## **Supporting Information**

## Alternating and Random-Sequence Polyesters with Distinct Physical Properties

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Figure S5. <sup>1</sup>H NMR spectra of 1b





Figure S9. Contact angle of p(A-alt-B)-1 and p(A-ran-B)-1 over 120 seconds



Figure S10. MALDI-MS of p(A-*alt*-B)-1. (The obtained signals correspond to the cyclic alternating polymers. The minor peaks in the spectra were analyzed in Figure S11.)



**Figure S11.** Enlarged view of the red dashed region in **Figure S10**. The minor distributions were formed by the addition of segment B or segment C to the major products. The formation of segments B and C was probably due to the presence of trace amount of impurities in monomer **2b** (shown in bottom right corner). Segment B could be generated by the reaction of monomer **1a** and trace amount of succinic anhydride ([M+Na]<sup>+</sup>: 123.0). Segment C could originate from trace amount of hydroxyacid monomer ([M+H]<sup>+</sup>: 377.2).







Figure S13. MALDI-MS of p(A-alt-B)-3.







Figure S15. MALDI-MS of p(A-ran-B)-2.





Table S1. Molecular Weight of Random and Sequence-Controlled Copolyesters

entry	polymer	M <sub>n</sub> (kDa) <sup>a</sup>	M <sub>w</sub> (kDa) <sup>a</sup>	$\frac{1}{2} \frac{1}{M_w/M_n}^a$	Ratio (A:B) <sup>b</sup>
1	p(A- <i>alt</i> -B)-1	27.7	56.0	2.0	49.9:50.1
2	p(A- <i>alt</i> -B)-2	8.2	10.5	1.3	50.0:50.0

3	p(A- <i>alt</i> -B)-3	19.1	38.0	2.0	50.8:49.2
4	p(A- <i>ran</i> -B)-1	27.9	54.2	1.9	48.7:51.3
5	p(A- <i>ran</i> -B)-2	31.1	53.9	1.7	48.5:51.5

<sup>a</sup>Molecular weight and polydispersity index were determined by SEC using DMF as the eluent and PS as the standard. <sup>b</sup>The ratio of the two components was determined by the integration of the <sup>1</sup>H NMR spectra.

Table S2. Water Absorption of p(A-alt-B)-1 and p(A-ran-B)-1 after 12, 24, 36 and 48 h

polymer	$H_2O\%_{12h}$	$H_2O\%_{24h}$	H <sub>2</sub> O‰ <sub>36h</sub>	$H_2O\%_{48h}$
p(A- <i>alt</i> -B)-1	4.2±0.9 %	5.3±1.2 %	6.1±1.0 %	6.3±0.9 %
p(A- <i>ran</i> -B)-1	4.1±1.0 %	6.3±1.1 %	6.3±1.1 %	6.4±1.1 %