Supporting Information

A Micellar Route to Layer-by-Layer Assembly of Hydrophobic Functional Polymers

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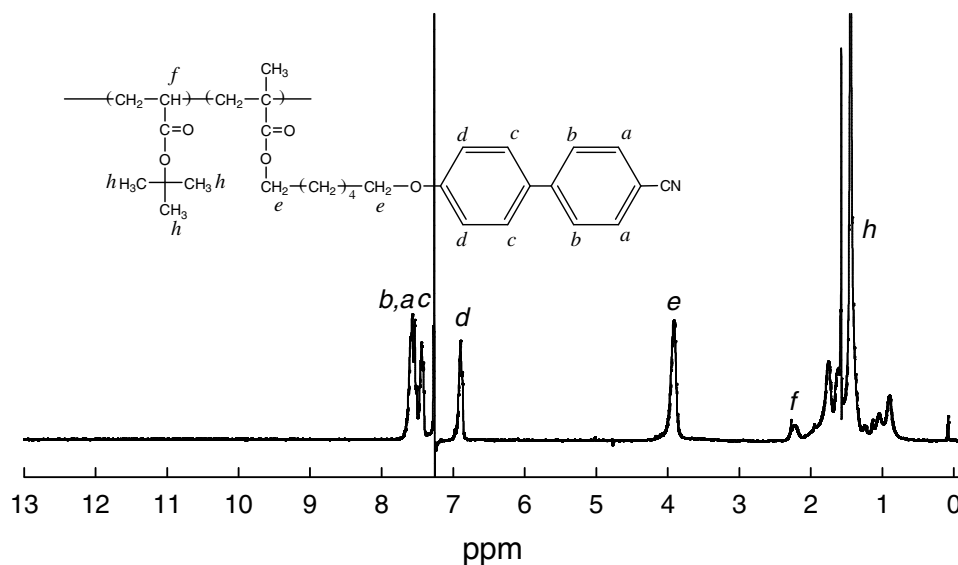## 1. ^{1}H NMR Spectra of Block Copolymers

Figure S1

Figure S1 shows the ^{1}H NMR spectrum of P*t*BA-*b*-PCMA in CDCl$_3$. The composition of the block copolymer was determined from the ratio of the integrals of the peak around 2.2 ppm of P*t*BA to the peak at about 3.8 ppm of PCMA. The average numbers of repeat units were estimated by combining M_n=4000 (GPC) for the P*t*BA macroinitiator and the composition determined from the ^{1}H NMR spectrum, resulting in P*t*BA$_{31}$-*b*-PCMA$_{60}$.

Figure S2 shows the ^{1}H NMR spectrum in DMSO-d6 of PAA-*b*-PCMA obtained by P*t*BA-*b*-PCMA hydrolysis. The almost complete disappearance of the characteristic strong peak at about 1.44 ppm of *t*-butyl groups indicates the successful hydrolysis reaction. The peak at ~ 12.2 ppm arises from protons of carboxylic acid groups.
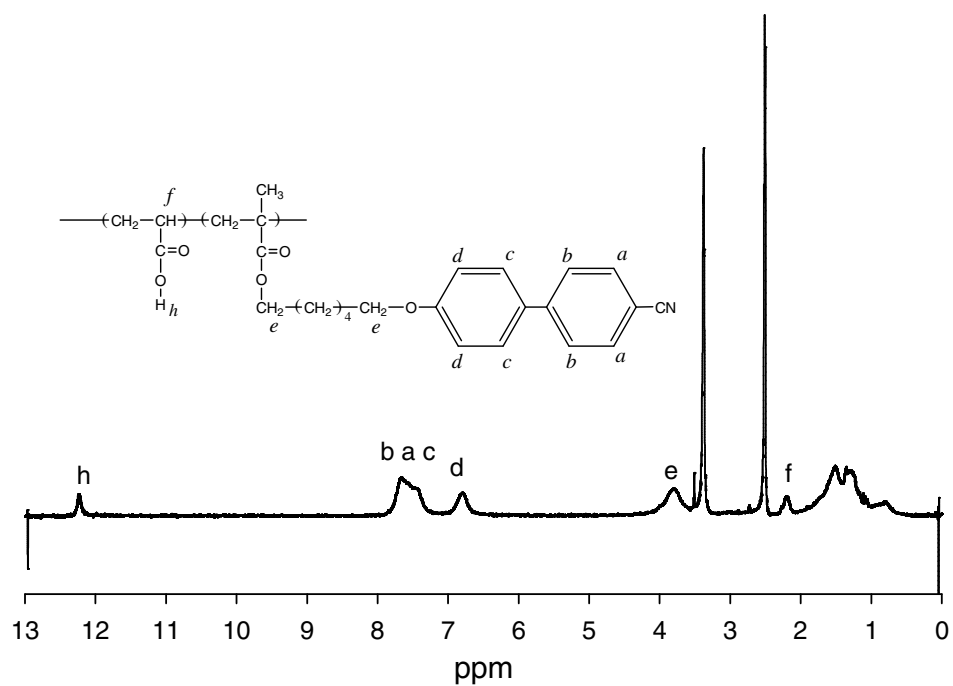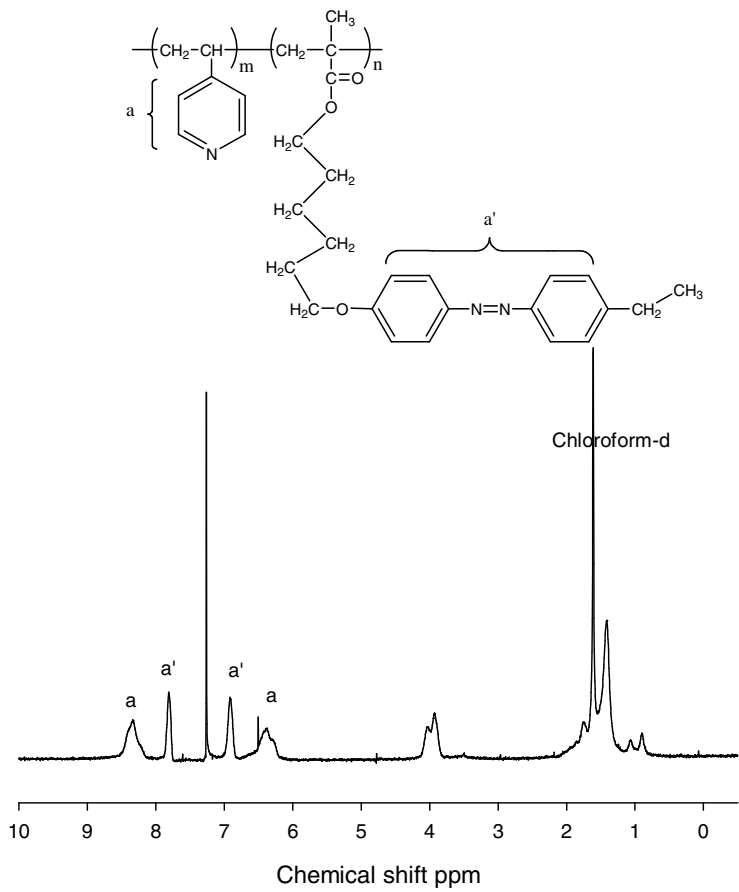
Figure S2

Figure S3

Figure S3 shows the ^{1}H NMR spectrum of P4VP-*b*-PAMA in CDCl$_3$. The composition of the block copolymer was determined from the integrals of the peaks assigned to protons of aromatic pyridine and benzene rings, in the region between 6 and 9 ppm. The numbers of monomeric units were estimated to be P4VP$_{22}$-*b*-PAMA$_{13}$ by combining the GPC value of M$_n$=7900 g mol^{-1} for the block copolymer (the P4VP macroinitiator is insoluble in the THF eluent) and the composition determined from the ^{1}H NMR spectrum. Note that this ^{1}H NMR spectrum was given in the Supporting Information of a previous paper reporting the fluorescence from micelles of this azobenzene-containing block copolymer.[1]
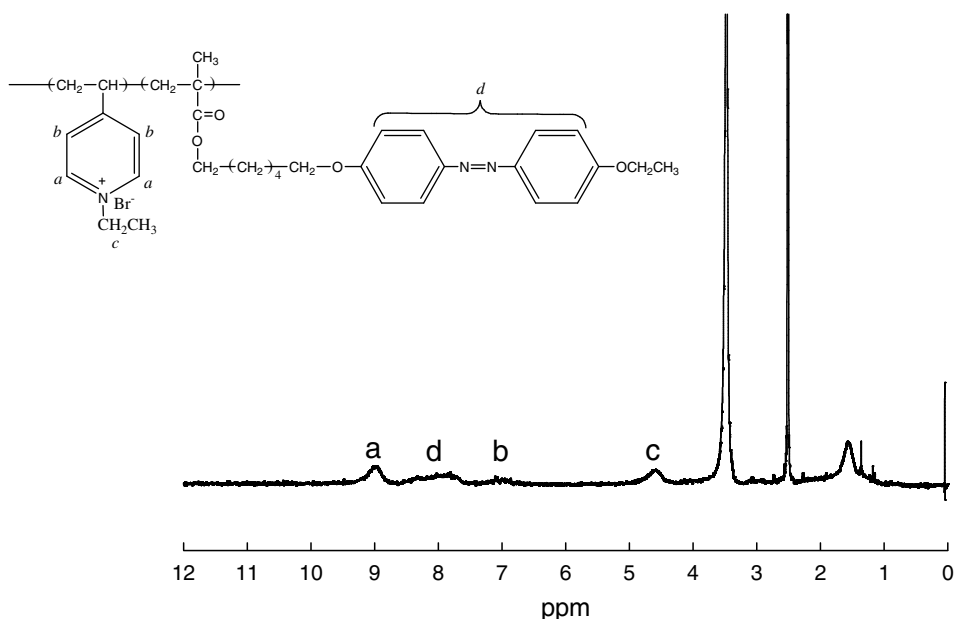

Figure S4

Figure S4 shows the ^{1}H NMR spectrum of P4VP-*b*-PAMA after quaternization. The resulting QP4VP-*b*-PAMA was poorly soluble in organic solvents at room temperature. The spectrum was obtained in DMSO-d6 solution, the poor solubility results in the broad peaks of aromatic protons; the peak at ~ 4.6 ppm was attributed to the methylene group of ethyl pyridinium.[2] Infrared analysis revealed a quaternization degree of about 95%.[1]

2. Dynamic Light Scattering Measurements

In addition to the direct observation by SEM and AFM of the two block copolymer micelles on the surface of LBL films, dynamic light scattering (DLC) measurements (using a Brookhaven
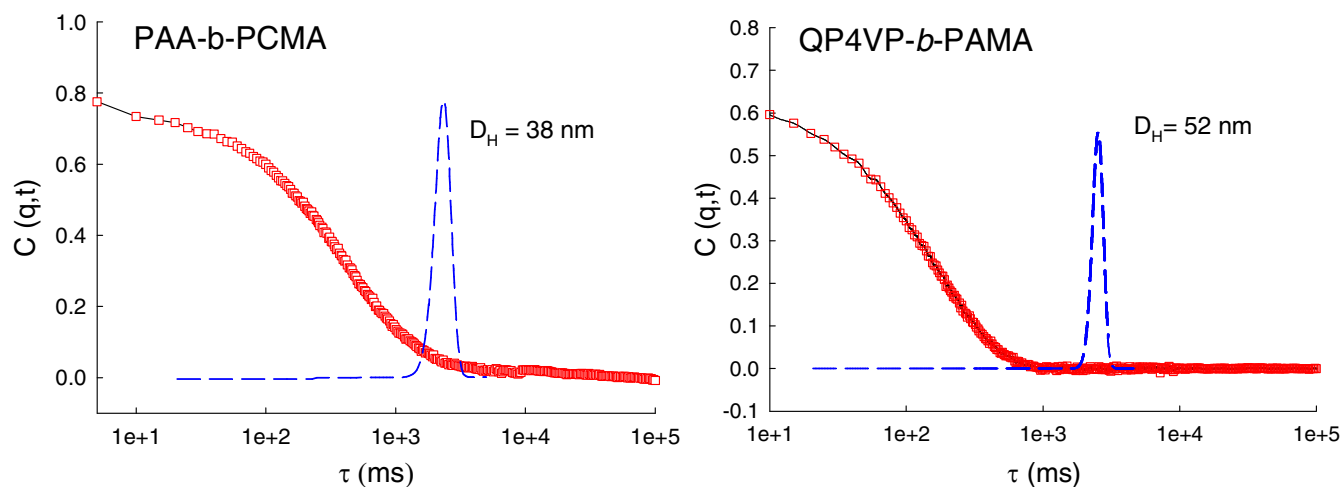
Figure S5

goniometer BI-200 equipped with a photodiode detector BI-APD and a digital correlator TurboCorr) also confirmed the formation of micelles in aqueous solutions (pH=12) used for the LBL assembly process. Figure S5 shows the auto-correlation functions and relaxation time distributions (CONTIN) for PAA-*b*-PCMA and QP4VP-*b*-PAMA indicating average hydrodynamic diameters of 38 and 52 nm respectively. These values are larger than the apparent sizes of most micelles viewed on SEM, the latter being in the dried state.

3. Critical Micelle Concentrations

Micelles of both amphiphilic block copolymers were prepared by adding water into their DMF solutions, followed by dialysis against water. This is the standard technique of preparing aqueous micellar solutions of block copolymers that are insoluble in water due to very small critical micelle concentrations (CMC). Nevertheless we tried to determine the CMC of PAA-*b*-PCMA and QP4VP-*b*-PAMA by using the well-known pyrene-probe method.[3] Figures S6 and S7 show the plots of I_1/I_3 (ratio of pyrene emission peaks) as a function of polymer contraction for PAA-*b*-PCMA and QP4VP-*b*-PAMA respectively. The CMC thus estimated is about 0.03 mg mL^{-1} for PAA-*b*-PCMA and 0.06 mg mL^{-1} for Q4VP-*b*-PAMA.
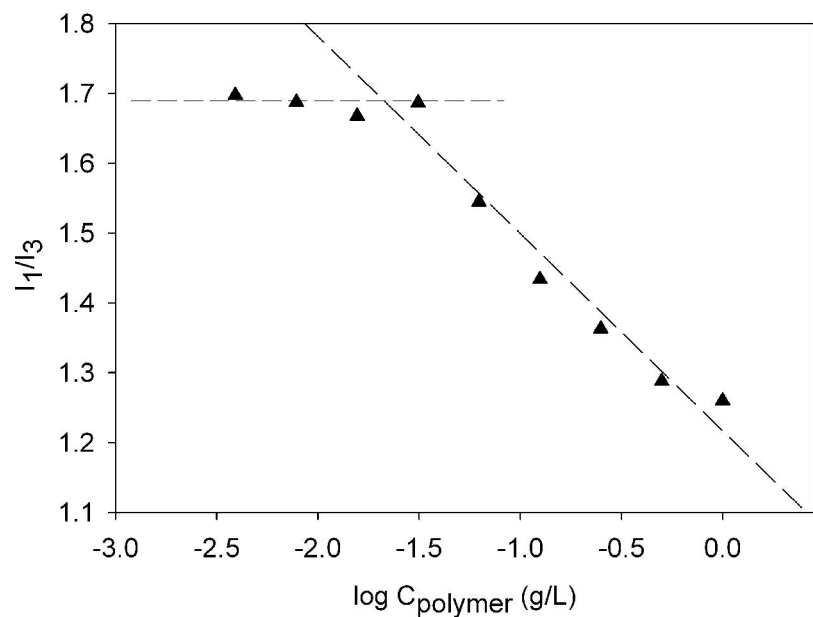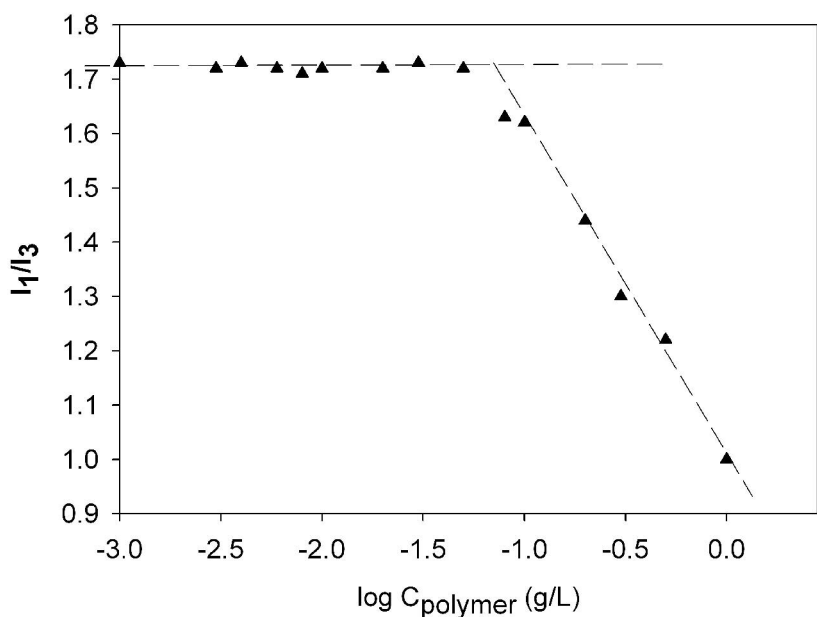
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Figure S6

Figure S7

References

1. Qi, B.; Zhao, Y. *Langmuir* **2007**, *23*, 5746.

2. Xiao, S. M; Lu, X; Lu, Q. M. *Macromolecules* **2007**, *40*, 7944.

3. Francis, M. F.; Piredda, M.; Cristea, M.; Winnik, F. M. *ACS Symp. Ser.* **2006**, *923*, 55.