

*Supporting Information for*

**Asymmetric Catalytic Emulsion Polymerization in Chiral Micelles**

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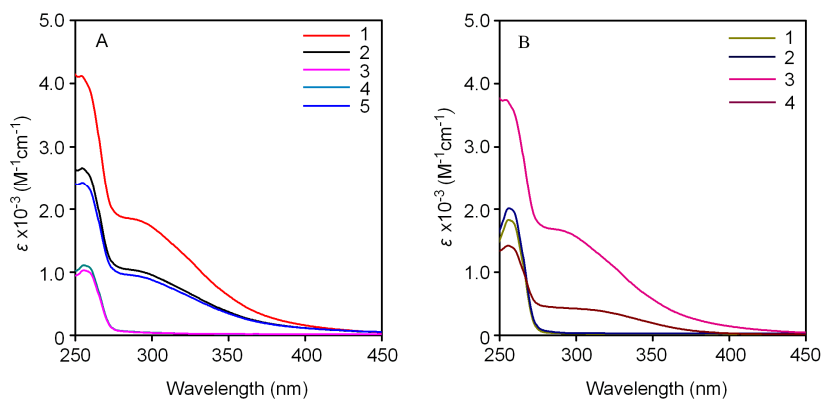
## Experimental Sections

**Materials.** The solvents were distilled under reduced pressure under argon atmosphere in advance. Deionized water was used for the polymerization. Monomers were prepared as introduced in previous reports.<sup>1</sup> (M1: Ref. 1a and b; M2: Ref. 1c) Phenylalanine (PA), serine (S), sodium dodecyl sulfate (SDS) and *N,N*-dimethylform amide (DMF), purchased from Aldrich, were used as received without further purification.  $(\text{nb})\text{Rh}^+\text{B}^-(\text{C}_6\text{H}_5)_4$  was prepared according to a procedure reported elsewhere.<sup>2</sup>

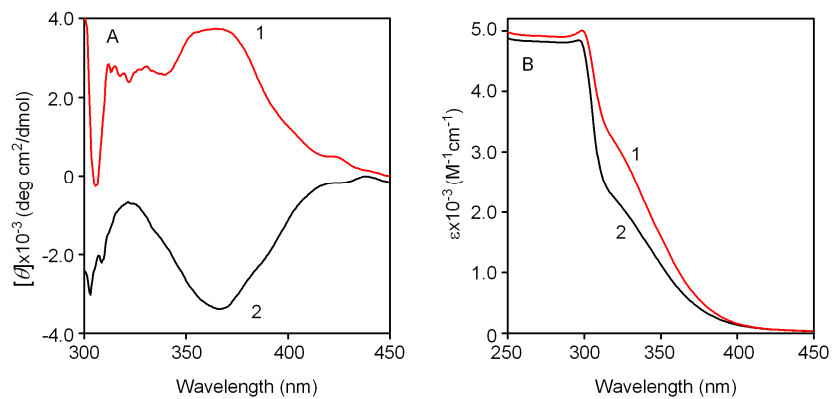
**Polymerization.** A typical polymerization was performed in a 50 mL double-walled glass reaction vessel with attached Teflon stirrer, reflux cooler, and a glass inlet. First the vessel was fed with 1.5 g (5.2 mmol) of SDS, 0.32 g (1.95 mmol) of phenylalanine (PA) and purged with argon for about 10 min. After that, 15 mL of water, which had been made oxygen-free by purging for about 10 min with argon, was added. The mixture was stirred at 600 rpm for 20 min at the reaction temperature of 30 °C to dissolve the surfactant under an argon atmosphere. Following this, 0.1 g (0.65 mmol) of monomer **1** dissolved in 3 mL of DMF was added. The mixture was stirred for a further 30 min to allow the monomer to be emulsified. The resulting monomer emulsion was initiated with 0.67 g (0.013 mmol) of Rh catalyst in 1 mL of DMF, and allowed to polymerize for 180 min. In order to acquire pure polymer particles, SDS was repeatedly excluded by centrifugation. A rotary evaporator was used to remove the water present in the emulsion. After centrifugation, the precipitation was dissolved in  $\text{CHCl}_3$  and filtered; the filtrate was then poured into a large amount of hexane and the polymers precipitated out. SDS and the amino acid cannot be dissolved in  $\text{CHCl}_3$ ,

so pure polymers were obtained.

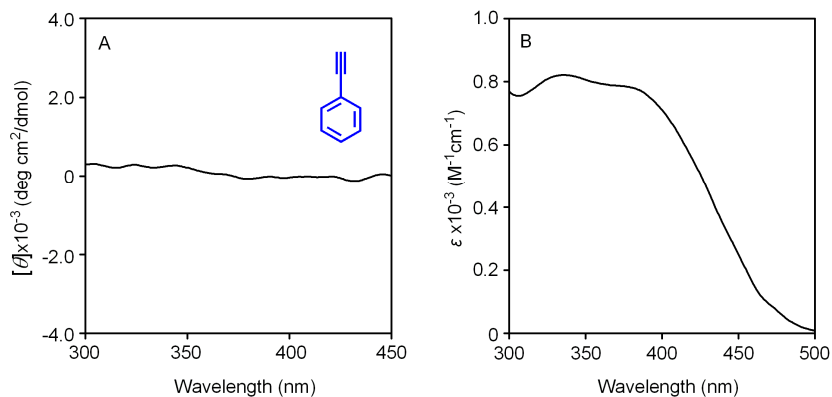
**Characterization.** Circular dichroism (CD) and UV-vis spectroscopy measurements were conducted on a Jasco 810 spectropolarimeter. For measuring CD and UV-vis spectra, the resulting polymer emulsions were diluted 30 times with deionized water in advance. The molecular weights and molecular weight polydispersities of the polymers were determined by GPC (Shodex KF-850 column) with polystyrenes standards and THF as the eluent. Raman spectra were obtained with a microscopic confocal Raman spectrometer spectrophotometer (Renishaw). The monomer conversions were determined gravimetrically. Transmission electron microscopy (TEM) was performed on the polymer emulsions with a HITACHI H-800 electron microscope. Emulsion particle sizes were determined from TEM images. Before carrying out the TEM experiments, the polymer emulsions were first diluted.



**Figure S1.** The UV-vis spectra of pa-poly(**1**) emulsions. In (A) : 1 and 5, poly(**1**) emulsions with *L*- and *D*-phenylalanine, respectively; 2, poly(**1**) emulsion without phenylalanine; 3 and 4, monomer **1** emulsions with *L*- and *D*-phenylalanine, respectively. In (B): 1 and 2, SDS solutions with *L*- and *D*-phenylalanine, respectively; 3, poly(**1**) emulsion with equal content of *L*-phenylalanine and *D*-phenylalanine; 4, poly(**1**) obtained from solution polymerization emulsified by SDS in the presence of chiral phenylalanine. All the original emulsions were diluted 20 times with deionized water. The concentration of polymer was approximately 0.11 mM (determined by the monomer unit). The spectra were recorded at 25 °C.



**Figure S2.** The (A) CD and (B) UV-vis spectra of s-poly(**1**) emulsions. 1 and 2, poly(**1**) emulsions with *L*- and *D*-serine, respectively. All the original emulsions were diluted 20 times with deionized water. The concentration of polymer was approximately 0.11 mM (determined by the monomer unit). The spectra were recorded at 25 °C.



**Figure S3.** The (A) CD and (B) UV-vis spectra of poly(phenylacetylene) emulsions in the presence of phenylalanine. All the original emulsions were diluted 20 times with deionized water. The concentration of polymer was approximately 0.11 mM (determined by the monomer unit). The spectra were recorded at 25 °C.

## References

- 1 (a) L. Ding, X. F. Jiao, J. P. Deng, W. G. Zhao and W. T. Yang, *Macromol. Rapid Commun.*, 2009, **30**, 120; (b) J. P. Deng, J. Tabei, M. Shiotsuki, F. Sanda and T. Masuda, *Macromolecules*, 2004, **37**, 5149; (c) J. P. Deng, X. F. Luo, W. G. Zhao and W. T. Yang, *J. Polym. Sci. Part A: Poly. Chem.*, 2008, **46**, 4112.
- 2 R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339–2343.