blending of **P2** and **P3** (1:1 molar ratio). B) Variable temperature turbidimetry analysis of **UB-A** (blue line), **M3** (purple line) and **M1** (orange line) at 3 mg mL⁻¹. C) Variable temperature turbidimetry analysis of **UB-B** (red line), **M3** (purple line) and **M2** (green line) at 3 mg mL⁻¹. In all cases, the solid trace represents the heating cycle and the dashed trace represents the cooling cycle. Heating and cooling rate = 1 °C min⁻¹.

To explore the effect of polymer architecture upon blending dynamics, **P4** ($T_{cp, M4} = 61$ °C) was blended with **P1** ($T_{cp, M1} = 32$ °C) (**Figure 3A** and Table S1). In contrast to **UB-A** and **UB-B**, two distinct cloud points were observed for blended diblock copolymer micellar solution **UB-C** (**Figure 3B**). Here, turbidimetry analysis suggested the presence of three populations of micelles: pure **M1**, pure p(OEGMA)-based diblock copolymer micelles (**M4**) and blended diblock copolymer micelles. Upon heating **UB-C**, a broad phase transition was initially observed at a $T_{cp} = 38$ °C which corresponded to the macroscopic precipitation of pure **M1**. Subsequently, a second phase transition was detected at a $T_{cp} = 60$ °C which was ascribed to the collapse of p(OEGMA) chains in solution. As outlined in **Figure 1B-I**, the presence of two cloud points for **UB-C** suggested the formation of two separate populations of copolymer micelles in solution as opposed to the formation of blended diblock copolymer micelles. However, an evident thermal hysteresis was observed for **UB-C**, which was in contrast to the turbidimetry data obtained for **UB-A** and **UB-B** (**Figure 2B** and **C**). As such, we attributed the initial increase in percentage transmittance upon cooling to the resuspension of pure **M4**. The second transition was assigned to the resuspension of pure **M1** and blended diblock copolymer micelles, with the p(DEAm) coronal chains rehydrated once the temperature of the solution reached the respective cloud point of **M1**. Overall, in comparison to **UB-A** and **UB-B**, the formation of blended diblock copolymer micelles for **UB-C** was disfavored to a degree, which was attributed to a low degree of miscibility between the two corona-forming blocks.

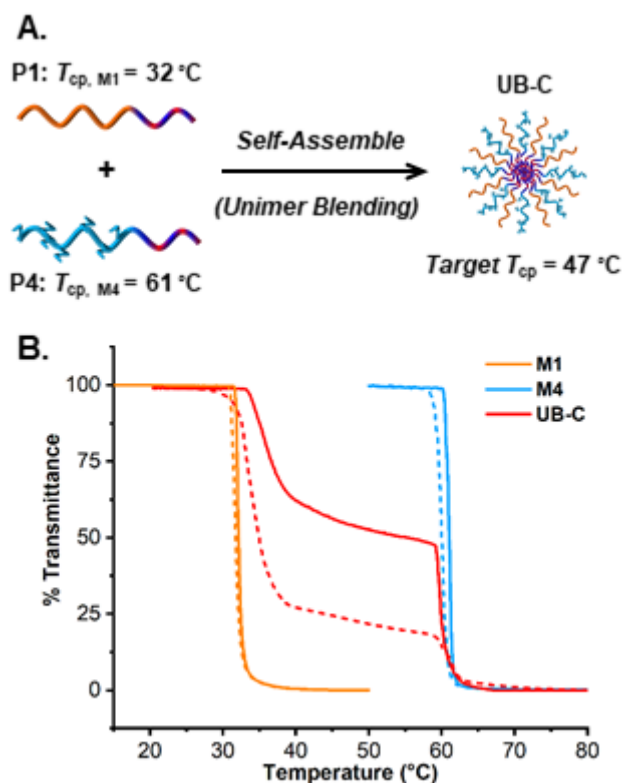


Figure 3. A) Preparation of blended diblock copolymer micellar solution **UB-C** *via* unimer blending of **P1** and **P4** (1:1 molar ratio). B) Variable temperature turbidimetry analysis of **UB-C** (red line), **M1** (orange line) and **M4** (light blue line) at 3 mg mL^{-1} . In each case, the solid trace represents the heating cycle and the dashed trace represents the cooling cycle. Heating and cooling rate = $1\text{ }^{\circ}\text{C min}^{-1}$.

Gibson and co-workers have reported that non-cooperative behavior was observed upon blending p(DEGMA) and p(OEGMA) homopolymers.^[32] Considering this, we further investigated whether the introduction of statistical p(*n*BA-*co*-DMA) core-forming block into the final diblock copolymer structures of **P3** and **P4** enabled the two thermoresponsive corona-forming blocks to interact in a cooperative manner due to comicellization. As such, blended diblock copolymer micellar solution **UB-D** was prepared by blending **P3** ($T_{cp, M3} = 20\text{ }^{\circ}\text{C}$) with **P4** ($T_{cp, M4} = 61\text{ }^{\circ}\text{C}$) in a 1:1 molar ratio (**Figure 4A-I** and Table S1). Turbidimetry

analysis of **UB-D** indicated the successful formation of one population of blended diblock copolymer micelles (Figure 4B). Significantly, no change in percentage transmittance was observed for **UB-D** at 20 °C or 61 °C, which correspond to the cloud point temperatures for pure **M3** and **M4**, respectively. Importantly, a broad phase transition was measured for **UB-D** at an intermediate temperature of 38 °C, which closely matched the targeted theoretical T_{cp} of 41 °C. Therefore, we surmised that the two thermoresponsive corona-forming blocks behaved in a cooperative manner upon comicellization, with the collapse of the p(OEGMA) chains occurring at a much lower temperature due to the close proximity of the collapsed p(DEGMA) chains within the micelle coronae. As such, we proposed that blended diblock copolymer micelles consisted of p(DEGMA)/p(OEGMA) mixed coronae instead of partially phase separated coronae due to negligible differences in both corona-forming block chemistry and architecture, which resulted in a high degree of miscibility between the two corona-forming blocks.

To further validate this unique result, we investigated whether the presence of a statistical p(*n*BA-*co*-DMA) core-forming block in the constituent diblock copolymer structures and subsequent comicellization was required for cooperative behavior. To this end, p(DEGMA)₆₇ (**P5**) and p(OEGMA)₆₄ (**P6**) homopolymers were synthesized *via* RAFT polymerization (Table S5 and Figure S1). Following this, a series of homopolymer mixtures (**UB-E-*n***) were prepared by blending **P5** and **P6** to target a range of *n*% p(OEGMA) incorporations (Figure 4A-II and Table S2). For blended homopolymer solutions **UB-E-30**, **UB-E-50** and **UB-E-70**, two relatively broad phase transitions were observed in each case which corresponded to the macroscopic precipitation of p(DEGMA) chains (**P5**) followed by p(OEGMA) chains (**P6**) in solution (Figure 4C). Whilst a slight increase in the measured T_{cp} for **P5** and **P6** with respect to increasing p(OEGMA) percentage incorporation was discovered, no change in percentage

transmittance was observed at the anticipated temperatures of 42 °C, 53 °C and 64 °C for **UB-E-30**, **UB-E-50** and **UB-E-70**, respectively (Table S2). Therefore, the two thermoresponsive homopolymers **P5** and **P6** exhibited non-cooperative behavior upon blending, which mirrored the thermoresponsive behavior previously observed by Gibson and co-workers for this specific polymer class.^[32]

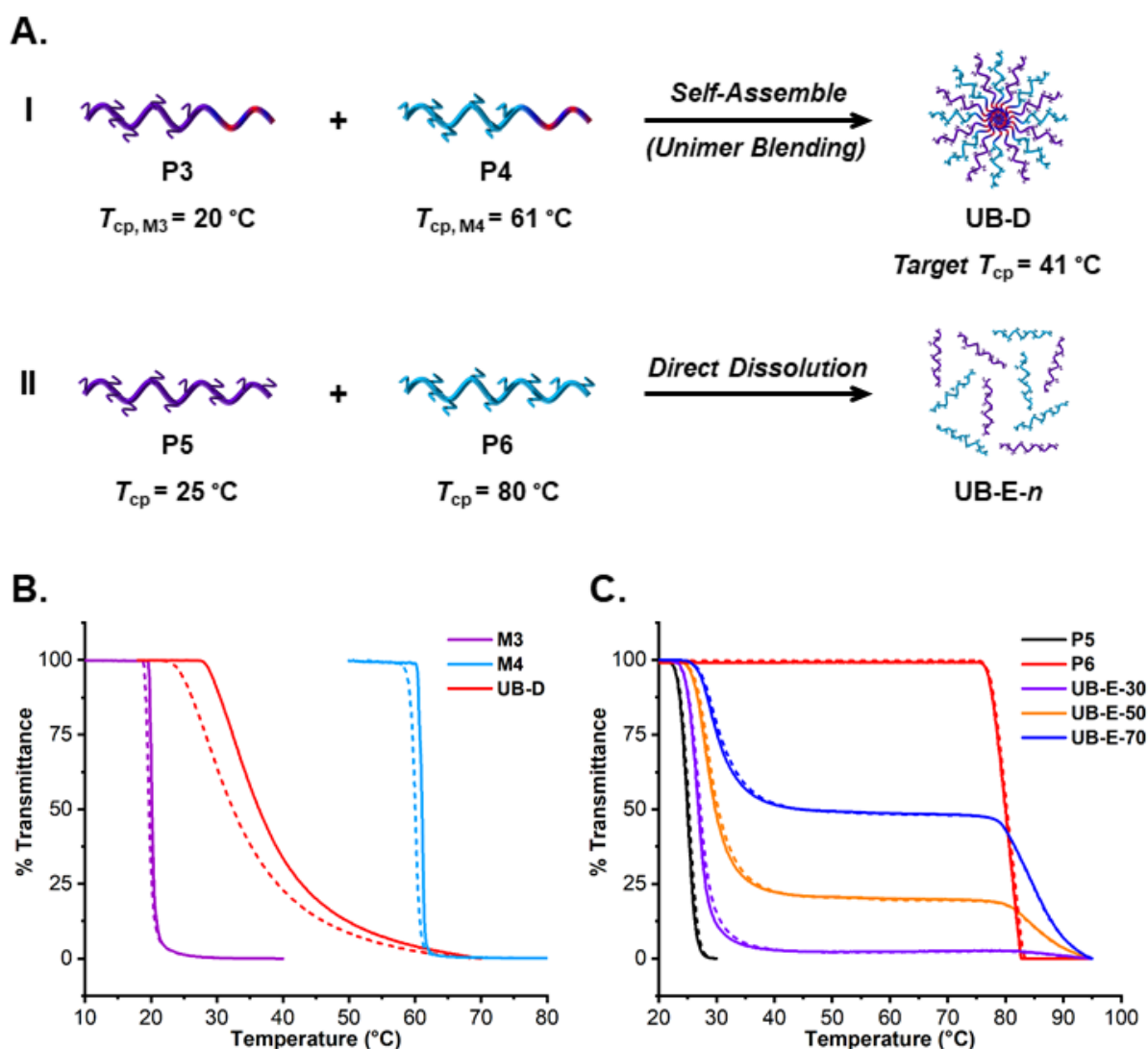


Figure 4. A) I) Preparation of blended diblock copolymer micellar solution **UB-D** via unimer blending of **P3** and **P4** (1:1 molar ratio). II) Preparation of blended homopolymer solutions **UB-E-n** via unimer blending of **P5** and **P6**. B) Variable temperature turbidimetry analysis of

UB-D (red line), **M3** (purple line) and **M4** (light blue line) at 3 mg mL⁻¹. C) Variable temperature turbidimetry analysis of **UB-E-30** (purple line), **UB-E-50** (orange line), **UB-E-70** (blue line), **P5** (black line), and **P6** (red line) at 3 mg mL⁻¹. In all cases, the solid trace represents the heating cycle and the dashed trace represents the cooling cycle. Heating and cooling rate = 1 °C min⁻¹.

In conclusion, the formation of blended diblock copolymer micelles was apparently favored provided that the chosen amphiphilic diblock copolymers were composed of short core-forming blocks, were relatively low in hydrophobic character, and possessed a relatively high degree of chain mobility. For blended diblock copolymer micelles with a coronal composition of brush-like p(DEGMA) and linear p(DEAm) or p(NIPAM), copolymer blending resulted in non-cooperative behavior with a broadening of the phase transition. In contrast, blended diblock copolymer micelles composed of a p(*n*BA-*co*-DMA) core and p(DEGMA)/p(OEGMA) mixed coronae displayed cooperative behavior with a single phase transition at an intermediate T_{cp} with respect to the constituent pure diblock copolymer micelles. Further investigation into the former diblock copolymer system revealed that incorporation of a p(*n*BA-*co*-DMA) core-forming block into the chemical structure of the constituent diblock copolymers was essential in facilitating this cooperativity. Overall, these findings highlight that the cloud point of a micellar solution could be modulated simply by blending two thermoresponsive amphiphilic diblock copolymers with similar coronal chemistry. This facile approach promises to open up new avenues in the design and preparation of responsive nanomaterials owing to its capability to allow for the predictable selection of stimuli-response.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest

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