Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Periodic Introduction of Hamilton Receptor into Polystyrene Backbone for Supramolecular Graft Copolymer with Regular Interval

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Mathematical model chosen to determine K_{ass}: The data were fitted to the following equation to provide K_{ass}:

$$\delta_{mix} = \delta_{ADADA} + \frac{(\delta_{\infty} - \delta_{ADADA})\left[\left([ADADA]+[DADDAD]+\frac{1}{K_{ass}}\right) - \sqrt{\left([ADADA]+[DADDAD]+\frac{1}{K_{ass}}\right)^2 - 4[ADADA][DADDAD]}\right]}{2[ADADA]}$$

, where the experimental parameters are as follows,

[ADADA] and [DADDAD]: molar concentrations of ADADA– and DADDAD–functionalized compounds (i.e., initiators or polymers)

δ_{mix}: a chemical shift for NH proton of ADADA–functionalized compound for an equimolar mixture with DADDAD counterpart in ^{1}H NMR spectrum (H^a in Figure 3);

δ_{ADADA}: a chemical shift for NH proton of ADADA–functionalized compound;

K_{ass}: an association constant;

δ_{∞}: a saturated chemical shift for NH proton of ADADA–functionalized compound when an excess molar of DADDAD counterpart was mixed. The value was calculated from curve fitting with third degree polynomial for plots with various mixing ratios.

Table S1. Parameters for K_{ass} Calculation in This Work

Combination	[ADA] and [DAD]	δ_{mix} / ppm	δ_{ADA} / ppm	δ_{∞} / ppm
$(PS_{DADDAD}8k)_n$-1and $PMMA_{ADADA}9k$[a]	2.0×10^{-3} mol/L	12.17	8.51	13.07[b]

[a]see Figure 3 for the interaction analyses by ^{1}H NMR ; [b]Calculated from curve fitting with third degree polynomial for plots with various mixing ratios (see Figure S1, respectively).

Table S2. Interaction analyses with DLS of $(PS_{DADDAD}8k)_n$-1 and equimolar mixture of $(PS_{DADDAD}8k)_n$-1 with $PMMA_{ADADA}5k$ or ADADA-free PMMA[a]

Entry	Samples	R_h, nm (n = 5)					Averaged R_h, nm[b]
1	$(PS_{DADDAD}8k)_n$-1 + $PMMA_{ADADA}5k$	13.6	16.7	17.2	17.6	19.1	17.2
2	$(PS_{DADDAD}8k)_n$-1 + ADADA-free PMMA	11.0	12.2	6.8	11.1	10.3	10.8

[a]All samples were prepared in $CHCl_3$ at 25 °C: $[(PS_{DADDAD}8k)_n\text{-}1] = 2$ mg/mL. [b]The number averaged hydrodynamic radius was estimated from selected 3 results exepting the maxium and minium value.

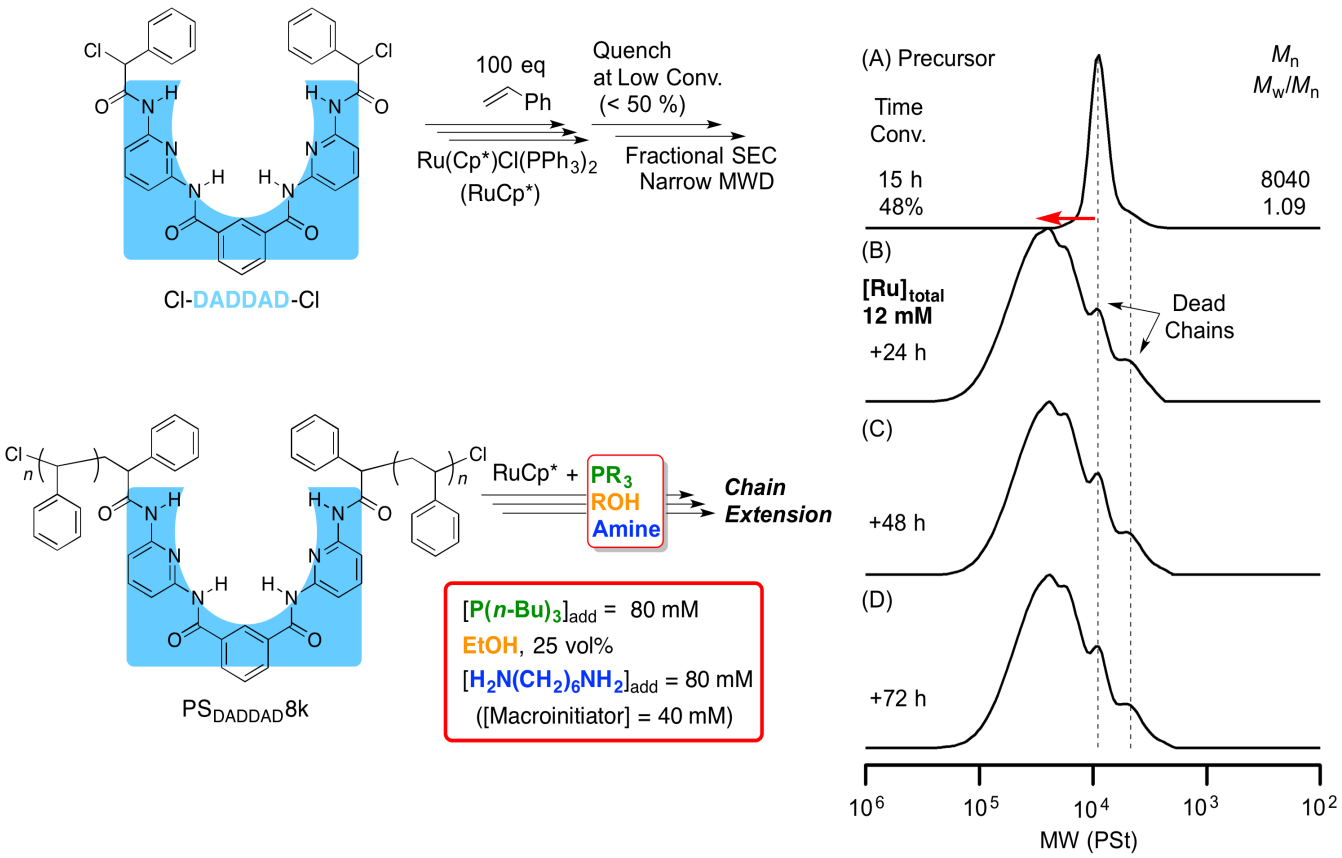

Figure S1. SEC curves (A) for Ru catalyzed living radical polymerization of styrene with Cl–DADDAD–Cl and radical coupling chain extension of the polystyene precursor for (B) 24 h, (C) 48 h, and (D) 72 h. Polymerization: $[\text{Monomer}]_0$ = 4.0 M; $[\text{Cl–DADDAD–Cl}]_0$ = 40 mM; $[\text{Ru(Cp*)Cl(PPh}_3)_2]_0$ = 4.0 mM; $[n\text{-BuNH}_2]_0$ = 40 mM in toluene at 100 °C. Radical coupling chain extension: [Precursor] = 40 mM; $[\text{Ru(Cp*)Cl(PPh}_3)_2]_0$ = 12 mM; $[\text{NH}_2\text{–(CH}_2)_6\text{–NH}_2]_0$ = 80 mM; $[\text{P}(n\text{-Bu})_3]_0$ = 80 mM in toluene/EtOH = 3/1 v/v % at 100 ˚C.

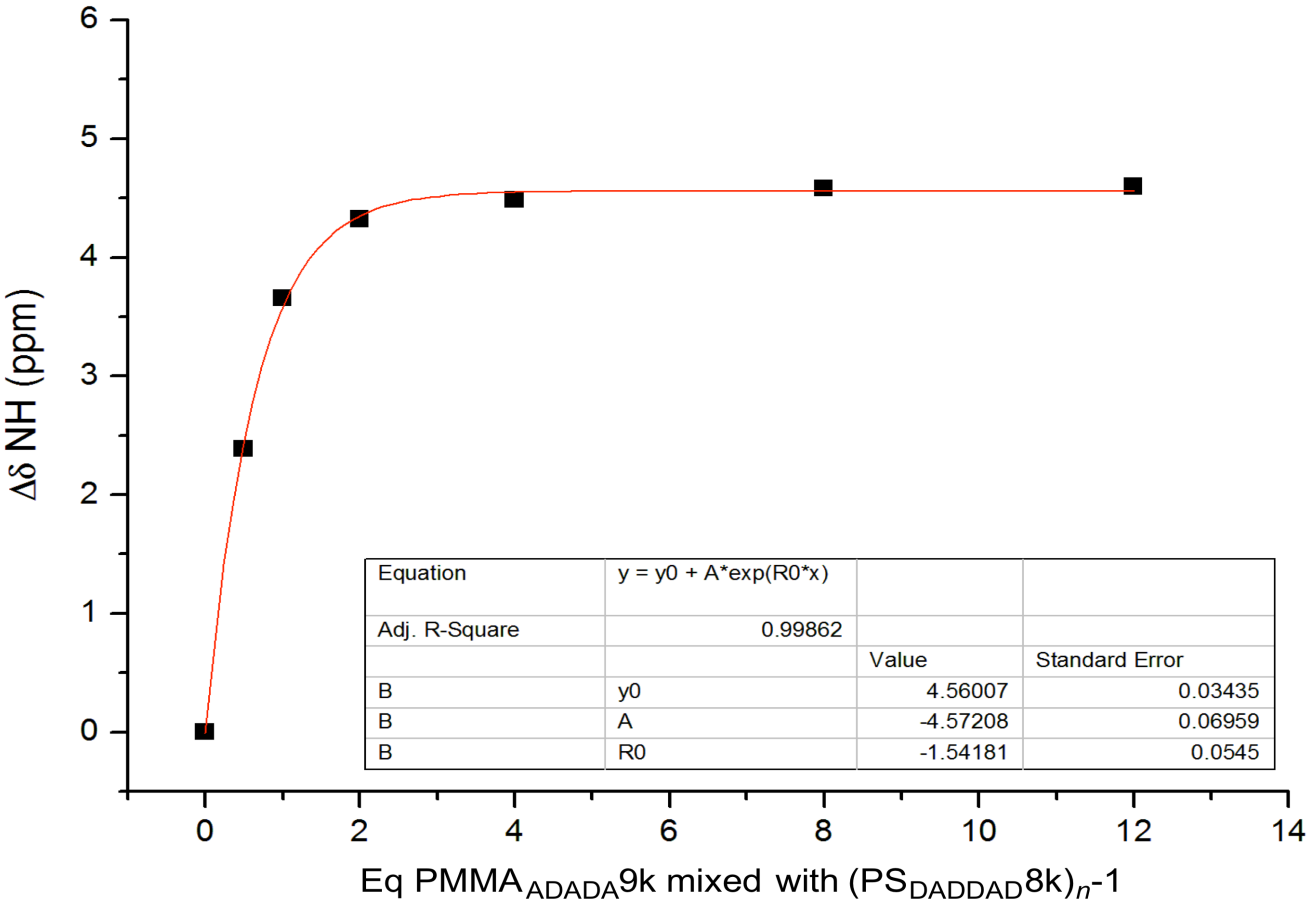

Figure S2. Plots of chemical shift change for NH proton of PMMA$_{ADADA}$9k mixed with (PS$_{DADDAD}$8k)$_n$-1 of various ratios in ^{1}H NMR spectrum (see Figure 3) to estimate δ_∞ for K_{ass}.

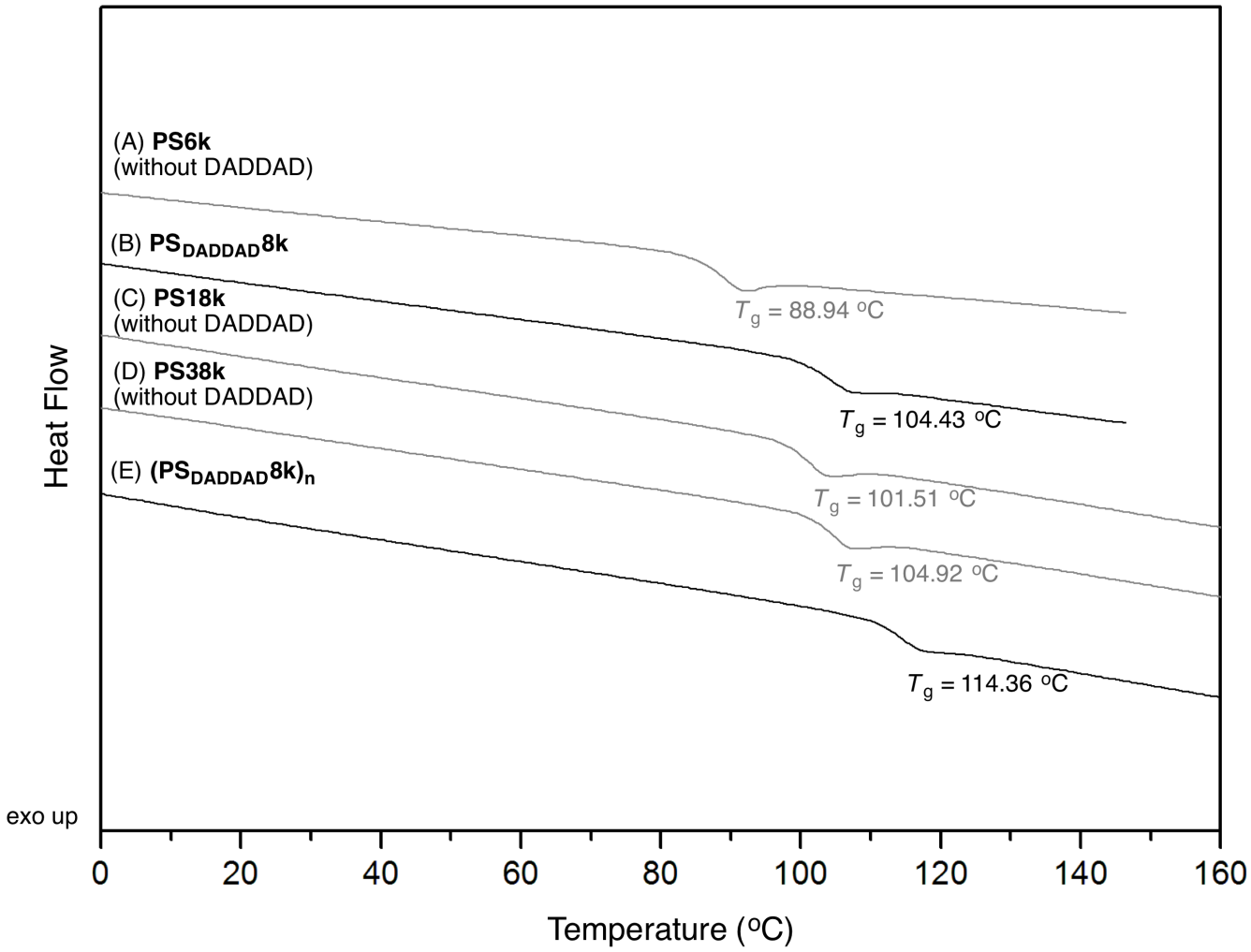

Figure S3. DSC thermograms (2nd heating process at 10 °C/min) of (A) DADDAD-free PS6k, (B) $PS_{DADDAD}8k$, (C) DADDAD-free PS18k, (D) DADDAD-free PS38k, and (E) $(PS_{DADDAD}8k)_n$.