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Multi-Morphological Complex Aggregates Formed from Amphiphilic Poly(ethylene oxide)-b-Polydimethylsiloxane-b-Poly(ethylene oxide) Triblock Copolymers

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Table S1, Figure S1-S9 and supplementary Experimental Section

Table S1. GPC results of polymers

Copolymer	$M_n(M_w/M_n)$ (PDMS)	$M_n(M_w/M_n)$ (PEO)	$M_n(M_w/M_n)$ (copolymer)
PEO_{10}-b-$PDMS_9$-b-PEO_{10}	726 (1.13)	468 (1.02)	1848 (1.08)
PEO_{95}-b-$PDMS_9$-b-PEO_{95}	726 (1.13)	4198 (1.04)	9122 (1.11)
PEO_{10}-b-$PDMS_{86}$-b-PEO_{10}	6405 (1.44)	468 (1.02)	7158 (1.52)
PEO_9-b-$PDMS_{51}$-b-PEO_9	3786 (1.32)	429 (1.01)	4579 (1.21)

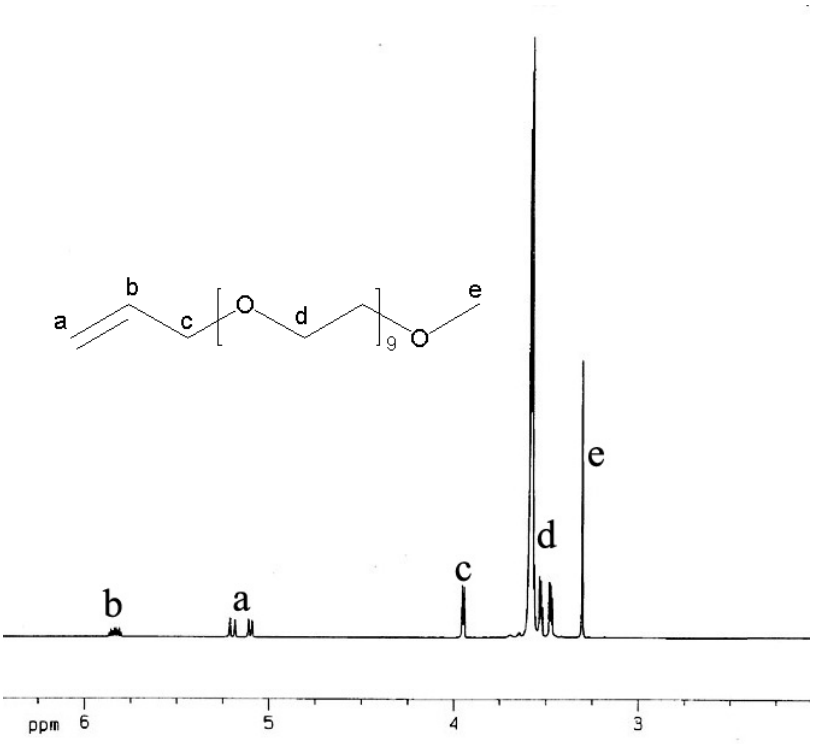

Figure S1. ^{1}H-NMR spectrum of PEO_{10} in $CDCl_3$

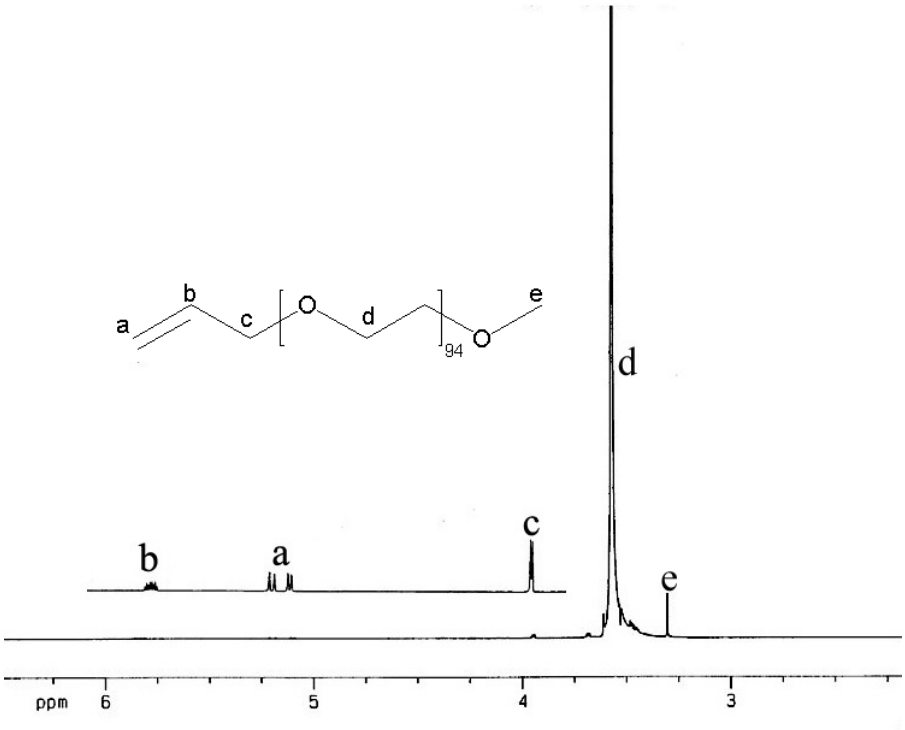

Figure S2. ^{1}H-NMR spectrum of PEO_{95} in $CDCl_3$

Figure S3. ^{1}H-NMR spectrum of PEO_9 (-OH) in $CDCl_3$

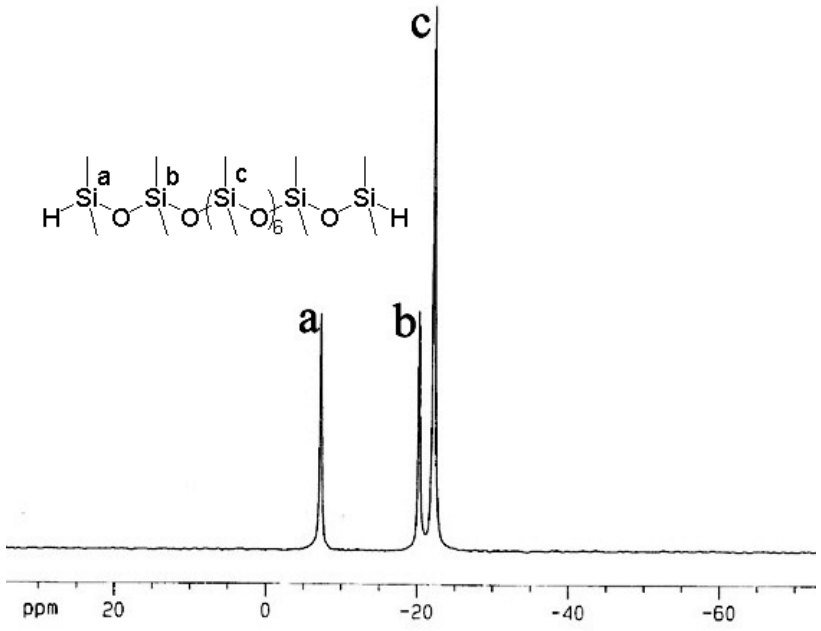

Figure S4. ^{29}Si-NMR spectrum of $PDMS_9$ in $CDCl_3$

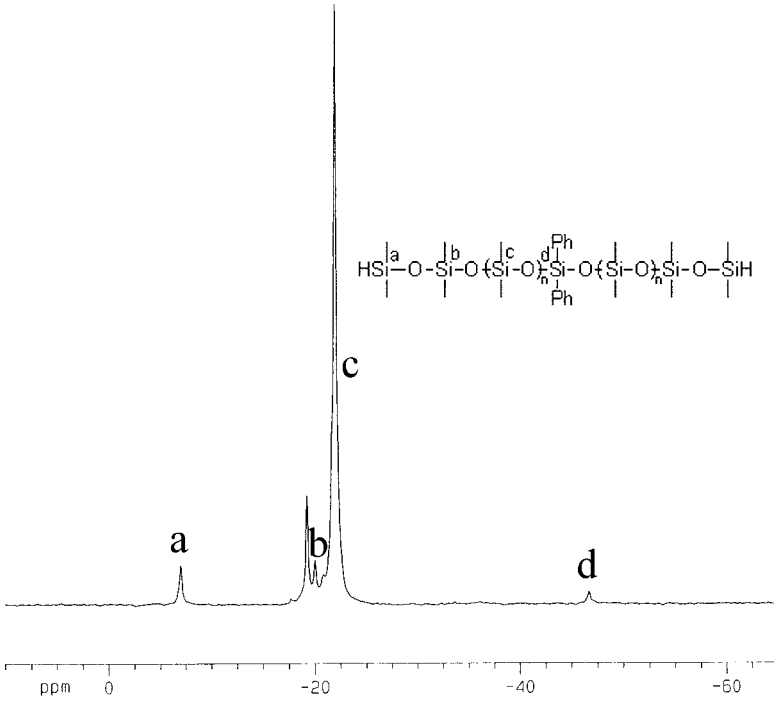

Figure S5. ^{29}Si-NMR spectrum of $PDMS_{86}$ in $CDCl_3$ (^{29}Si-NMR spectrum of $PDMS_{51}$ was not shown as it is similar to **Figure S5**))

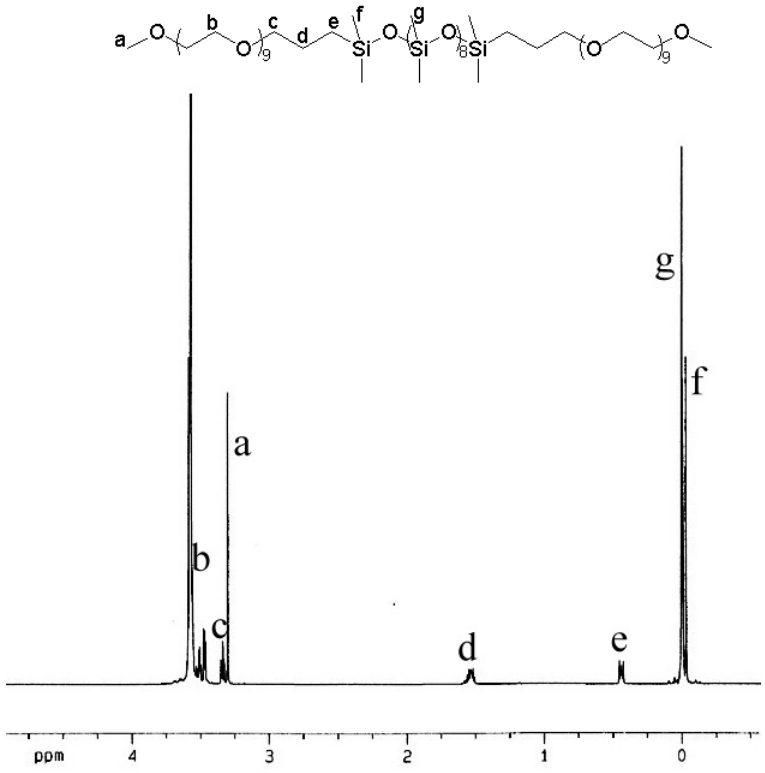

Figure S6. ^{1}H-NMR spectrum of PEO_{10}-b-$PDMS_{9}$-b-PEO_{10} in $CDCl_3$

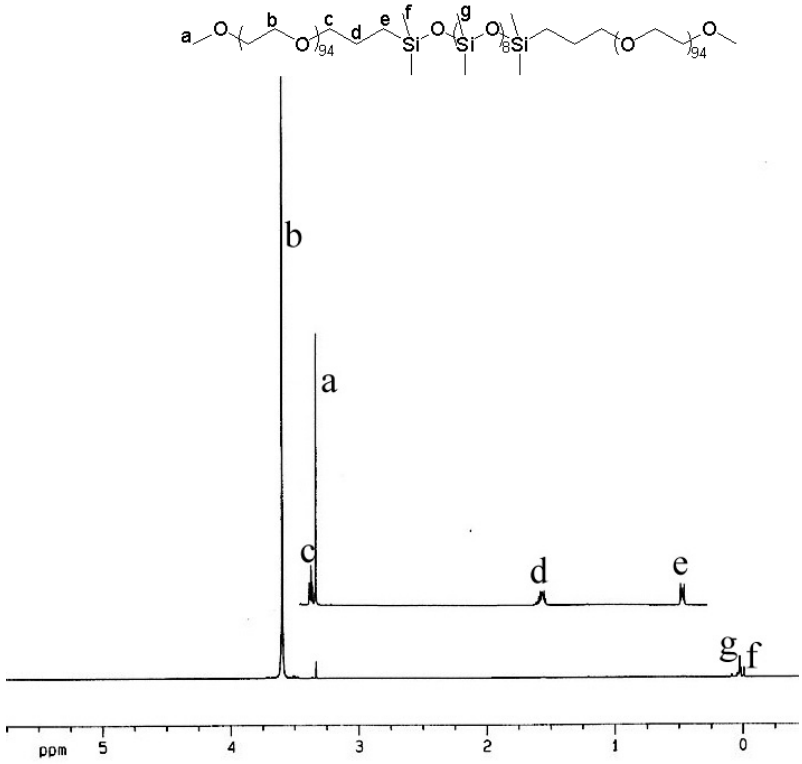

Figure S7. ^{1}H-NMR spectrum of PEO_{95}-b-$PDMS_{9}$-b-PEO_{95} in $CDCl_3$

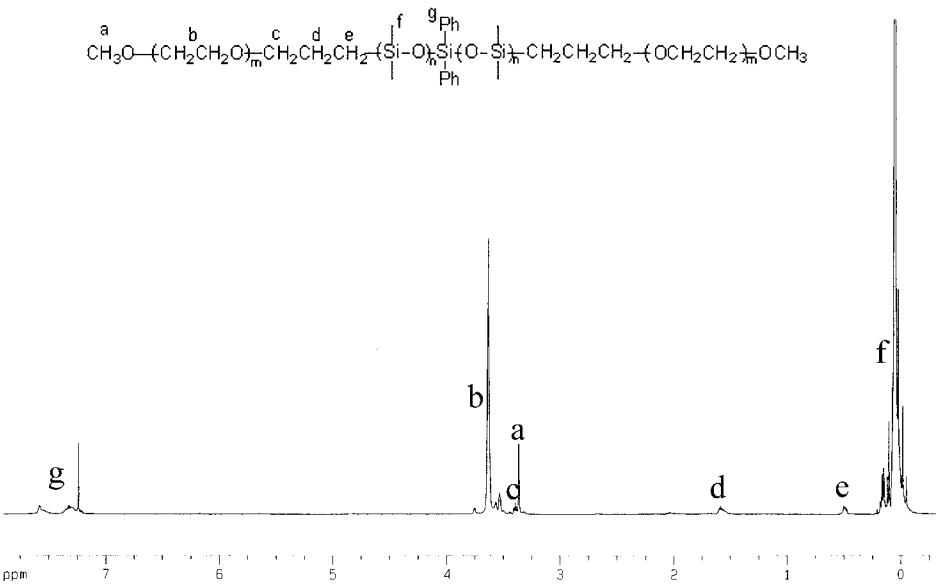

Figure S8. ^{1}H-NMR spectrum of PEO_{10}-b-$PDMS_{86}$-b-PEO_{10} in $CDCl_3$

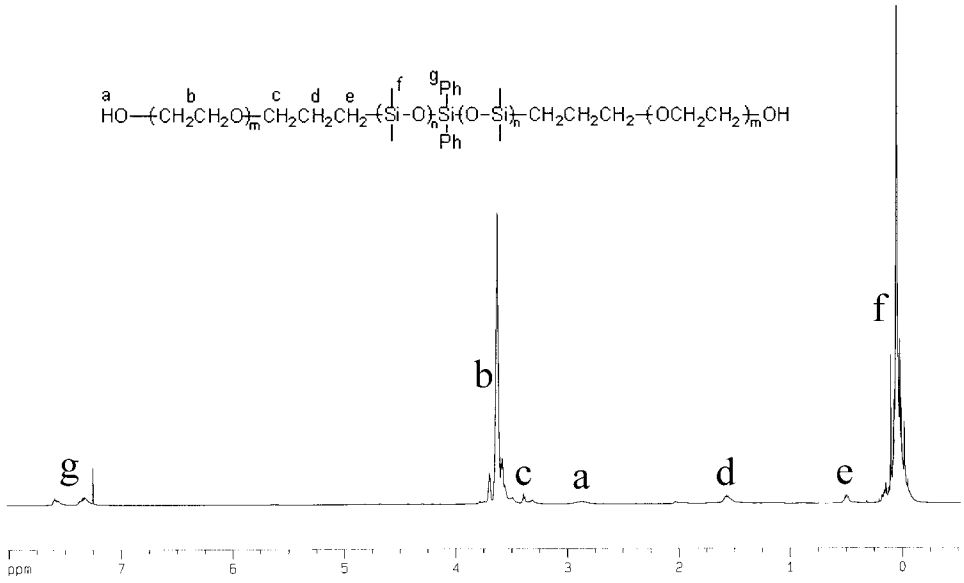

Figure S9. ^{1}H-NMR spectrum of (HO-) PEO_9-b-$PDMS_{51}$-b-PEO_9 (-OH) in $CDCl_3$

Experimental Procedure for the Synthesis and Characterization of the Triblock

Copolymers PEO-b-PDMS-b-PEO

Materials

D_4 was dried over CaH_2 and distilled under nitrogen. 1,1,2,2-tetramethyldisiloxane (MM^H) and dimethylchlorosilane were distilled under nitrogen. Diphenylsilanediol ($Ph_2Si(OH)_2$) was prepared according to the literature [17]. Benzene, THF, and Toluene (Beijing Chemical Reagent Company, A.R.) was dried from refluxing with sodium and distilled prior to use. Potassium is cut into small pieces in nitrogen prior to use. N-methyl-2-pyrrolidinone (NMP) were dried over sodium and collected by trap-to-trap distillation under reduced pressure. Poly(ethylene oxide)s (PEOs, M_n = 468, 4198, and 429, Nanjing JLPC Tenside Chemical & Technical Ltd. Co.) were dried at 30^{o}C in vacuum oven overnight prior to use.

Synthesis of the Difuntional H-Si-terminated Polydimethylsiloxane ($PDMS_9$)

To the flask charged with D_4 (74.2g, 0.25mol) and MM^H (16.8g, 0.125mol) was added the catalyst (H_2SO_4, 98%, 1mL). The mixture was stirred vigorously at room temperature for 6h. Then the solution was washed with deionized water for three times and the organic phase was dried over anhydrous $NaSO_4$ overnight, filtered, and removed of low molecular weight moiety at 80^{o}C under 1mmHg pressure.

Synthesis of dipotassium diphenylsilanediolate

To a mixture of (12.8g, 0.33mol) potassium and benzene (60ml) was added a THF (60ml) solution of diphenylsilanediol (32.0g, 0.15mol) dropwise over 6h at room temperature under nitrogen. After stirred overnight, the solution turned into homogeneous milky emulsion. Removed of the unreacted potassium, the solution was stored under nitrogen. The titration of the resulting solution with HCl gave the concentration of 1.190M.

Synthesis of the Difuntional H-Si-terminated Polydimethylsiloxanes ($PDMS_{86}$ and $PDMS_{51}$)

To the flask charged with D_4 (10ml, 0.03mol) was added dipotassium diphenylsilanediolate ((1ml, 0.0012mol) or (2ml, 0.0023mol)) by a syringe. When the promoter was injected into the flask, the system turned clear immediately. After stirred at 30 for 40min (or 25min), the reaction mixture was quenched with an excess amount of dimethylchlorosilane. Then the solution was washed with deionized water for three times and the organic phase was dried over anhydrous Na_2SO_4 overnight, filtered and submitted to ^{29}Si-NMR and GPC measurement.

Synthesis of ABA triblock copolymers

To the flask charged with PEO and PDMS was injected toluene. The catalyst ($H_2PtCl_6.6H_2O$) solution (1.0% g/ml) in isopropanol was added into the mixture at 90 , then the solution was heated to 110 and stirred for 5h. After adsorption of catalyst by active carbon and removal of toluene by distillation under reduced pressure, the product was measured by ^{1}H-NMR and GPC.

Characterization of Polymers

GPC measurements in toluene were performed with a Waters system including a 515 high-pressure liquid chromatography (HPLC) pump, a 2410 differential refractive-index detector, and Styragel columns (HR) at 40^{o}C at a rate of 1.0 ml/min with linear polystyrene standards.

^{1}H-NMR and ^{29}Si-NMR spectra were recorded on a Bruker AV600 instrument operating at 600 and 119 MHz respectively.