Supporting Information

Formation of Multilayers by Star Polyelectrolytes: Effect of Number of Arms on Chain Interpenetration

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Synthesis of star poly(*tert*-butyl acrylate) (P*t*BA)

Initiator, *t*-BA, PMDETA, CuBr, and acetone were added into a 25 mL glass tube. After three freeze-vacuum-thaw cycles, the tube was sealed under vacuum, and then immersed in an oil bath thermostated at 60 °C. After a certain time, the polymerization was quenched by rapidly cooling the mixture to room temperature and exposing it to air. The mixture was filtered through neutral alumina to remove the catalyst using THF as the eluent. The polymer was precipitated by pouring the solution into the mixture of CH_3OH and H_2O (1:1/v:v). The product was dried under vacuum at 40 °C.

Synthesis of star PAA by the hydrolysis of star P*t*BA

Trifluoroacetic acid (TFA, 6.0 mL, 80.8 mmol) in 10.0 mL of CH_2Cl_2 was added dropwise to a solution of P*t*BA (1.5 g) in 30.0 mL of CH_2Cl_2. The mixture was allowed to stir at room temperature for 24 h. Then, the CH_2Cl_2 and excess TFA were removed in vacuum. The obtained solid was dissolved in water, and dialyzed against water for 3 days. Afterwards, the star PAA solution was lyophilized to give a white powder.

Synthesis of star PDEM

Initiator, DEM, CuCl, o-phen, acetone, and water were added into a 25 mL glass tube. After three freeze-vacuum-thaw cycles, the tube was sealed under vacuum and stirred at room temperature. After a certain time, the mixture was exposed to the air and diluted with THF, then filtered through neutral alumina to remove the catalyst using THF as the eluent. The polymer was precipitated by pouring the solution into cold hexane. The product was dried under vacuum at 40 °C.

Characterization of star PAA and PDEM using ^{1}H NMR

All proton nuclear magnetic resonance (^{1}H NMR) spectra were determined on a Bruker DMX-500 instrument with $CDCl_3$ or D_2O as solvent and tetramethylsilane (TMS) as internal standard. The ^{1}H NMR spectra of star PAA and PDEM are shown in Figures S1 and S2, respectively.

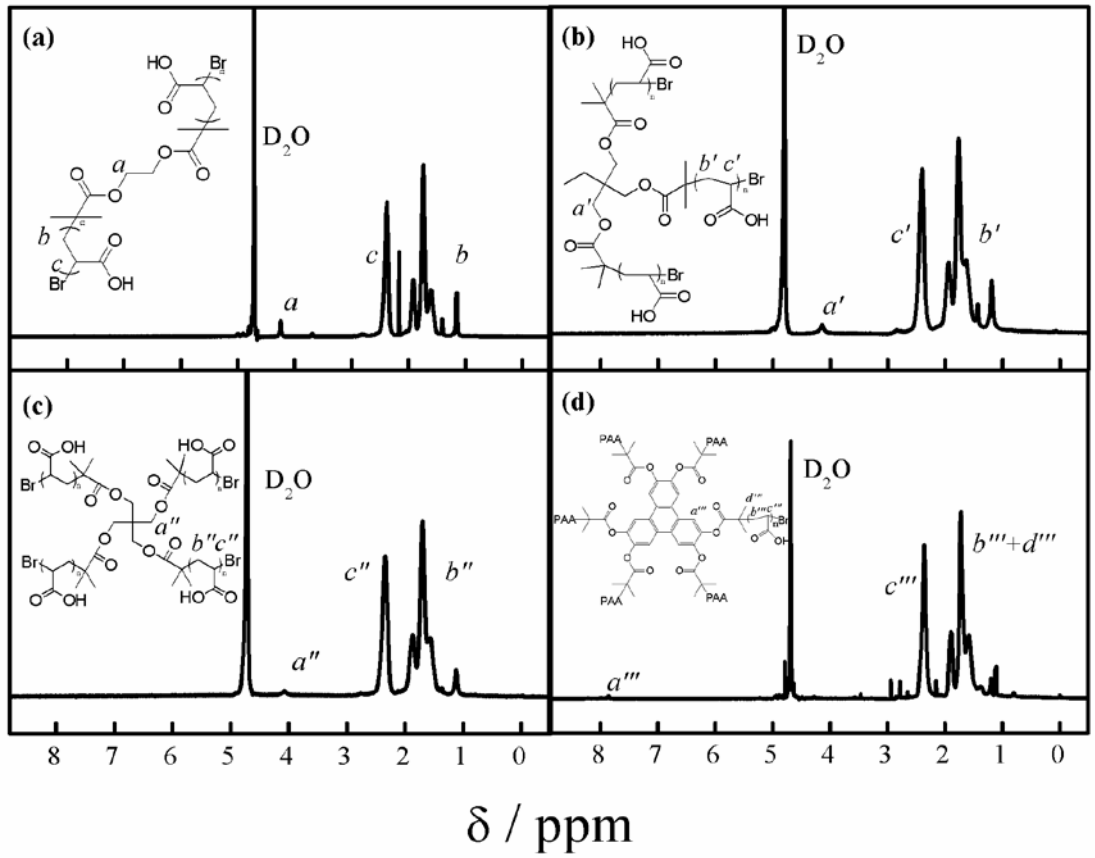


Figure S1 ^{1}H NMR spectra of star PAA. (a) 2-arm, (b) 3-arm, (c) 4-arm, and (d) 6-arm. The corresponding assignments for the signals can be found from the chemical structure of the star PAA in the figure. The ^{1}H NMR spectra indicates the successful synthesis of the star PAA with different arm numbers.

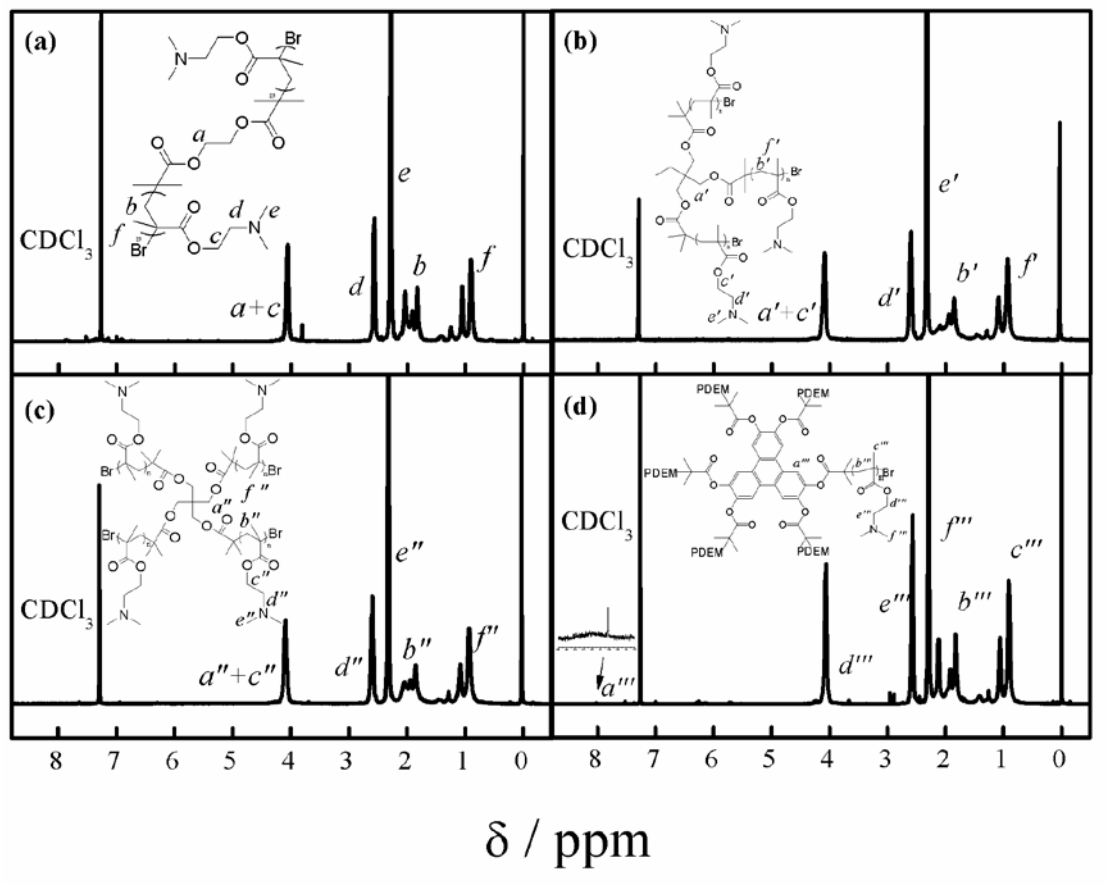
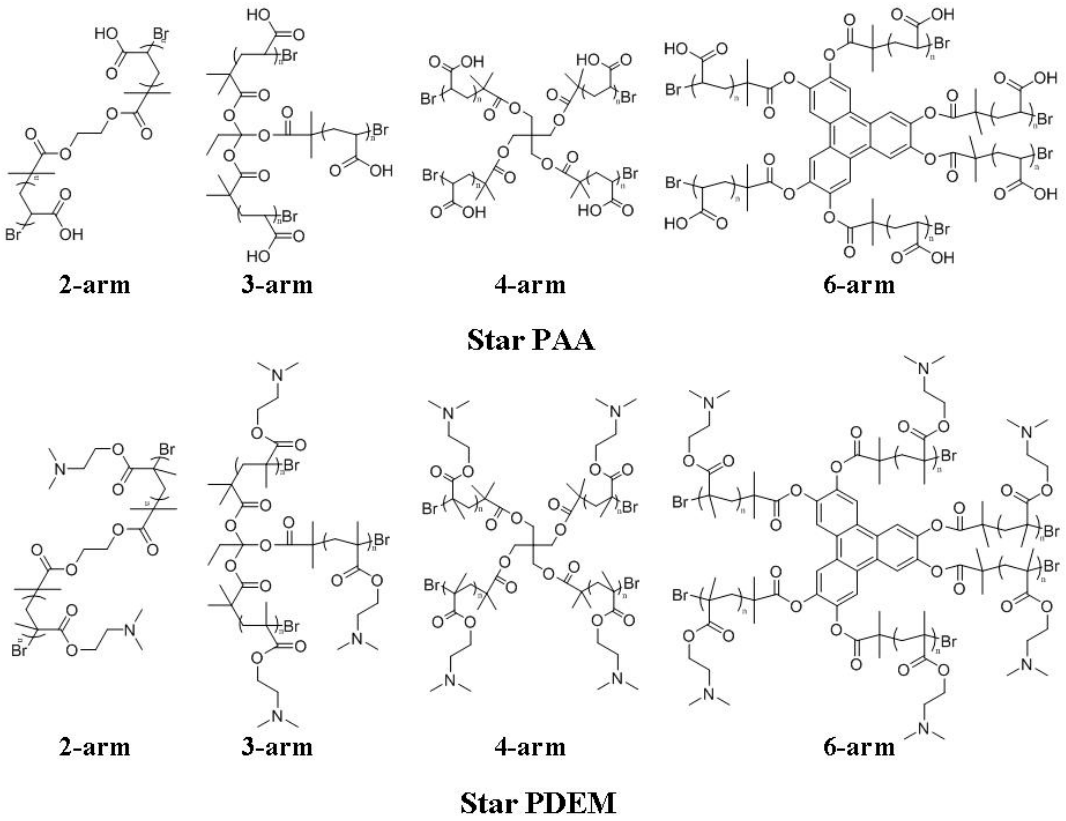


Figure S2 ^{1}H NMR spectra of star PDEM. (a) 2-arm, (b) 3-arm, (c) 4-arm, and (d) 6-arm. The corresponding assignments for the signals can be found from the chemical structure of the star PDEM in the figure. The ^{1}H NMR spectra indicates the successful synthesis of the star PDEM with different arm numbers.



Scheme S1 The chemical structures of star PAA and PDEM with different arm numbers.

Calculation of Chain Persistence Length

Generally, the conformation of polyelectrolytes is determined by the total chain persistence length (l_p) which represents the effective rigidity of the polyelectrolyte chain.[S1] l_p is the sum of the intrinsic persistence length (l_0) and the electrostatic persistence length (l_e):[S2]

$$l_p = l_0 + l_e = l_0 + \frac{l_B \tau^2}{4\kappa^2}$$

where l_B, τ, and κ^{-1} are the Bjerrum length, the linear charge density, and the Debye length, respectively. τ is defined as: $\tau = f/b$, where f is the charge fraction of polymer chain and b is the bond length. The l_0 for PDEM and PAA is ~ 0.9 and ~ 0.7 nm, respectively.[S3,S4] At the NaCl concentration of 0.5 M and pH of 5.3 at 25 °C, κ^{-1} and l_B are ~ 0.4 and ~ 0.7 nm, respectively. b is ~ 0.154 nm for the C-C bond length.

For the PDEM with the charge fraction of 100% (e.g., from 2-arm to 6-arm PDEM):

$$l_p = l_0 + \frac{l_B \tau^2}{4\kappa^2} = 0.9 + \frac{0.7(1/0.154)^2}{4(1/0.4)^2} = 0.9 + 1.2 = 2.1\ nm$$

For the PAA with the charge fraction of 100% (e.g., 2-arm PAA):

$$l_p = l_0 + \frac{l_B \tau^2}{4\kappa^2} = 0.7 + \frac{0.7(1/0.154)^2}{4(1/0.4)^2} = 0.7 + 1.2 = 1.9\ nm$$

For the PAA with the charge fraction of 50% (e.g., 6-arm PAA):

$$l_p = l_0 + \frac{l_B \tau^2}{4\kappa^2} = 0.7 + \frac{0.7(0.5/0.154)^2}{4(1/0.4)^2} = 0.7 + 0.3 = 1.0\ nm$$

Consequently, the conformation of the arm chains does not exhibit an obvious change with the increasing arm number of PDEM, whereas the arm chains may adopt a more coiled conformation as the arm number of star PAA increases.

References:

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(S2) Dobrynin, A. V. *Macromolecules* **2005**, *38*, 9304-9314.

(S3) Manning, G. S. *Biophys. J.* **2006**, *91*, 3607-3616.

(S4) Gao, Y. "*Polymolecular and Unimolecular Micelles of Triblock Copolymers*", 2011, PhD Thesis, Queen's University, Canada.