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Supporting Information

Sequence-regulated vinyl copolymers with acid and base monomer units via atom transfer radical addition and alternating radical copolymerization

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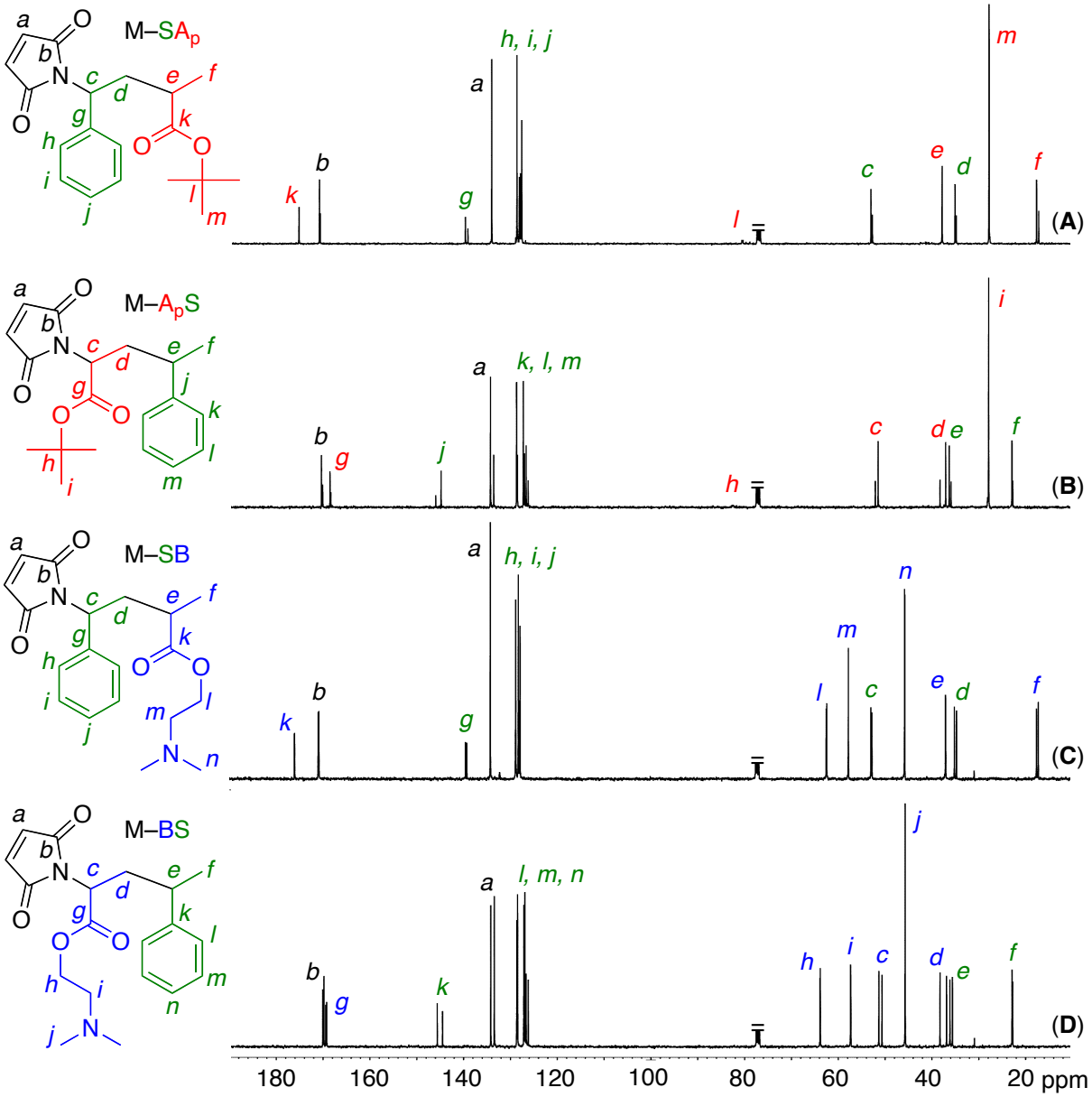

Fig. S1. ^{13}C NMR spectra ($CDCl_3$, r.t.) of a series of maleimide-ended sequence-regulated oligomonomers (M–SA_p (A), M–A_pS (B), M–SB (C), M–BS (D)).

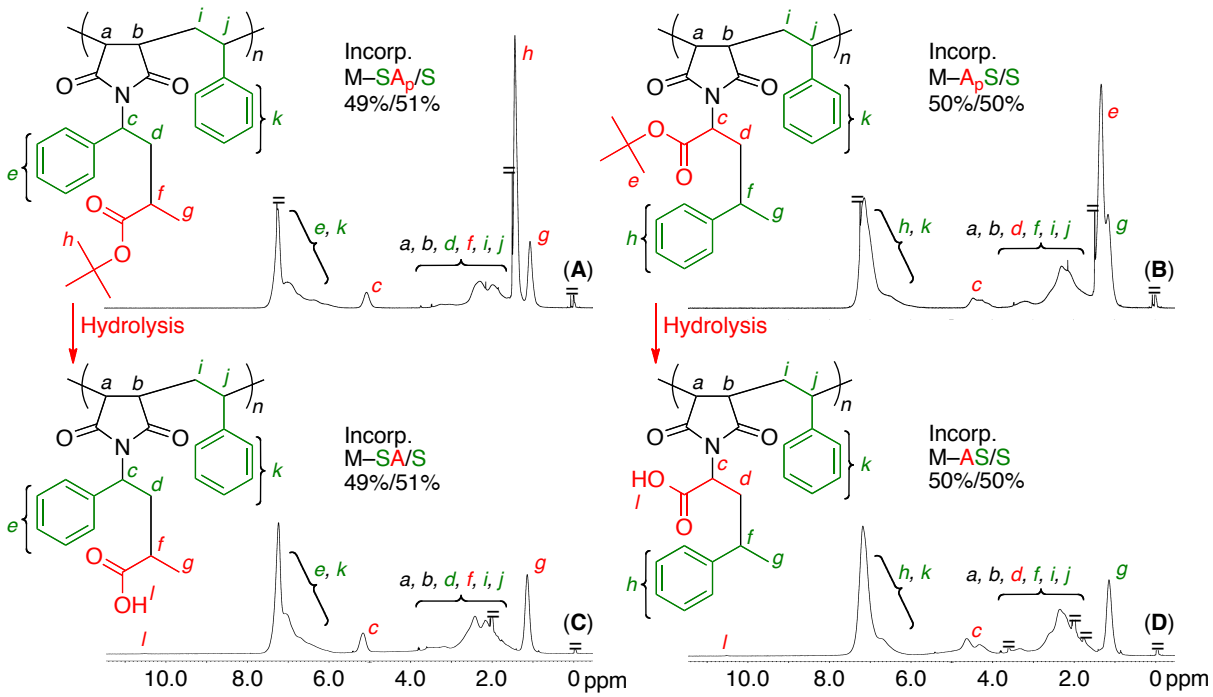

Fig. S2. ^{1}H NMR spectra of a series of main- and side-chain sequence-regulated acid-functionalized vinyl copolymers (poly(M_1-*alt*-S)) obtained in alternating free radical copolymerization of maleimide-ended functional oligomonomers and styrene with AIBN in toluene at 60 ºC ($[M_1]_0$ = $[S]_0$ = 1.0 M, $[AIBN]_0$ = 20 mM) and after deprotections of *t*Bu ester. M_1: M–SA_p (A), M–A_pS (B), M–SA (A), M–AS (D).

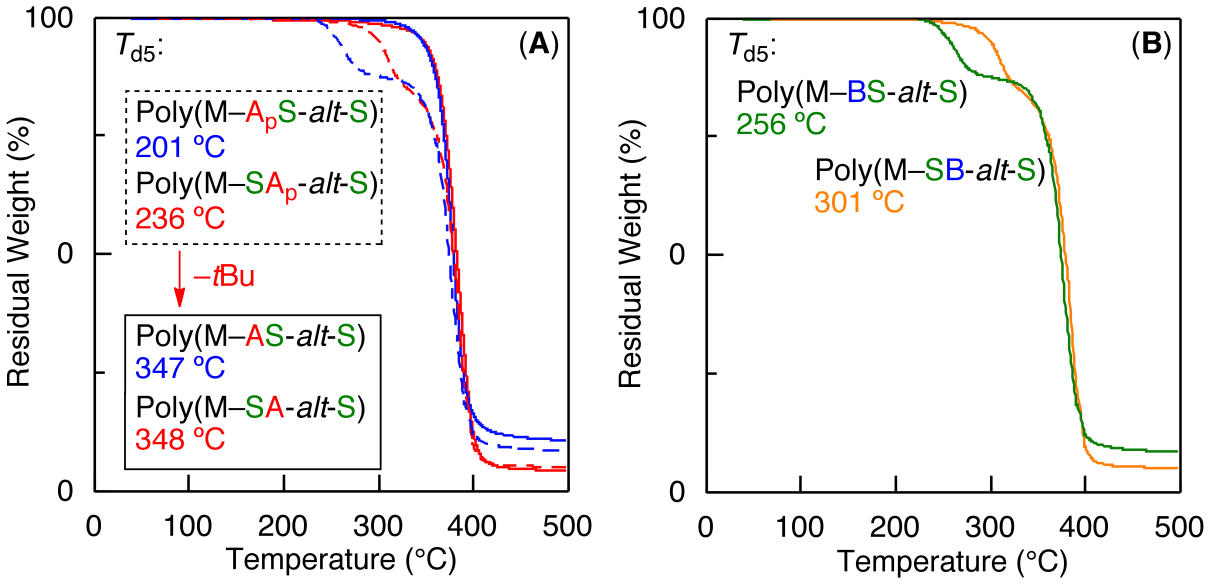

Fig. S3. TGA curves and T_{d5} values a series of main- and side-chain sequence-regulated functional vinyl copolymers (poly(M_1-*alt*-S)) obtained in alternating free radical copolymerization of sequence-regulated maleimide-ended oligomonomers and styrene. (A) dotted lines: poly(M–SA_p-*alt*-S) and poly(M–A_pS-*alt*-S). solid lines: poly(M–SA-*alt*-S) and poly(M–AS-*alt*-S). (B) poly(M–SB-*alt*-S) and poly(M–BS-*alt*-S).

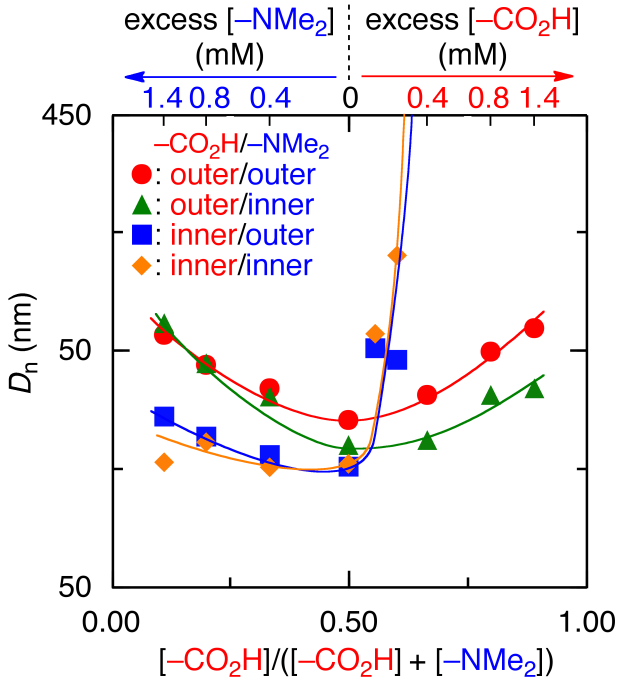

Fig. S4. DLS analysis of mixture of acid- and base-functionalized sequence-regulated vinyl copolymers at different ratios in $CHCl_3$ at 20 °C. $[–CO_2H] = [–NMe_2] = 0.20$ mM at $[–CO_2H]/([–CO_2H] + [–NMe_2]) = 0.50$.

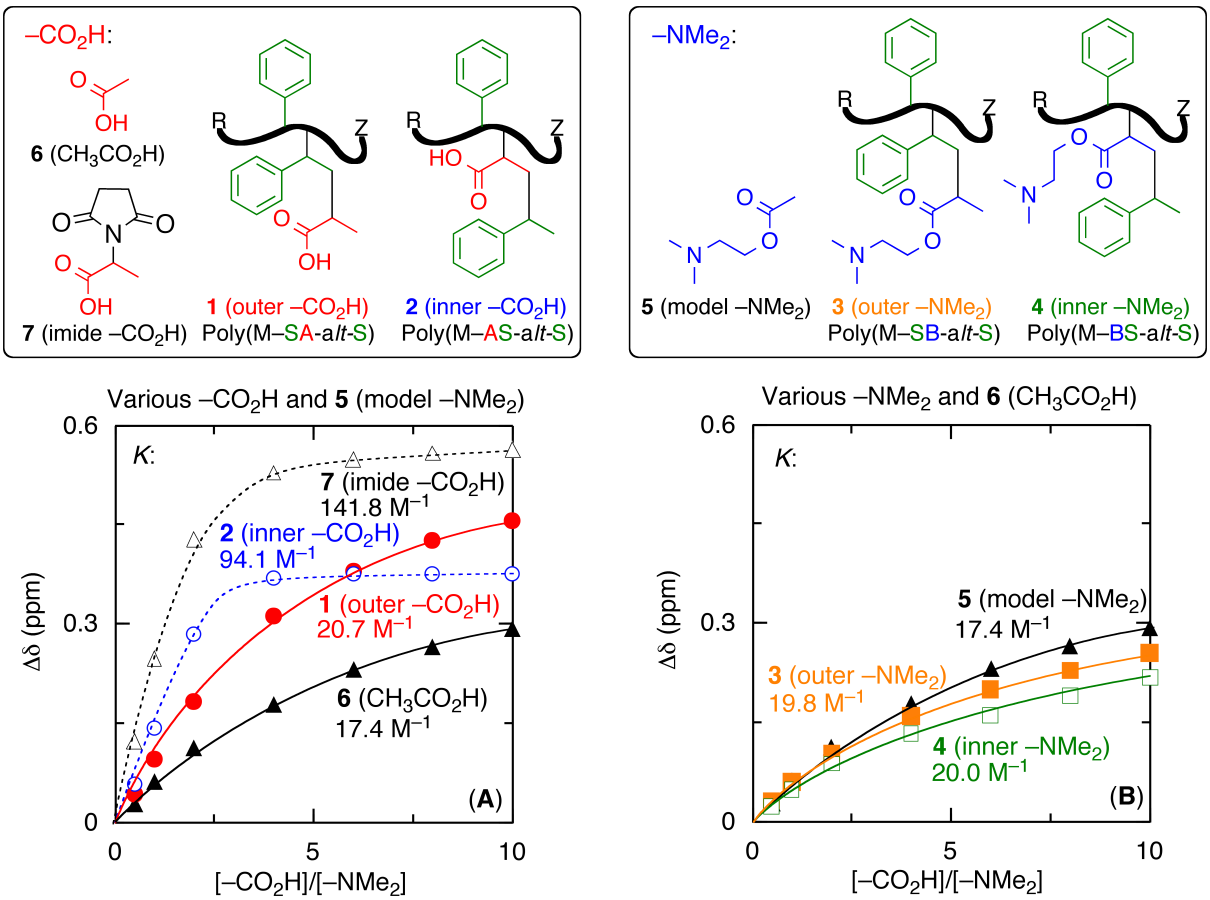

Fig. S5. NMR titration and equilibrium constants (*K*) between sequence-regulated acid-functionalized oligomonomers and model amine (**5**) (A) or base-functionalized oligomonomers and CH_3CO_2H (**6**) (B) obtained by the changes in chemical shifts (ppm) of methyl protons of dimethylamino groups in $CDCl_3$ at 20 ºC. [$–NMe_2$] =10 mM.

Table S1. Alternating RAFT copolymerization of sequence-regulated functional oligomonomers (M_1) and Styrene (S)

Entry	M_1	$([M_1]_0+[S]_0)/[CDB]_0$	Time, h	Conv., %[c] M_1/S	M_n[d]	M_w/M_n[d]	Incorp. %[c] M_1/S
1[a]	M–SA_p	100	24	95/96	15900	1.16	49/51
2[a]	M–A_pS	100	24	92/95	16000	1.17	49/51
3[b]	M–SB	100	24	96/94	12100	1.34	50/50
4[b]	M–BS	100	24	96/97	11800	1.24	50/50

Polymerization condition: [a]$[M_1]_0/[S]_0/[CDB]_0/[AIBN]_0$ = 1000/1000/20/5.0 mM in toluene at 60 °C. [b]$[M_1]_0/[S]_0/[CDB]_0/[V\text{-}70]_0$ = 1000/1000/20/5.0 mM in $PhC(CF_3)_2OH$ at 20 °C. [c]Determined by ^{1}H NMR. [d]Determined by SEC.