Electronic Supplementary Information for

Hairy cylinders based on a coil-comb-coil copolymer

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1. Figures and Scheme

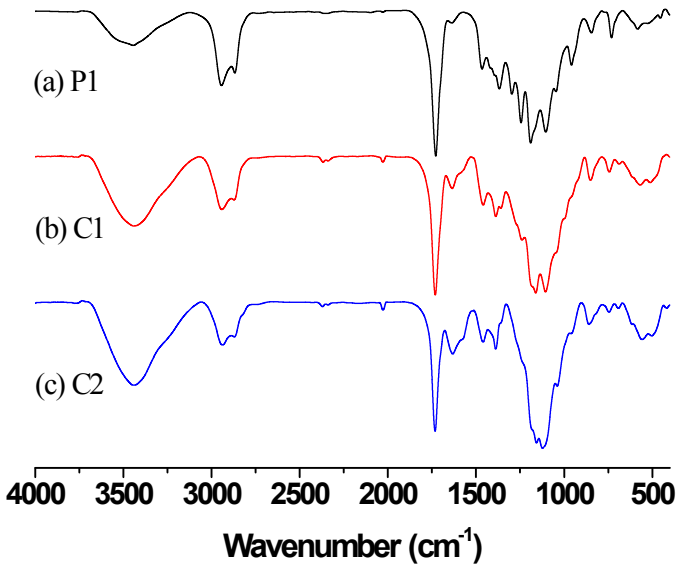


Fig. S1 IR spectra of P1, C1 and C2.

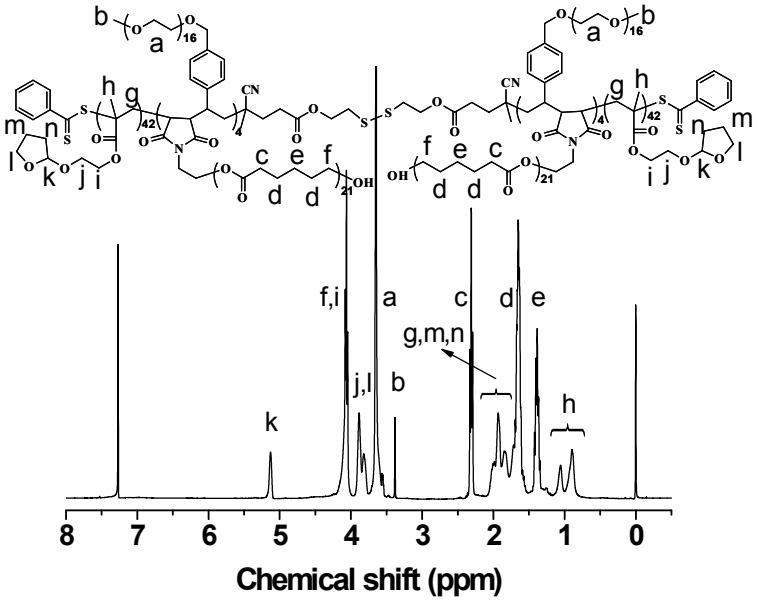


Fig. S2 ^{1}H NMR spectrum of $PTMA_{42}$-*b*-[(St-PEG_{16})-*alt*-(MI-PCL_{21})]$_4$-S-S-[(St-PEG_{16})-*alt*-(MI-PCL_{21})]$_4$–*b*-$PTMA_{42}$ copolymer (C1).

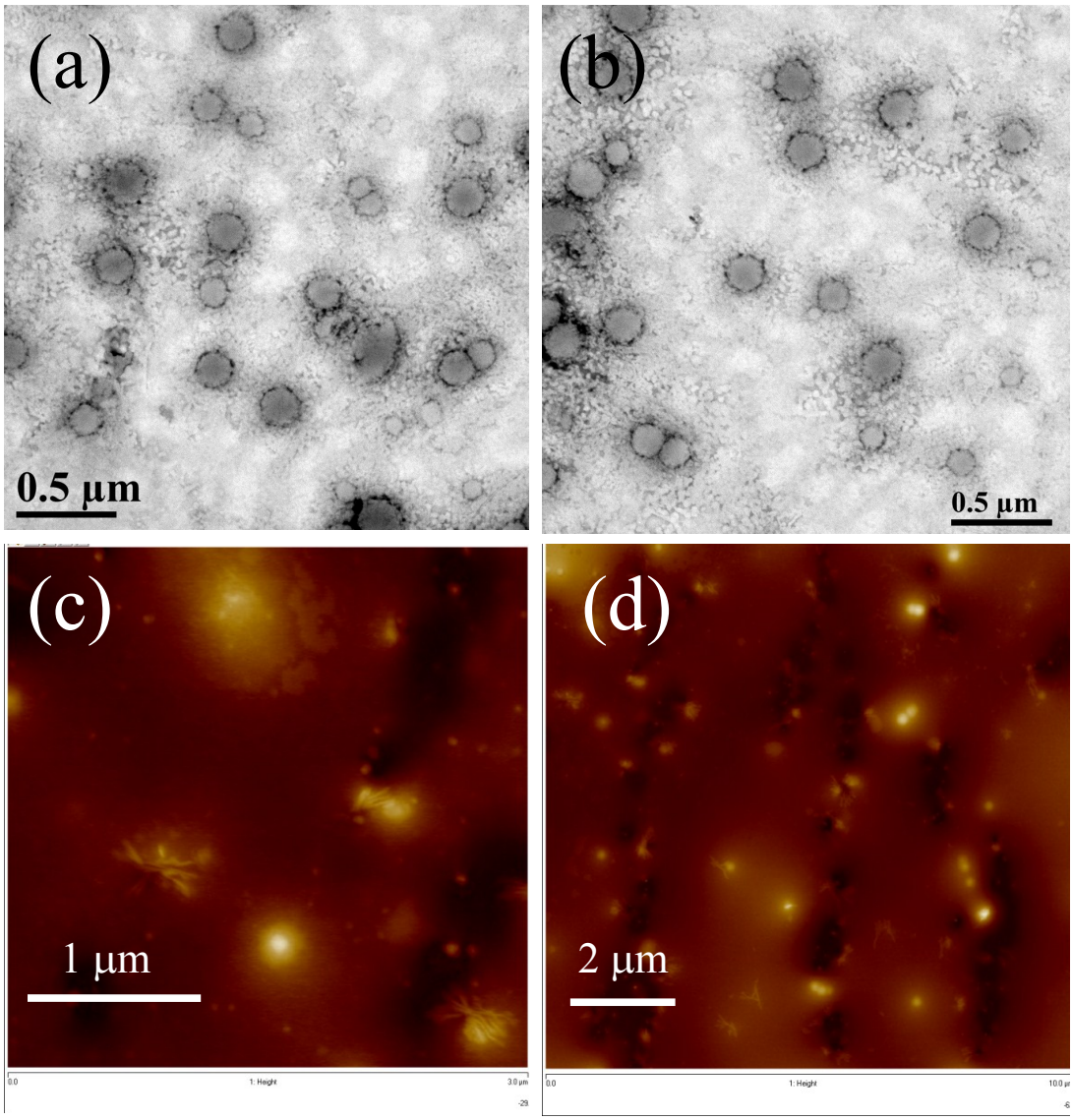


Fig. S3 Additional TEM (a-b) and AFM (c-d) images of C1 hairy nanoparticles at r = 2:1.

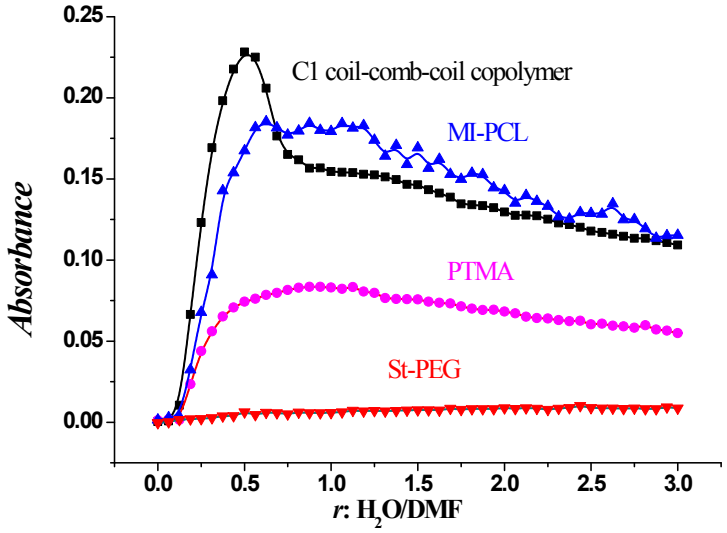


Fig. S4 The turbidity studies in the mixture solution of H_2O/DMF (r, v/v) of C1 coil-comb-coil copolymer and corresponding homopolymers of St-PEG, MI-PCL and PTMA with the same concentration as that of C1 during self-assembly.

The turbidity studies[1, 2] of C1 coil-comb-coil copolymer and corresponding homopolymers of St-PEG, MI-PCL and PTMA with the same concentration as that of C1 during self-assembly were performed to explore the possible transition pathway of different morphologies with different water contents (*r*). The absorbance at 650 nm were recorded. As one may expected, the absorbance of St-PEG homopolymer kept constant with increasing water content. For the case of MI-PCL homopolymer, adding a very small amount of water caused a fast increase in the absorbance. The maximum absorbance appeared when *r* is up to 0.625. Similarly, the turbidity of PTMA homopolymer presented analogous pathway with the maximum absorbance at $r = 1$. The turbidity showed different pathways when the three homopolymers formed a copolymer. When *r* is less than 0.5, the absorbance increased quickly, similar to that of MI-PCL and PTMA. Interestingly, the absorbance decreased quickly after r is up to 0.5 and decreased gradually after *r* is up to 0.75, which are corresponding to the morphology transition detected by TEM when cylinders turned into hairy cylinders at *r* from 0.5 to 0.7. The morphology transition is also reflected in the increase of cylinders diameter at different *r* (Table 2). With more and more water adding, PTMA and MI-PCL becomes more and more insoluble, and the less hydrophobic PTMA joins the core of the cylinders, leading to the increase of cylinders diameter, and essentially promoting the formation of hairy cylinders due to the synergic effect with comb-like structure which will be discussed later.

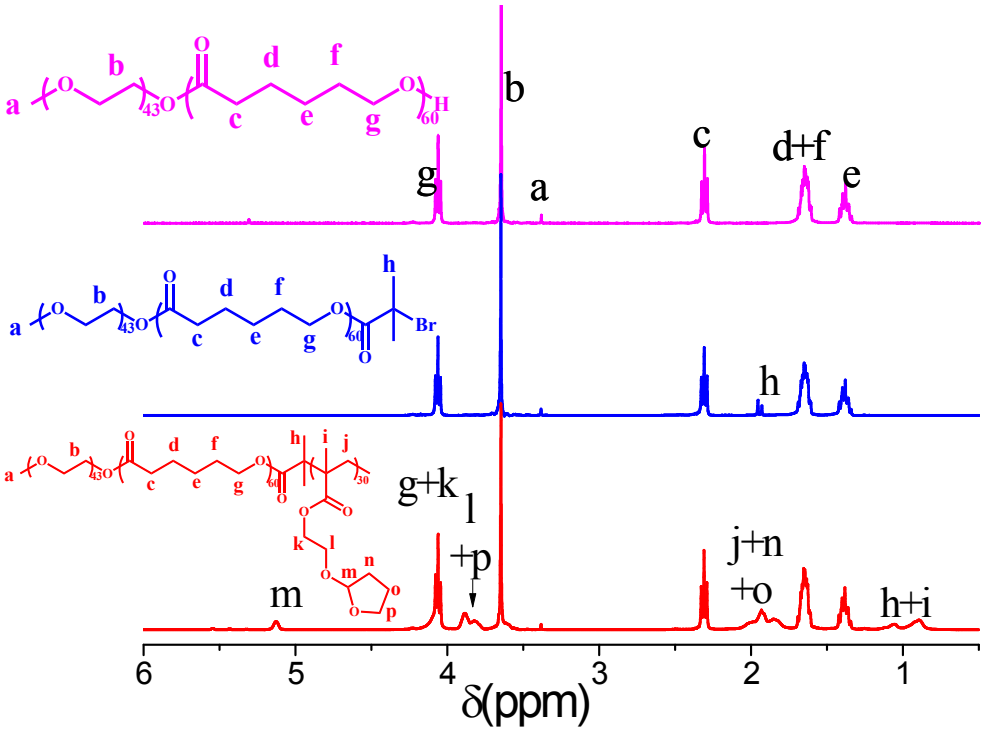


Fig. S5 ^{1}H NMR spectrum of PEG_{43}-*b*-PCL_{60}-*b*-$PTMA_{30}$ (L1).

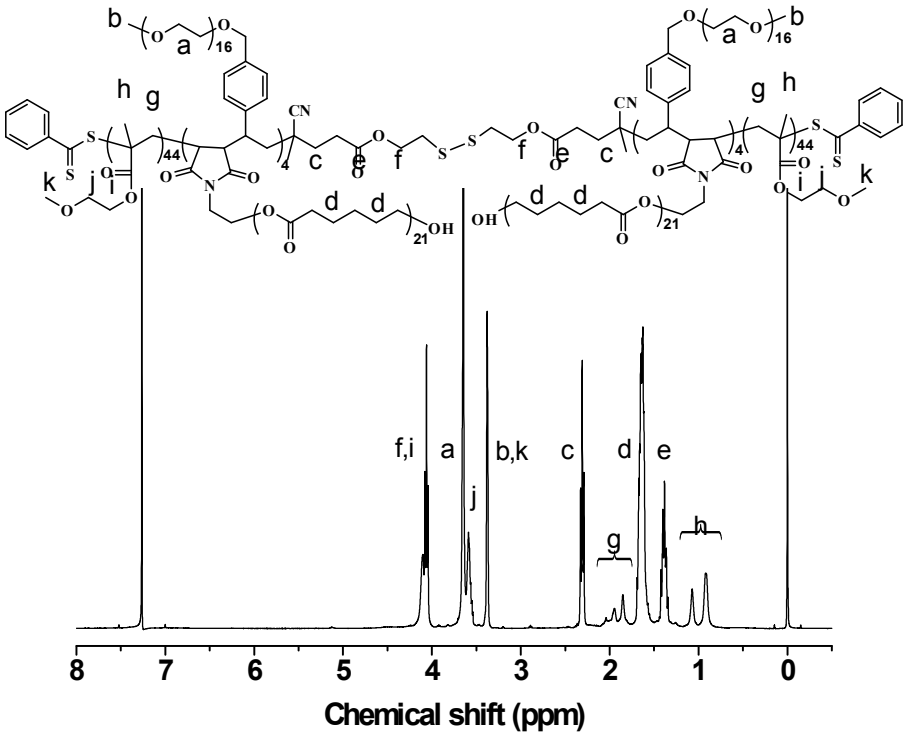


Fig. S6 ^{1}H NMR spectrum of $PMEMA_{44}$–*b*–[(St-PEG_{16})-*alt*-(MI-PCL_{21})]$_4$–S–S–[(St-PEG_{16})-*alt*-(MI-PCL_{21})]$_4$–*b*–$PMEMA_{44}$ copolymer (C2).

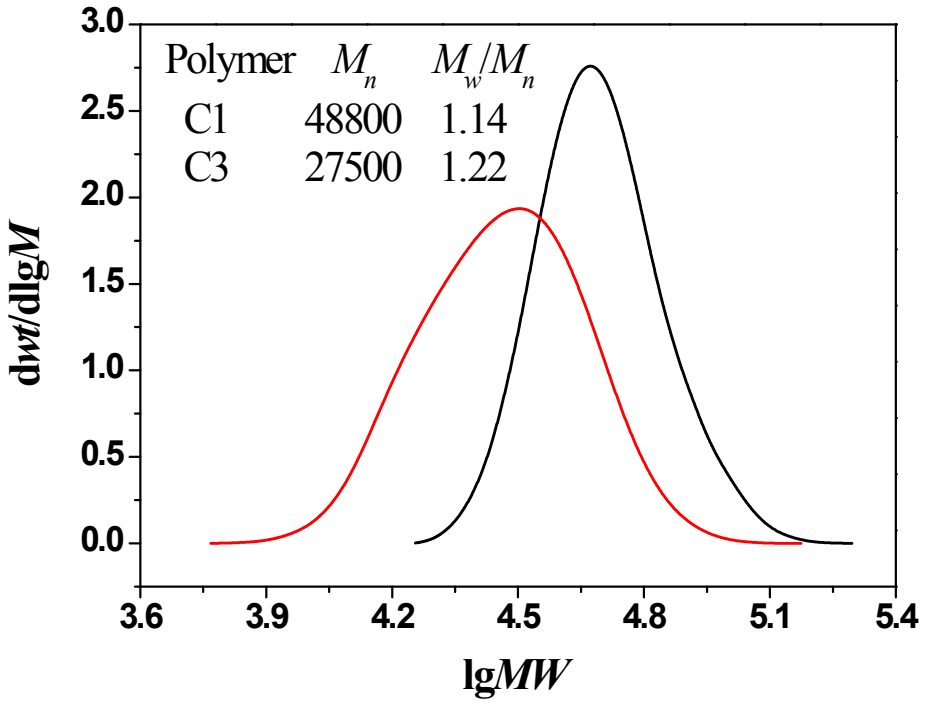
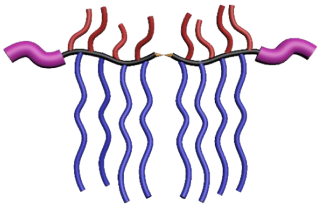
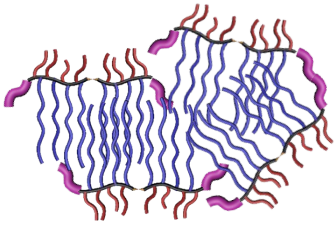


Fig. S7 GPC traces of C3 after reduction of C1 to cleave the disulfide linkage.

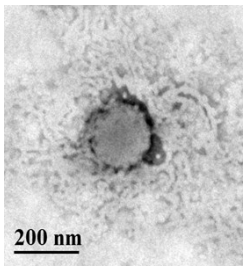
Scheme S1 Structure-dependent cylinders arrangement.

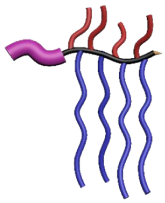


Coil-Comb-Coil copolymer C1

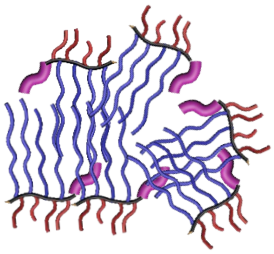


Cylinders ending is more difficult than cylinders elongation and branching.

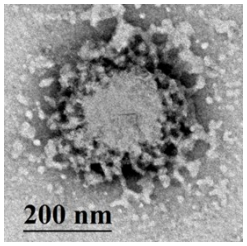




Coil-Comb copolymer C3



Molecule is more flexible and can easily adjust its conformation to end cylinders elongation.



2. Calculations

2.1 Calculation of the contour length of the main chain and side chains of C1.

The calculation by accumulating the length of carbon-carbon and carbon-oxygen covalent bonds at a specific angle was based on our previous method.[3] The main process is showing below:

The angle of carbon-carbon covalent bonds is 109.28°.

The angle of carbon-oxygen covalent bonds is 120°.

$$l_{PEG} = \left(l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times n_{c-c} + l_{c-o} \times \cos\left(\frac{180° - \theta_{c-o}}{2}\right) \times n \right.$$
$$\times 16 \approx 6.0\ nm$$

$$l_{PCL} = \left(l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times n_{c-c} + l_{c-o} \times \cos\left(\frac{180° - \theta_{c-o}}{2}\right) \times n$$
$$\times 21 \approx 18.4\ nm$$

$$l_{PTMA} = l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times DP = 0.154\ nm \times \cos\left(\frac{180° - 109.28}{2}\right.$$

$$l_{PMEMA} = l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times DP = 0.154\ nm \times \cos\left(\frac{180° - 109.28°}{2}\right) \times 44 \approx 5.5\ nm$$

The contour length of the main chain is calculated by accumulating the length of carbon-carbon, carbon-oxygen and carbon-sulfur covalent bonds at a specific angle:

The angle of carbon-sulfur covalent bonds is 120 °.

$$l_{main\ chain} = l_{spacer} + 2 \times l_{half\ brush} + 2 \times l_{end\ group} + 2 \times l_{PTMA}$$

$$l_{spacer} = \left(l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times n_{c-c} + l_{c-o} \times \cos\left(\frac{180° - \theta_{c-o}}{2}\right) \times n$$
$$\times 2 + l_{s-s} \times \cos\left(\frac{180° - \theta_{s-s}}{2}\right) \times n_{s-s}$$
$$= \left(0.154\ nm \times \cos\left(\frac{180° - 109.28°}{2}\right) \times 4 + 0.143\ nm \times \cos\left(\frac{180°\right.\right.$$
$$\times 2 + 0.207\ nm \times \cos\left(\frac{180° - 120°}{2}\right) \times 1 \approx 2.0\ \ nm$$

$$l_{half\ brush} = l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times n_{c-c} \times DP = 0.154\ nm \times \cos\left(\frac{180° -\right.$$
$$\times 4 \approx 2.0\ nm$$

$$l_{end\ group} = l_{c-c} \times \cos\left(\frac{180° - \theta_{c-c}}{2}\right) \times n_{c-c} + l_{c-s} \times \cos\left(\frac{180° - \theta_{c-s}}{2}\right) \times n_c$$

$$= 0.154\ nm \times \cos\left(\frac{180° - 109.28°}{2}\right) \times 1 + 0.182\ nm \times \cos\left(\frac{180° - 12}{2}\right.$$

$$+ 0.266\ nm \approx 0.7\ nm$$

$$l_{main\ chain} = l_{spacer} + 2 \times l_{half\ brush} + 2 \times l_{end\ group} + 2 \times l_{PTMA}$$

$$= 2.0\ nm + 2 \times 2.0\ nm + 2 \times 0.7\ nm + 2 \times 5.3 = 18\ nm$$

2.2 Weight fractions of St-PEG, MI-PCL and PTMA in the C1 coil-comb-coil copolymers.

The M_n value of P1 determined by ^{1}H NMR was $M_{n,P1}$ = 30900 g mol^{-1} , and the M_n value of C1 determined by ^{1}H NMR was $M_{n,C1}$ = 47600 g mol^{-1}. The numbers of St-PEG ($M_{n,PEG}$ = 870 g mol^{-1}, PDI = 1.04)[4] and MI-PCL ($M_{n,PCL}$ = 2560 g mol^{-1})[5] grafts per comb were determined to n_{PEG} = 8.9 and n_{PCL} = 8.8 by ^{1}H NMR analysis. Thus the weight fractions were calculated as below:

$w_{PEG} = m_{PEG}/ m_{C1} = n_{PEG} \times M_{n,PEG} / M_{n,C1} = 8.9 \times 870 / 47600 = 16.2\%$

$w_{PCL} = m_{PCL}/ m_{C1} = n_{PCL} \times M_{n,PCL} / M_{n,C1} = 8.8 \times 2560 / 47600 = 47.3\%$

$w_{PTMA} = m_{PTMA}/ m_{C1} = (M_{n,C1} - M_{n,P1}) / M_{n,C1} = (47600-30900) / 30900 = 35.1\%$

$w_{main\ chain} = 1 - w_{PEG} - w_{PCL} - w_{PTMA} = 1.4\%$

3. References

1 L. Zhang and A. Eisenberg, *Science*, 1995, **268**, 1728-1731.

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3 Q. T. Huang, B. Yang, H. H. Liu, Y. L. Zhao and J. Z. Du, *Polym. Chem.*, 2015, **6**, 886-890.

4 H. Zhu, G. Deng and Y. Chen, *Polymer*, 2008, **49**, 405-411.

5 M. J. Zhang, H. H. Liu, W. Shao, K. Miao and Y. L. Zhao, *Macromolecules*, 2013, **46**, 1325-1336.