Supporting Information for *Macromol. Rapid Commun*. **2006**, *27*, 1838.

Morphological Transformation and Photophysical Proeprties of Poly[2,7-(9,9-dihexylfluorene)]-*block*-poly(acrylic acid) (PF-*b*-PAA) Rod-Coil Copolymers in Solution

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Experimental Section

Materials

The monomer, *tert*-butyl acrylate (*t*BA, Aldrich, 98%), was distilled under vacuum in prior to polymerization. *N*,*N*,*N*′,*N*′,*N*′′-Pentamethyldiethylenetriamine PMDETA (Acros, 99+%) was used as received. CuBr (99+%), 2,7-Dibromo-9,9-dihexylfluorene, 4-bromobenzyl alcohol, 2-bromoisobutyryl bromide, tetra(kisphenylphosphine)palladium(0), *N*,*N*-dimethylacetamide (DMAc), anisole, and sodium carbonate were purchased from Aldrich and used without purification.

Synthesis

The preparation of the block copolymer is shown in Scheme S1. The polyfluorene precursor (**3**) was synthesized by the Suzuki coupling reaction with 4-bromobenzyl alcohol as the end-capper was prepared according to a method reported by Müllen et al.[1]

α-{4-[2-(2-Bromo-2-methylpropoyloxy)methyl]phenyl}-ω-bromo-poly[2,7-(9,9-dihexyl-fluorene)] (PF-Br, **4**). 2.0 mL of 2-bromoisobutyryl bromide (16.0 mmol) was added dropwisely to a solution of 1.34 g (0.36 mmol) of **3** and 4.0 ml (38.2 mmol) of triethylamine in 20 ml of dry THF, and the reaction mixture was stirred at room temperature for 24 h. After the mixture was poured into 200 ml of cold methanol, a solid was obtained. The solid was then re-dissolved into 5 ml of THF and re-precipitated twice into 200 ml of cold methanol to afford 1.18 g of a white power of **4**.

Hydrolysis of PF-b-PtBA

PF-*b*-PtBA (250mg, 2.5mmole) was dissolved into 25 ml of dichloromethane. To the reaction mixture, excess trifluoroacetic acid (TFA) was added. After reaction at room temperature for 24 h, a precipitate was obtained upon addition of n-hexane into the concentrated reaction

mixture. The polymer finally obtained after drying under vacuum at 40 °C for 48 h.

Measurements

^{1}H nuclear magnetic resonance (NMR) data was obtained by a Bruker AV 300 MHz spectrometer. Gel permeation chromatographic analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD Gmbh. All GPC analyses were performed on polymer/THF solution at a flow rate of 1 ml/min at 40 °C and calibrated with polystyrene. UV-visible absorption and photoluminescence (PL) spectra were recoded on a Jasco model UV/VIS/NIR V-570 spectrometer and Fluorolog-3 spectrofluorometer (Jobin Yvon), respectively. The fluorescence quantum yields (ψ_f) of the polymers in solutions were recorded by using the diluted quinoline solution in 0.1 N H_2SO_4 as the standard, assuming that the fluorescence quantum yield was 0.546 with the excitation wavelength of 365 nm. ψ_f was calculated according to the following equation:[2]

$$\Phi_S = \Phi_R \left(\frac{A_R}{A_S}\right)\left(\frac{I_S}{I_R}\right)\left(\frac{n_S^2}{n_R^2}\right)$$

where ψ_R and ψ_S are the fluorescence quantum yields of quinoline and the polymers, respectively; A_R and A_S are the absorbances of quinoline and the polymers at the excitation wavelength, respectively; I_R and I_S are the integrated emission intensities of quinoline and the polymers, respectively; and n_R and n_S are refractive indices of the corresponding solvents of the solutions, respectively (pure solvents were assumed). In the cases of mixed solvents were employed, the refractive indices of the mixed solvents were calculated according to

$$n_{mix}^2 = f_A n_A^2 + f_B n_B^2$$

where f_A and f_B are the fractions (vol/vol) of solvents A and B, respectively.

Polymer Structure Characterization

Figure S1 shows the ^{1}H NMR spectra of PF_7-*b*-PAA_{70} in $CDCl_3$, which agrees well with the proposed structure. Figure S2 shows the FT-IR spectra of the diblock copolymer PF-PtBA before and after hydrolysis. After hydrolysis, the carboxylic group is clearly observed as the broad absorbance from 2800 to 3600 cm^{-1}, which indicates the successful hydrolysis of PtBA to PAA. The GPC traces revealed the molecular weights and distribution of the molecular weight of the final block copolymers are shown in Figure S3 and Table S1.

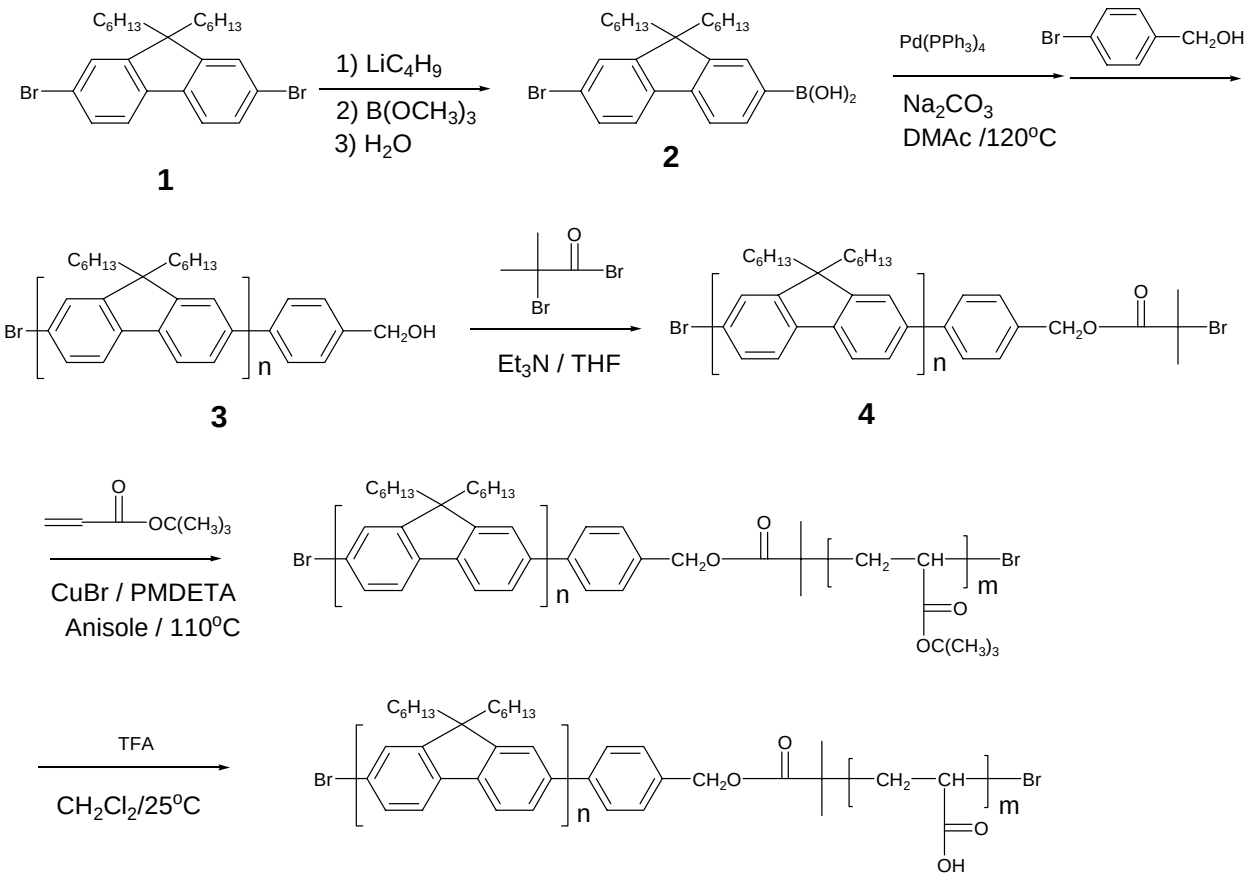
Thermal Properties

The thermal properties of the synthesized copolymer were studied by differential scanning calorimetry (DSC) and thermal gram analysis (TGA) using PF_7-*b*-PAA_{70} as an example. Figure S4(a) shows the TGA curve of the PF_7-*b*-PAA_{70} at a heating rate of 10 ^{0}C/min under nitrogen atmosphere. It exhibits two thermal degradation temperatures at 220 and 290 °C, which are attributed to the decomposition of polyacrylic acid and polyfluorene, respectively .The DSC curve of the PF_7-*b*-PAA_{70} at a heating rate of 20 °C/min under nitrogen atmosphere is shown in Figure S4(b). It exhibits a glass transition temperature(T_g) at 52.3 °C and the melting endotherm at 132 °C, which is attributed to polyfluorene reported in the literature.[3] The small melting peak at 186 °C requires further characterization to understand its origin.

[1] D. Marsitzky, M. Klapper, K. Müllen, *Macromolecules* **1999**, *32*, 8685

[2] D. F. Eaton, *Pure Appl. Chem.* **1988**, *60*, 1107.

[3] W. J. Lin, W. C. Chen, W. C. Wu, Y. H. Niu, Alex K. Y. Jen, *Macromolecules* **2004**, *37*, 2335.



1 **2** **3** **4**

P1: n = 7, m = 26
P2: n = 7, m = 50
P3: n = 7, m = 70

Scheme S1. Synthetic of PF-*b*-PAA rod-coil diblock copolymers.

Table S1. The experimental conditions [a] and properties of rod-coil diblock copolymers

Sample	$[M]_0/[I]_0$ [b]	Time (hr)	*M*n (GPC)[c]/g mole^{-1}			PDI [d]	PAA (vol%)	Expected composition
			PF	P*t*BA	PAA			
P1	50	8	2200	3328	1872	1.20	0.46	PF_7-*b*-PAA_{26}
P2	100	8	2200	6400	3600	1.20	0.62	PF_7-*b*-PAA_{50}
P3	200	24	2200	8960	5040	1.25	0.70	PF_7-*b*-PAA_{70}

a) [Initiator]:[PMDETA]:[CuBr] = 1:2:2. Polymerization temperature is 110°C.

b) Feed molar ratio of the monomer $[M]_0$ to initiator $[I]_0$.

c) Number average molecular weight determined by GPC(THF, calibration with polystyrene standards).

d) Polydispersity determined by GPC.

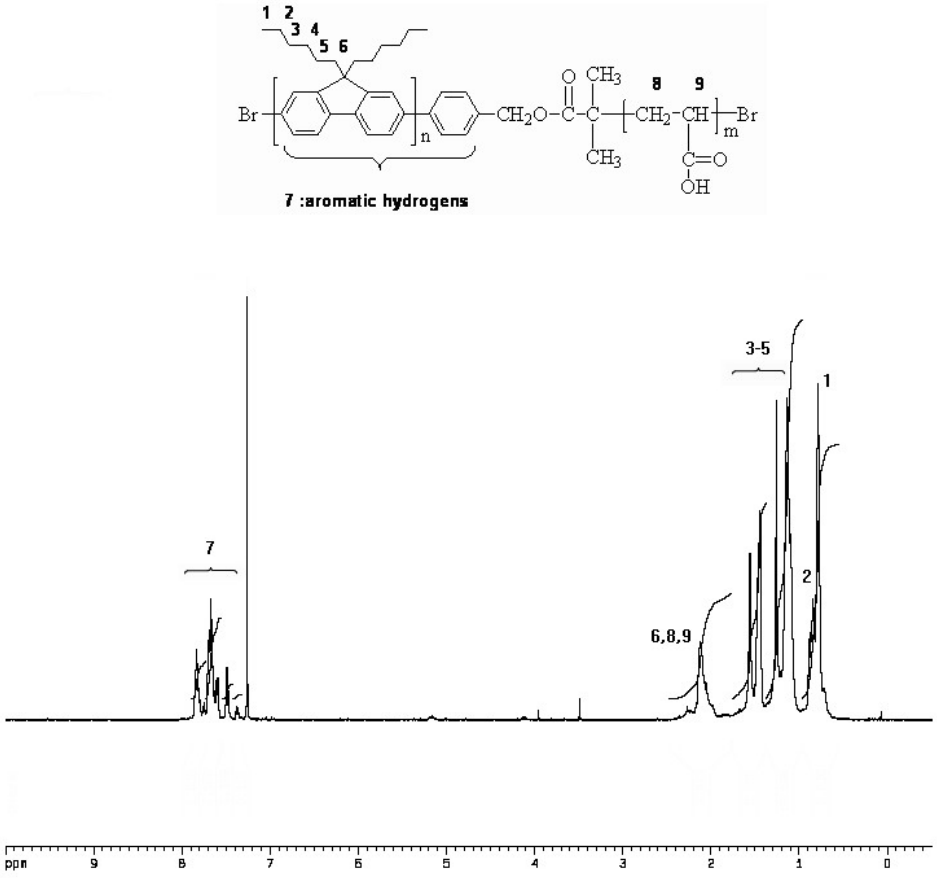


Figure S1. ^{1}H NMR spectrum of the PF_7-*b*-PAA_{70} in $CDCl_{3,}$.

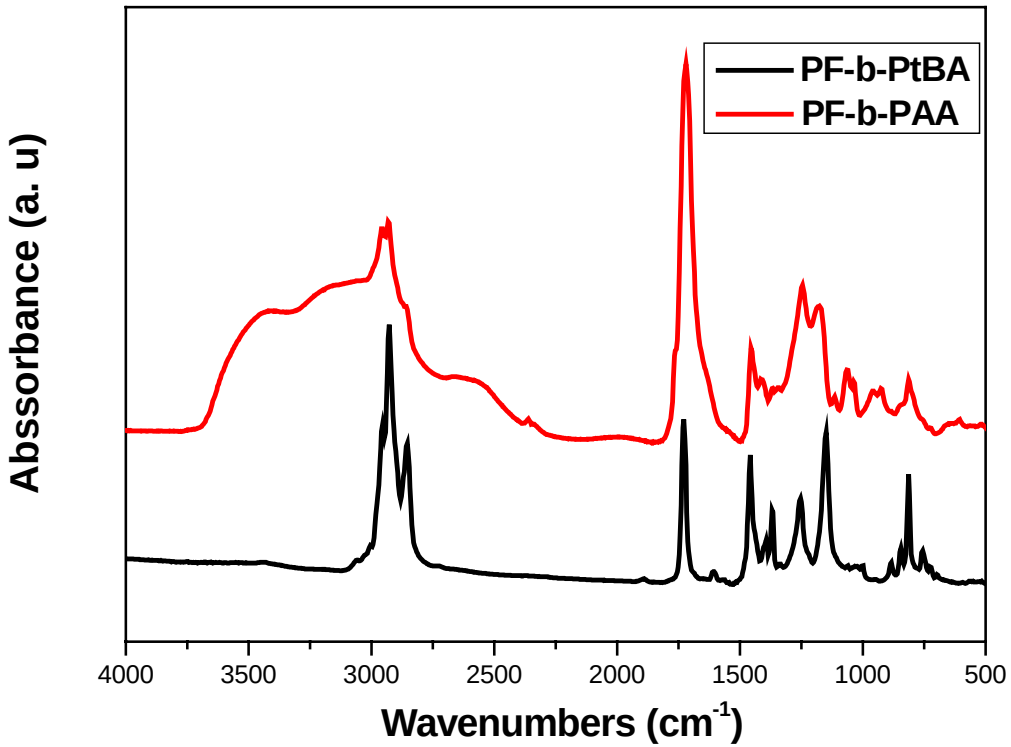


Figure S2. FT-IR spectra of PF-*b*-PtBA before (dotted line) and after hydrolysis (solid line) on KBr.

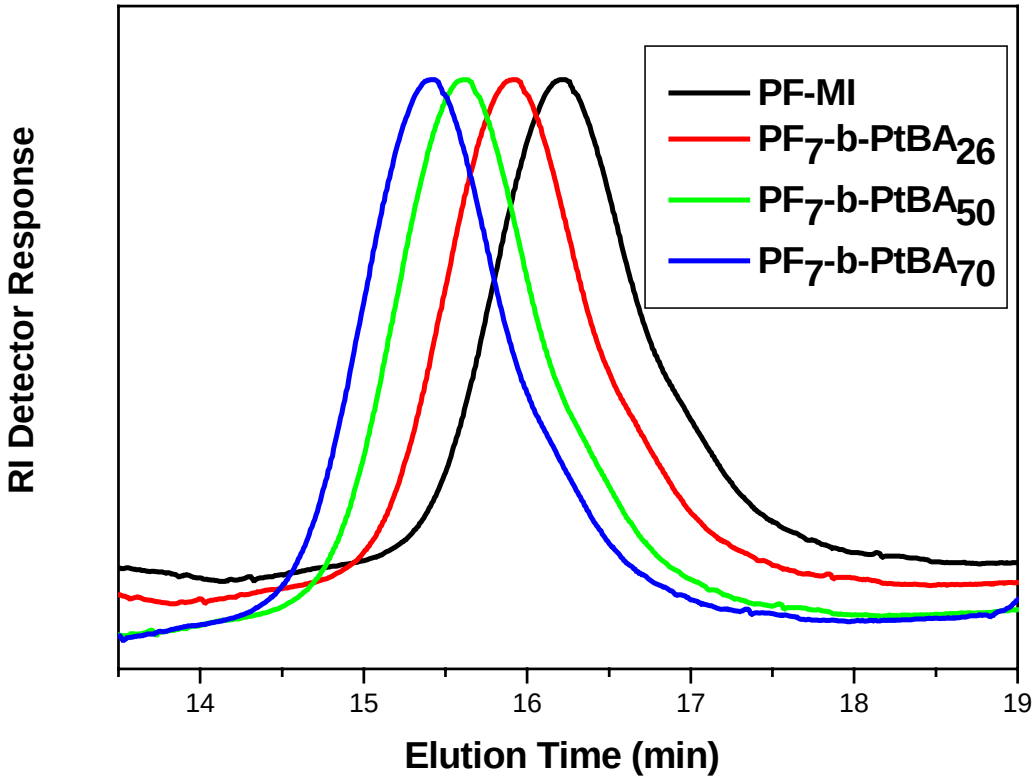
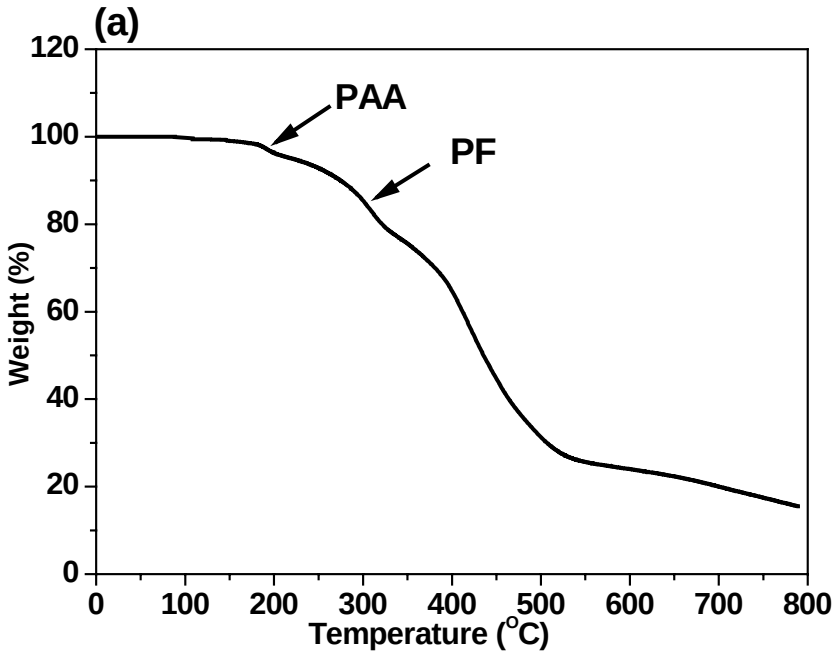


Figure S3.GPC traces of the PF macroinitator and PF-*b*-P*t*BA block copolymers.


(a)
120
100
80
60
40
20
0
Weight (%)
PAA
PF
0
100
200
300
400
500
600
700
800
Temperature (°C)

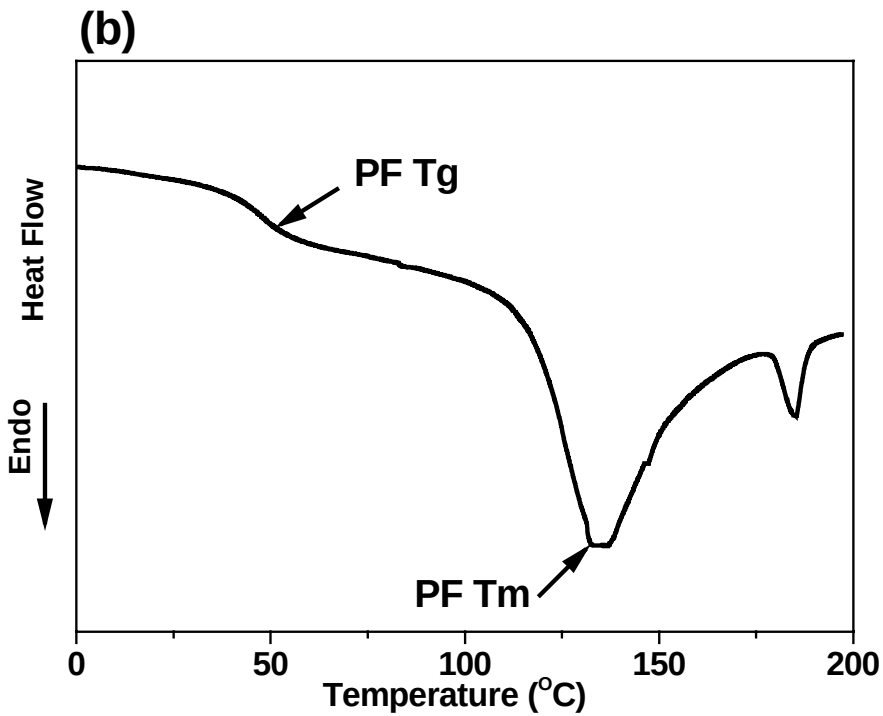


Figure S4. (a)TGA and (b) DSC curves of the PF_7-*b*-PAA_{70} diblock copolymers at a heating rate of 10 and 20 ^{0}C/min under nitrogen atmosphere, respectively.