Regulation of cis and trans microstructures of isoprene units in alternating copolymers

via "Space-Limited" living species in anionic polymerization

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The alternating copolymers obtained have performed on SEC test, and the SEC curves were shown as follow. These curves were single peak with narrow distribution.



Fig. S1 The SEC curves of the poly(isoprene-*alt*-DPE-2SiH) copolymers: *a*) the alternating copolymers (A, B and C in Table 1) with medium *trans* modified by THF; *b*) the alternating copolymers (D, E, F and G in Table 1) with high *cis* modified by RONa; *c*) the alternating copolymers (H and I in Table 1) with high *trans* modified by ROK.

The MALDI-TOF MS test results of alternating copolymers modified with NaODP and *t*-BuOK were shown in Fig. S2-S3, and the alternating sequence can be demonstrated.



Fig. S2 The MALDI-TOF MS test results of poly(isoprene-alt-DPE-2SiH) copolymers modified with 1.0 eqv. NaODP (E in Table 1).



Fig. S3 The MALDI-TOF MS test results of poly(isoprene-alt-DPE-2SiH) copolymers modified with 1.0 eqv. t-BuOK (H in Table 1).

The test results of ¹³C NMR spectra were shown in Fig. S4, and the peaks of methyl groups of *cis* or *trans* isoprene units were attributed to peak at 23.9 ppm and 16.3 ppm in ¹³C NMR spectra, respectively.



Fig. S4 The ¹³C NMR spectra of poly(isoprene-alt-DPE-2SiH) copolymers modified with different additives.