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Directional effect on the fusion of ellipsoidal morphologies into nanorods and nanotubes†

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Particle fusion is well-recognized as an important spontaneous process to produce higher-order nanostructures during morphology transition in polymerization-induced self-assembly (PISA). However, to our knowledge, the directional contact, adhesion, and fusion of adjacent nanoparticles have been rarely elucidated in PISA. Herein, a directional fusion of ellipsoidal morphologies was demonstrated during PISA of semi-fluorinated liquid-crystalline (SFLC) block copolymers. The ellipsoidal nanostructures, including micelles and vesicles, preferred to undergo a directional fusion in a head-to-head model, leading to the formation of nanorods and nanotubes, respectively. We believe the directional fusion will offer insightful guidance in PISA to the preparation of complicated functional nanostructures.

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Introduction

Over the past few decades, the solution self-assembly of block copolymers (BCPs) as a versatile approach to constructing nanostructures has been greatly developed.^{1–9} However, traditional self-assembly of BCPs suffers from recognized limitations, such as a low concentration (below 1 wt% solids) and multiple-step process,^{1,10} which severely impede the scalable production of BCP nanomaterials. In contrast, polymerization-induced self-assembly (PISA) *via* reversible addition–fragmentation chain transfer (RAFT)-mediated dispersion polymerization has been well-established as a reliable strategy for efficient production of BCP nanoparticles with tailorable properties.^{11–17} During a typical dispersion polymerization, a stabilizer homopolymer is chain-extended by polymerizing a soluble monomer to produce amphiphilic BCPs, which *in situ* self-assemble to form nanoparticles with diverse morphologies. The morphology evolution during PISA has been systematically investigated, providing guiding principles for predicting BCP morphologies. Generally, in a typical PISA process, the spheres fused into worms, lamellas, and all the way to high-order vesicles with the growth of core-forming blocks.¹⁸ As a consequence, the formation of nanorods and nanotubes is highly sensitive to synthetic conditions such as solids contents, polymerization solvents,

and block compositions.¹⁹ Although a few researchers have developed novel PISA strategies for polymeric worms, nanowires, and nanotubes,^{20–26} it is still challenging to produce nanorods and nanotubes through the self-assembly of amorphous coil–coil BCPs.

Recently, liquid-crystalline (LC) block copolymers have been broadly employed to mediate the self-assembly behaviors of BCPs. In particular, it was well-demonstrated that self-assembly of LC block copolymers facilitated the formation of cylindrical nanostructures.^{27,28} For example, Li and co-workers found that BCPs comprising a cholesteryl LC core-forming block preferred to form cylindrical micelles.²⁹ Winnik *et al.* described that the self-assembly of BCPs comprising a polyferrocenylsilane block can readily produce rod-like micelles within a broad range of BCP composition window.³⁰ Among various liquid-crystalline polymers, fluorinated polymers are remarkable materials because of their unique properties and wide applications in several areas.^{29–33} Particularly, semi-fluorinated poly(meth)acrylates bearing side groups with high numbers of fluorocarbons (≥ 7) exhibit excellent LC nature because F-alkyl chains are much bulkier and more rigid than alkyl chains.^{34,35} In recent years, the self-assembly of semi-fluorinated liquid-crystalline (SLFC) BCPs for constructing cylindrical nanostructures has been systematically developed. For example, Liu and co-workers demonstrated that triblock terpolymers bearing a fluorinated block can readily self-assemble into cylindrical micelles.³⁶ Manners *et al.* reported that the self-assembly of a SLFC BCP afforded monodisperse cylindrical micelles through a fragmentation-thermal annealing process.³⁷ Yuan and co-workers found that cylindrical micelles could be readily prepared by PISA of semi-fluorinated-containing monomer in a wide range of lengths of core-forming block.³⁸ However, the dynamic process

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of morphology evolution for the formation of cylindrical micelles was not discussed. Despite significant progress, the unique advantage of BCPs with a LC block in forming cylindrical nanostructures compared with coil-coil BCPs need further elucidation.

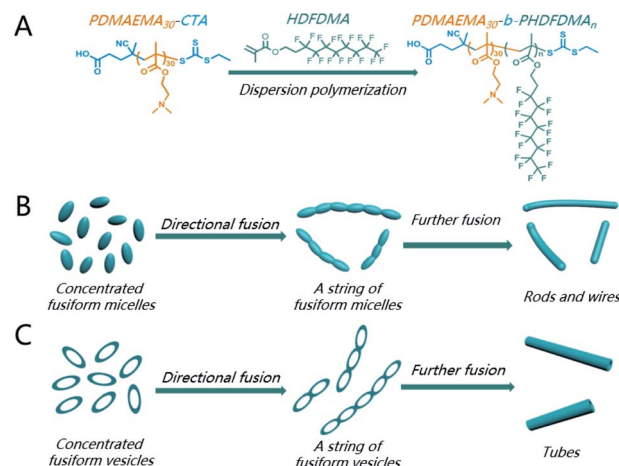
Recently, a few researchers have reported that ellipsoidal morphologies can be readily obtained through PISA of rigid rod-coil BCPs with a LC block.³⁹ For instance, Chen and co-workers presented an efficient approach to forming a series of anisotropic morphologies, including ellipsoidal vesicles *via* polymerization-induced hierarchical self-assembly of azobenzene-containing BCPs.⁴⁰ Shen and co-workers reported that facile preparation of ellipsoidal micelles can be achieved in the dispersion polymerization of heptadecafluorodecyl methacrylate (HDFDMA) employing several macromolecular chain transfer agents (macro-CTAs) in a wide selection of solvents.⁴¹ In contrast, the PISA of amorphous coil-coil BCPs usually results in isotropic spheres.

Fusion is an important spontaneous process to generate higher-order structures during morphology evolution in PISA.⁴² For instance, spheres fuse to worms¹⁸ and vesicles fuse to form tubes, compound vesicles,⁴³ and tetrapod polymersomes.⁴⁴ Cai and co-workers have well-demonstrated that one-dimensional nanowires readily formed *via* the fusion of spindle-like micelles along the long axis of the micelles.^{45,46} We envision that it might also undergo a directional fusion of ellipsoidal morphologies during the formation of cylindrical nanostructures *via* PISA of BCPs containing a LC block. However, to the best of our knowledge, the directional fusion effect on the formation of cylindrical nanostructures has been rarely discussed in PISA. Although Lv *et al.* reported that the fusion of vesicles in one dimension can occur to form nanotubes in their PISA protocol,⁴³ the directional contact, adhesion, and fusion of adjacent nanoparticles was not elucidated. Herein, we aim to verify the directional effect on the fusion of ellipsoidal morphologies during dispersion polymerization of HDFDMA using poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA₃₀) as the macro-CTA.

Results and discussion

As demonstrated in Scheme 1A, a PDMAEMA₃₀ macro-CTA was employed to mediate the reversible addition–fragmentation chain transfer (RAFT) dispersion polymerization of HDFDMA. The PDMAEMA₃₀-CTA was first synthesized *via* RAFT homogeneous polymerization of DMAEMA in *N,N*-dimethylformamide (DMF) at 70 °C. After dialysis against ethanol for two days, the degree of the polymerization (DP) of DMAEMA was calculated to be 30 by comparing the integral ratio of signal *h* ($\delta = 4.09$ ppm) and *b* ($\delta = 3.27$ ppm) (Fig. 1A). GPC analysis in Fig. 1B shows a narrow molecular weight distribution ($M_w/M_n = 1.12$) and good agreement between theoretical and experimental molecular weights ($M_{n,NMR} = 4973$ g mol^{−1}, $M_{n,GPC} = 5077$ g mol^{−1}), indicating good control of molecular weight distributions.

Then, the PDMAEMA₃₀ macro-CTA was chain-extended through RAFT dispersion polymerization of HDFDMA in ethanol at 70 °C at 20% w/v solids content. The polymerization



Scheme 1 (A) RAFT PISA process for BCPs nano-objects containing a SFLC block *via* chain-extension of PDMAEMA₃₀ macro-CTA; (B) formation of nanorods through the directional fusion of ellipsoidal micelles and (C) formation of nanotubes through the directional fusion of ellipsoidal vesicles.

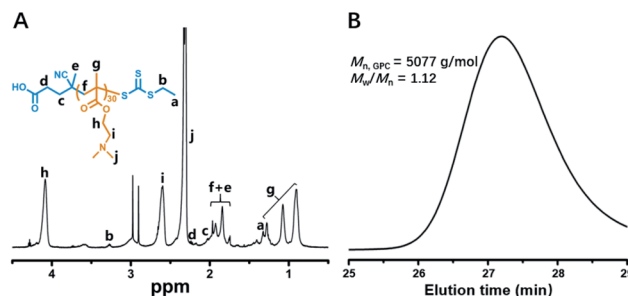


Fig. 1 ¹H NMR spectrum (A) and GPC trace (B) of PDMAEMA₃₀ macro-CTA.

condition and results were summarized in Table 1. ¹H NMR spectra confirmed that near quantitative HDFDMA conversions were accomplished within 11–23 h. The BCPs compositions can

Table 1 Summary of the dispersion polymerization of HDFDMA in ethanol mediated by PDMAEMA₃₀-CTA at 70 °C

Feed ratio ^a	Solids%	Conv. ^b %	$D_{h,app}$ ^c	PDI ^c
1/50/0.3	20	99	126	0.18
1/60/0.3	20	99	140	0.11
1/70/0.3	20	99	164	0.08
1/80/0.3	20	99	191	0.08
1/90/0.5	20	99	200	0.15
1/100/0.5	20	99	280	0.43
1/100/0.5	15	99	230	0.34
1/100/0.5	30	99	350	0.49
1/105/0.5	30	99	618	0.35

^a Molar ratio (PDMAEMA₃₀-CTA/HDFDMA/AIBN). ^b Monomer conversions determined by ¹H NMR spectroscopy in CDCl₃. ^c The average value of apparent hydrodynamic diameter ($D_{h,app}$) and the polydispersity index (PDI) of particle size confirmed by DLS characterizations with the block copolymer concentration of 0.1% (1 mg mL^{−1}).



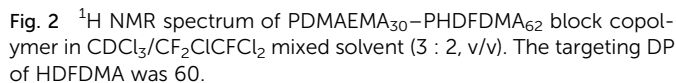


Fig. 2 ^1H NMR spectrum of PDMAEMA₃₀–PHDFDMA₆₂ block copolymer in $\text{CDCl}_3/\text{CF}_2\text{ClCFCl}_2$ mixed solvent (3 : 2, v/v). The targeting DP of HDFDMA was 60.

The morphologies of BCP nanostructures were analysed by transmission electron microscopy (TEM). The corresponding size distributions of the PDMAEMA₃₀-PHDFDMA_{*n*} nano-objects were characterized by dynamic light scattering (DLS). As shown in Fig. 3A, the dispersion polymerization targeting a DP of 50 resulted in a mixture of anisotropic ellipsoidal micelles with different sizes. The DLS results in Fig. 4 (the black line) indicated an average value of the apparent hydrodynamic diameter

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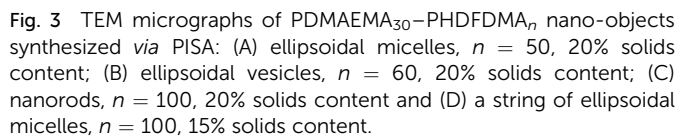


Fig. 3 TEM micrographs of PDMAEMA₃₀-PHDFDMA_{*n*} nano-objects synthesized *via* PISA: (A) ellipsoidal micelles, *n* = 50, 20% solids content; (B) ellipsoidal vesicles, *n* = 60, 20% solids content; (C) nanorods, *n* = 100, 20% solids content and (D) a string of ellipsoidal micelles, *n* = 100, 15% solids content.

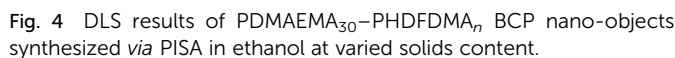


Fig. 4 DLS results of PDMAEMA₃₀-PHDFDMA_n BCP nano-objects synthesized *via* PISA in ethanol at varied solids content.

Interestingly, with a further increase of DP of HFDfDMA to 100, nanorods with varied length formed (Fig. 3C). Besides nanorods, ellipsoidal micelles can also be clearly observed. DLS results in Fig. 4 (the blue line) also demonstrated a wide distribution of size ($PDI = 0.43$). The peak at 1189 nm corresponded to long rods while the peak at 177 nm corresponded to the mixture of short rods and ellipsoidal micelles. The statistical analysis in Fig. S5† demonstrated that the average width of nanorods (108 nm) is basically consistent with the short axis of the ellipsoidal micelles, suggesting that nanorods were resulted from the directional fusion of the ellipsoidal micelles along the long axis. As is well-recognized, the solids content is one of the critical factors influencing the morphology evolution process in PISA. In principle, low solid contents will retard the morphology evolution by decreasing the probability of collision and fusion of nanoparticles.^{47–49} To acquire more convincing evidence for a directional fusion of ellipsoidal micelles, the PISA of

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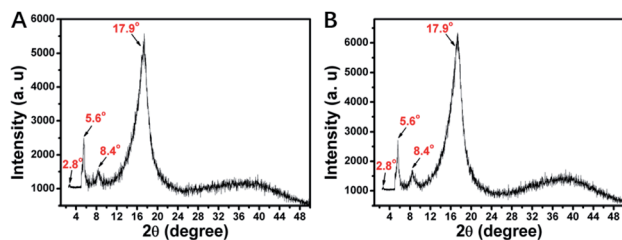


Fig. 6 X-ray diffraction patterns for (A) PDMAEMA₃₀-PHDFDMA₅₀ and (B) PDMAEMA₃₀-PHDFDMA₁₀₀ fluoro-containing block copolymer nanoparticles.

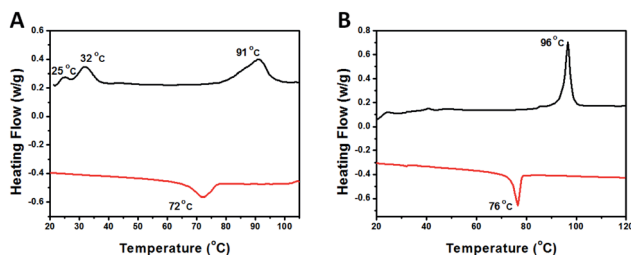


Fig. 7 DSC traces for (A) PDMAEMA₃₀-PHDFDMA₁₀₀ fluoro-containing block copolymer nano-objects and (B) PHDFDMA₅₀ homopolymer. The red and black lines refer to the heating half-cycle and cooling half-cycle, respectively.

perfluoroalkyl chain length.⁵¹ This provides convincing evidence that HDFDMA blocks formed an ordered smectic B (SmB) phase. As Lv *et al.* reported, the temperature of polymerization (T_p) in PISA is crucial for morphological evolution because the mobility of core-forming block can be affected by T_p .⁴³ They found that when T_p of PISA was appropriately lower than or close to the glass transition temperature (T_g), the mobility of the core-forming block was retarded, facilitating the one-dimension fusion of vesicles into tubes. In our work, the T_p for all PISA formulations were set to be 70 °C, a commonly used temperature for most RAFT-PISA protocols. To check if the T_p we utilized is appropriately lower than or close to the SmB-to-isotropic phase transition temperature of PHDFDMA blocks, the DSC measurements were conducted. As indicated in Fig. 7, a SmB to isotropic phase transition at 72 °C for PDMAEMA₃₀-PHDFDMA₁₀₀ was revealed, suggesting that T_p at 70 °C is appropriate in our PISA system. In order to better explain directional fusion mechanism for ellipsoidal morphologies, we performed a PISA of PDMAEMA₃₀-PHDFDMA₁₀₀ with 20% solids content at 76 °C. TEM micrograph in Fig. S9† demonstrated that only spherical particles formed and no fusion of nanoparticles was observed. Since the T_p at 76 °C is higher than the SmB-to-isotropic phase transition temperature, the ellipsoidal morphologies were not produced and no directional fusion can be observed.

Conclusions

In summary, a directional effect on the fusion of ellipsoidal morphologies into nanorods and nanotubes was demonstrated

in our work. The ellipsoidal micelles and vesicles can be readily prepared *via* the dispersion polymerizations of HDFDMA mediated by PDMAEMA₃₀ due to the LC ordering of the SFCLC blocks. In addition, the ellipsoidal morphologies preferred to fuse in a head-to-head manner, affording the lowest membrane curvature and tension. Thus, nanorods and nanotubes can be readily generated *via* the directional fusion of ellipsoidal micelles and vesicles, respectively. We believe the directional effect on nanoparticle fusion will offer insightful guidance to the preparation of complicated functional nanostructures.⁴⁴

Experimental

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN, 99%) were purchased from Sigma-Aldrich. Heptadecafluorodecyl methacrylate (HDFDMA, 98%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%) were purchased from Shanghai Aladdin Bio-Chem Technology. CDCl₃ (99.8%) was purchased from J&K Scientific. CF₂ClCFCl₂ (99.5%) was purchased from Shanghai Macklin Biochemical. All the monomers were passed through an Al₂O₃ column to remove the inhibitor prior to polymerizations. The chain transfer agent 4-cyano-4-(ethylthiocarbonothioylthio) pentanoic acid (CEPA) was synthesized according to a previously published procedure.⁵²

Characterization

The monomer conversions (HDFDMA and DMAEMA) and chemical structure of the synthesized polymers, including PDMAEMA₃₀-CTA and PDMAEMA₃₀-PHDFDMA_n, were analyzed by ¹H NMR spectroscopy on a Bruker AV 400 MHz spectrometer. CF₂ClCFCl₂ was utilized as a cosolvent together with a suitable deuterated solvent to sufficiently dissolve fluoro-containing block copolymer nanoparticles. Gel permeation chromatography (GPC) measurements were performed on a Waters Alliance e2695 GPC system equipped with a Styragel guard column (WAT054415, 30 × 4.6 mm), two org separation columns consisting of D2500 (300 × 8 mm) and D5000 (300 × 8 mm). Detection was made with a 2414 refractive index detector (Waters Alliance), a Viscotek 302/305 UV detector (Malvern Instruments), and a Viscotek TDA 305-020 LALS/RALS detector (Malvern Instruments). DMF (HPLC grade, containing 1 mg mL⁻¹ LiBr) was used as the eluent at a flow rate of 0.8 mL min⁻¹. GPC samples were prepared by dissolving 3–5 mg dry polymer powder in 1 mL DMF and filtered through a 0.20 μm Millipore filter. The temperature of the columns and detector was set at 65 °C and 45 °C, respectively. Analysis of molecular weight and dispersity was carried out using Empower 2 software against polymethyl methacrylate (PMMA) standards (molecular weight range 2.4 × 10² to 1.0 × 10⁶ g mol⁻¹). Dynamic light scattering (DLS) analysis was performed on a Malvern ZS90 with a He-Ne laser (633 nm, 4 mW) at a 90° angle. The as-synthesized nanoparticle dispersions *via* PISA were diluted to 0.1% (1 mg mL⁻¹) in a disposable cuvette using ethanol and analyzed after 30 minutes. The viscosity was 1.748 cP and the refractive index was 1.366. The temperature for all DLS characterizations was 25 °C



and the equilibration time was 120 seconds. Autocorrelation functions were analyzed by the cumulants method to calculate the z-average hydrodynamic diameter and polydispersity index (PDI). The morphology of the nanoparticles was analyzed by transmission electron microscopy (TEM) conducted on a Jeol 200CX microscope (200 kV). Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC214 instrument under N₂ protection at a scanning rate of 10 °C min⁻¹. X-ray diffraction (XRD) measurements were carried out on a Rigaku Dmax 2500 PC diffractometer using Cu K α radiation (λ = 0.154 nm).

Synthesis of PDMAEMA₃₀ macro-chain transfer agent

Macromolecular chain transfer agent was synthesized according to a previously published procedure.⁵³ In brief, DMAEMA (3.14 g, 20.0 mmol), CEPA (0.132 g, 0.5 mmol), and AIBN (8.2 mg, 0.05 mmol) were added into a glass vial and subsequently dissolved in 6.5 mL DMF. After the solution was purged with nitrogen for 30 minutes, the glass vial was placed into an oil bath at 70 °C and stirred at 500 rpm. After 3 h of polymerization under nitrogen, the glass vial was removed from the oil bath and the resulting solution was exposed to air to terminate the polymerization. The monomer conversion was determined to be 70% by ¹H NMR spectroscopy. The polymer was purified in a dialysis bag (MWCO 1.0 kg mol⁻¹) against ethanol for two days. After rotary evaporation and drying under vacuum, polymer sample with high purity was obtained.

Synthesis procedure for the dispersion polymerization of HFDMA mediated by PDMAEMA₃₀-CTA

A certain amount of PDMAEMA₃₀-CTA and HFDMA were added into a glass vial and dissolved in ethanol. After the solution was degassed for 30 minutes in an ice bath, a certain amount of AIBN dissolved in ethanol was injected into the reaction mixture under N₂ atmosphere and the glass vial was placed into an oil bath at 70 °C with a stirring speed of 500 rpm. After a certain time of polymerization under nitrogen atmosphere, the glass vial was removed from the oil bath and the solution was exposed to air to terminate the polymerizations. The monomer conversion was determined by ¹H NMR spectroscopy in CDCl₃. Purified copolymers were obtained by precipitation in diethyl ether and drying under vacuum. The BCPs compositions were characterized by ¹H NMR spectroscopy in a mixture of CDCl₃/CF₂ClCFCl₂ (3 : 2, v/v). The actual repeat unit of HFDMA was determined by comparing the integral of signal *h'* (δ = 4.30 ppm) and *h* (δ = 4.14 ppm).

Author contributions

Yahui Li, Qunzan Lu and Qiumeng Chen performed the experiments. Xuan Wu, Jianliang Shen and Liangliang Shen designed the project and performed the data analysis. Lianliang Shen wrote the paper. All authors discussed the results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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