Supplementary information

Hydrogen Atom–Coupled Electron Transfer-Driven Anionic Polymerization under Aerobic Conditions

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1. Supplementary Methods

Materials

All monomers were purchased from TCI (stabilized with 4-*tert*-butylcatehol, TBC), except for methyl methacrylate and 4-methoxy styrene, which were obtained from BTC and Alfa Aesar, respectively. All monomers, reagents, and solvents from commercial sources were used as received without additional purification prior to polymerization. Potassium-*tert*-butoxide (KO^tBu) was purchased from Alfa Aesar. 18-crown-6-ether (**18-c-6**) was sourced from AK Scientific. 15-crown-5-ether (**15-c-5**), 12-crown-4-ether (**12-c-4**), triethylsilane ($HSiEt_3$), phenylsilane (H_3SiPh) and triphenylsilane ($HSiPh_3$) were purchased from BeanTown Chemical, Inc. Diphenylsilane (H_2SiPh_2) was purchased from STREM Chemicals, Inc. Diethylsilane (H_2SiEt_2) was acquired from GELEST, Inc. Note: diethylsilane (bp 56 °C and density 0.686 g/mL) is volatile.

Methods

Fourier Transform Near-infrared (FT-NIR) Spectroscopy. The progress of polymerization was monitored by Fourier transform near-infrared spectroscopy (FT-NIR), enabling time-resolved measurement of monomer consumption. Conversion was tracked by monitoring the disappearance of signal at 6136 cm^{-1} and 6171 cm^{-1}, corresponding to the C=C bond stretching vibration of vinyl group in styrene and methacrylate, respectively. FT-NIR measurements were performed at resolution of 8 and 16 cm^{-1}, with sample and baseline scan time 8 set. Peak analysis was conducted within the spectral range of 6210-6050 cm^{-1}. Monomer conversion and first-order kinetic were determined based on peak intensity changes. All real-time FT-NIR monitoring was conducted using a Bruker MPA FT-NIR Spectrophotometer, with baseline corrections and data analysis performed by OPUS software. Conversion and ln ($[M_0]/[M_t]$) were derived from the C=C bond stretching vibration peaks, and first-order kinetic plots were generated using linear fitting. Conversions and first-order kinetic plots were calculated through equations 1 and 2.

$$\text{Conversion yield (\%)}: \frac{I_0 - I_t}{I_0} \times 100\ (\%) \qquad (1)$$

$$\ln\left([M_0]/[M_t]\right): \ln\frac{I_0}{I_t} \qquad (2)$$

Where I is the intensity at a specific peak according to substituent-styrene. I_0 is an initial intensity, and it is intensity value over time, which is an important experimental parameter commonly used to prove the monomer conversion of polymerization.

Gel Permeation Chromatography (GPC) Analysis. GPC analysis was carried out to investigate the molecular weight and dispersity (*Đ*) of polymers, using liquid chromatography line consisting of M510 pump, U6K universal injector and Viscotek 250 dual refractometer/viscometer detector (Viscotek/Malvern Corporation) Tetrahydrofuran (THF) was used as a mobile phase with a flow rate of 0.8 mL/min. The samples were dissolved in THF (1 mL) and filtered through 0.22 μm PTFE filters. The detection was performed at 280 nm employing a Waters 486 tunable absorbance detector (Waters Corporation) incorporated in the detector sequence. The separation was conducted over a set of three 5 μm Styragel columns (HR 2, 3, and 5, Waters Corporation). Molecular weights were calculated by a calibration curve constructed with 17 narrow dispersity polystyrene standards with molecular masses between 0.162 kDa and 956 kDa (Polymer Standards Service) and Viscotek OmniSEC 3.1 software (Malvern Panalytical Inc., Westborough, MA, USA).

Nuclear Magnetic Resonance (NMR) Spectroscopy. All polymers were characterized by ^{1}H and ^{19}F NMR. ^{1}H NMR spectra were recorded using $CDCl_3$ as solvent by using a Bruker AVANCE III HD 600 MHz and JEOL 500 MHz equipped. ^{1}H NMR chemical shifts are referenced to chloroform (7.26 ppm). The following abbreviations are used to describe signals: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment (e.g., CH_aH_b). Before and after the reaction, the crude samples (100 μL) were diluted in $CDCl_3$ (0.6 mL). The solid styrene polymers were obtained by precipitation in cold methanol after reaction and dried. The methyl methacrylate polymers were obtained by precipitation in cold hexane after polymerization. The products were then dissolved in $CDCl_3$ for NMR analysis. The NMR spectra were processed with Bruker TopSpin 4.1.4 software.

IRC Calculations and Charge Analysis. Intrinsic reaction coordinate (IRC) calculations were carried out at the uB3LYP-D3(BJ)/6-31+G(d) level of theory, starting from the optimized TS geometry. A total of 30 steps, with a step size of 0.1 Bohr, were propagated in both the forward and reverse directions along the IRC reaction path. For each IRC geometry obtained, natural bond orbital (NBO) population analyses[1] were performed at the same level of theory. While IRC calculations as well as all geometry optimizations performed above were conducted on the singlet energy surface, the NBO analyses were evaluated using the triplet single point calculations. This combined singlet/triplet treatment was employed to better characterize the singly occupied molecular orbitals particularly in the vicinity of the TS.

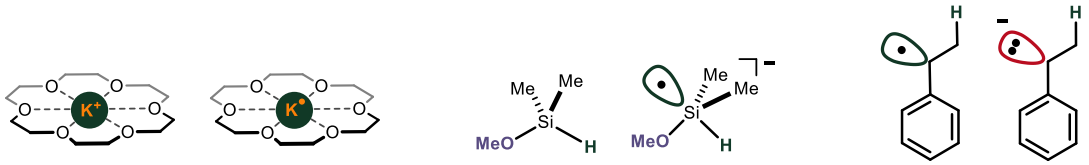
Standard reduction potentials. Reduction potentials were calculated from the free energy values obtained at the uB3LYP-D3(BJ)/6-31+G(d,p) level of theory according to Eq. S1[2].

$$E^0 = -\frac{\Delta G_0}{nF} - E^{SHE} \qquad \text{(Eq. S1)}$$

where E^0 is the standard reduction potential, ΔG_0 is standard free energy change associated with the reduction process, F is the Faraday constant, n is the number of electrons transferred (i.e., n = 1), and E^{SHE} is the reduction potential of the standard hydrogen electrode (4.43 V)[3]. The calculated reduction potentials are summarized in Table 1.

2. Reduction Potentials of Key Redox-Relevant Species.

Supplementary Table 1. Standard reduction potentials. The free energy change ΔG_0 was computed as the difference between each species and its corresponding reduced form using the uB3LYP-D3(BJ)/6-31+G(d,p) method with implicit solvation in THF. Experimental reduction potentials measured in aqueous solution.[3]



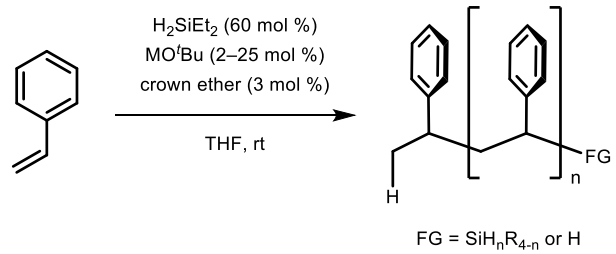
K^+(18-c-6) **silane** **styrene**

species	calculated (V)	experimental (V)[16]
K^+	−2.9	−2.8
K^+(**18-c-6**)	−3.4	-
hydrosilane	−4.1	-
styrene	−1.9	-

3. Optimization of Key Reaction Parameters for Styrene Polymerization.

Styrene (92 μL, 0.8 mmol), crown ether (0.02 mmol, 3 mol %), and THF (3 mL, 0.3 M) were added to a screw cap vial. H_2SiEt_2 (70 μL, 0.5 mmol, 60 mol %) was then added to the solution, and the reaction mixture was gently swirled at room temperature. Alkali metal Lewis base (2–25 mol %) was subsequently added to the solution. Upon completion of the reaction, the mixture was precipitated into cold methanol. This precipitation was repeated once or twice to further purify the polymer. The final polymer was dried in a vacuum oven. The conversions of the monomers were determined by real-time FT-NIR monitoring, and M_n and $Đ$ were measured by using GPC.

Supplementary Table 2. Optimization of styrene polymerization using an alkali metal Lewis base–crown ether pair.



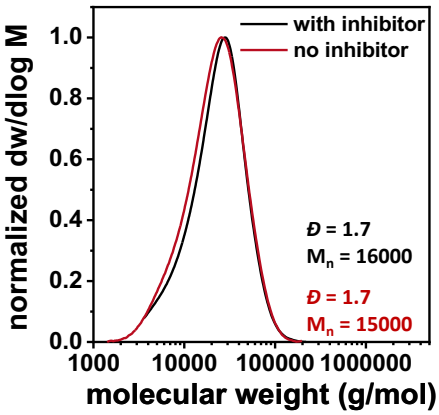
entry	alkali metal Lewis base (mol %)	crown ether	conv.* (%)	M_n	$Đ$
1	LiO^{t}Bu (25)	12-c-4	<10	n.d	n.d
2	NaO^{t}Bu (25)	15-c-5	<15	n.d	n.d
3	KO^{t}Bu (2)	18-c-6	<35	29000	3.2
4	KO^{t}Bu (4)	18-c-6	<40	27000	3.0
5	KO^{t}Bu (5)	18-c-6	<50	21000	2.4
6	KO^{t}Bu (6)	18-c-6	<95	19000	2.1
7	KO^{t}Bu (10)	18-c-6	>95	17000	1.7
8	KO^{t}Bu (20)	18-c-6	>99	15000	1.9
9	KO^{t}Bu (25)	18-c-6	>99	16000	1.7

*conv.: conversion, M_n: number average molecular weight, $Đ$: dispersity, n.d: not determined.

Supplementary Table 3. Effect of K^+(**18-c-6**) complex coordination on the HOMO and LUMO energies of reactant species.

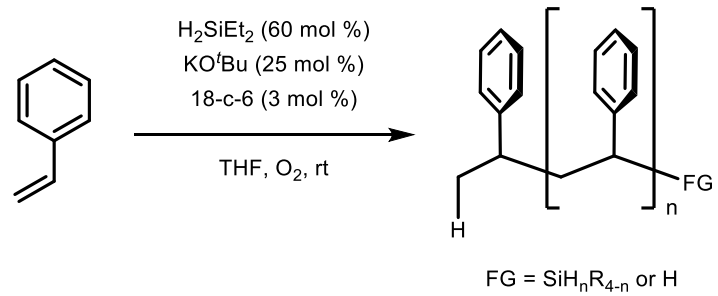
species	K^+(**18-c-6**)	E_{LUMO} (Hartree)	E_{HOMO} (Hartree)
styrene	−	−0.05013	-
	+	−0.06338	-
styryl anion	−	-	−0.09353
	+	-	−0.11000

To assess the influence of inhibitor residues, polymerization was conducted using unpurified styrene (i.e., without removal of the monomer inhibitor – TBC) under standard conditions. The resulting polymer exhibited comparable molecular weight ($M_n \approx 16000$) and dispersity ($Đ = 1.7$) to that obtained from purified monomer ($M_n \approx 15000$, $Đ = 1.7$). These results suggest that trace inhibitors have a minimal impact on the efficiency and control of the HAP process.



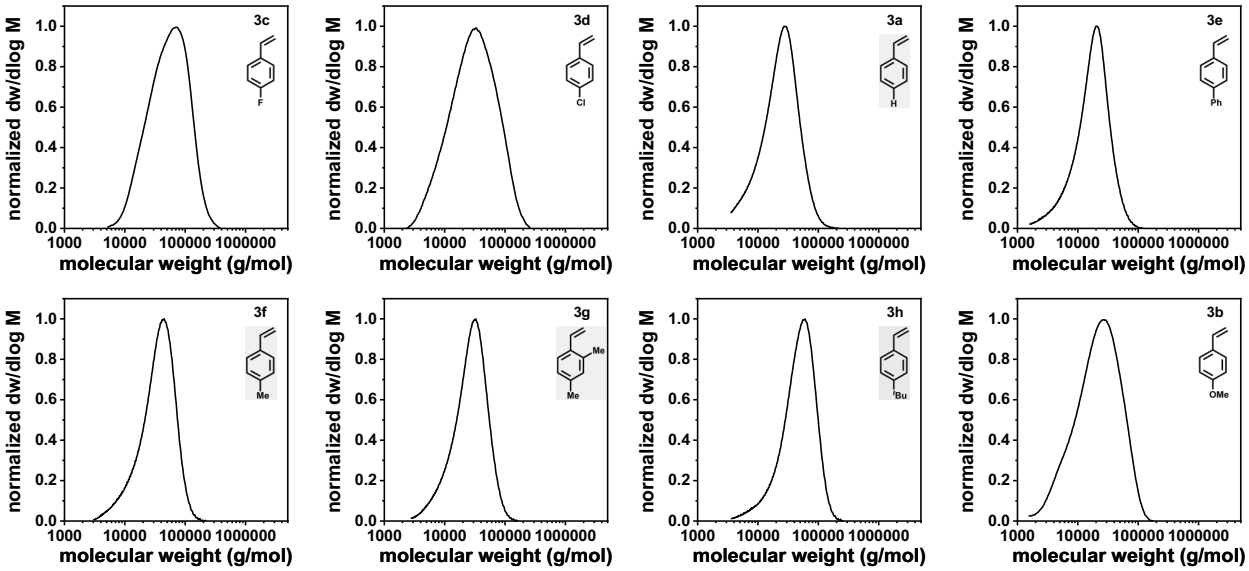
Supplementary Figure 1. GPC traces of two poly(styrene)s synthesized from the same styrene monomer in the presence and absence of an inhibitor.

The impact of oxygen on HAP reactivity was evaluated under pure O_2 atmosphere to determine its oxygen tolerance (Fig. 2d entry 3). Polymerization proceeded slower than under standard conditions; nevertheless, monomer conversion was nearly complete (>95%), indicating that HAP is fully tolerant to oxygen. The resulting polymer exhibited a lower M_n (5,300) and dispersity ($Đ = 1.6$).



Supplementary Figure 2. Oxygen tolerance of HAP.

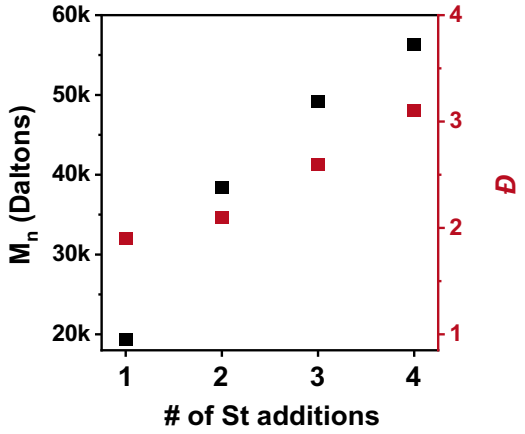
4. Monomer Scope of HAP



Supplementary Figure 3. GPC traces of synthesized poly(styrene)s (Fig. 3a).

5. Homopolymerization

Styrene (92 μL, 0.8 mmol), **18-c-6** (4.9 mg, 0.02 mmol, 3 mol %), and THF (3 mL, 0.3 M) were introduced into a screw cap vial. H_2SiEt_2 (70 μL, 0.5 mmol, 60 mol %) was then added, and the mixture was gently swirled at room temperature to ensure homogeneity. KO^{t}Bu (200 μL, 25 mol %) was introduced into the reaction mixture. After completion of the initial polymerization of styrene (1 min), additional styrene monomer (0.8 mmol per portion) was sequentially added at approximately 100 s intervals to continue the homopolymerization process. Upon completion of the reaction, the mixture was precipitated into cold methanol to isolate the polymer. The precipitation was repeated once or twice to further purify the polymer. The resulting polymer was dried in a vacuum oven to afford the final product. Polymer conversion was determined by real-time FT-NIR monitoring.



Supplementary Figure 4. Number average molecular weight (M_n) and dispersity ($Đ$) as a function of the number of monomer additions.

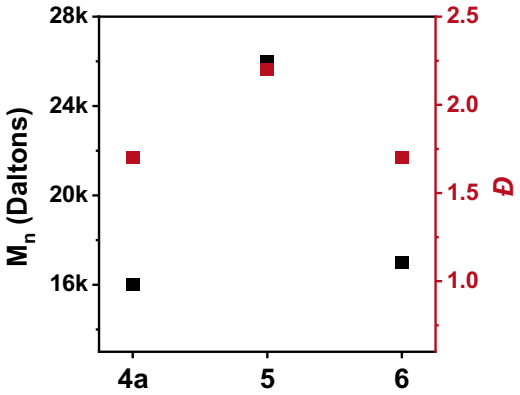
Supplementary Table 4. GPC results of homopolymerization via HAP.

sample	M_w	M_n	$Đ$	DP
standard	27000	16000	1.7	154
m^{1st}	74000	35000	2.1	337
m^{2nd}	104000	40000	2.6	385
m^{3rd}	164000	52000	3.1	500

*DP: Degree of polymerization ($M_n/M_{repeating\ unit}$).

6. Block Copolymerization

Styrene (92 µL, 0.8 mmol), **18-c-6** (4.9 mg, 0.02 mmol, 3 mol %), and THF (3 mL, 0.3 M) were added into a screw cap vial. H_2SiEt_2 (70 µL, 0.5 mmol, 60 mol %) was added to the solution, and the mixture was gently swirled at room temperature. Next, KO^{t}Bu (200 µL, 25 mol %) was introduced into the solution. After completion of the initial polymerization of styrene (~1 min), a second monomer [0.8 mmol, 4-chlorostyrene (4-Cl-St) or methyl methacrylate (MMA)] was added sequentially to afford block copolymers poly(St-*b*-4-Cl-St) (**5**), and poly(St-*b*-MMA) (**6**), respectively. After completion of the reaction, the mixture was poured into cold methanol to precipitate the polymer. The precipitated polymer was collected, and the precipitation was repeated once or twice to enhance its purity. The purified polymer was then dried in a vacuum oven to obtain the final product.



Supplementary Figure 5. Number average molecular weight (M_n) and dispersity ($Đ$) of block copolymers. **4a**: PS, **5**: poly(St-*b*-4-Cl-St), and **6**: poly(St-*b*-MMA).

Supplementary Table 5. GPC results of block copolymerization.

sample	M_w	M_n	$Đ$
4a	27000	16000	1.7
5	55000	26000	2.2
6	29000	17000	1.7

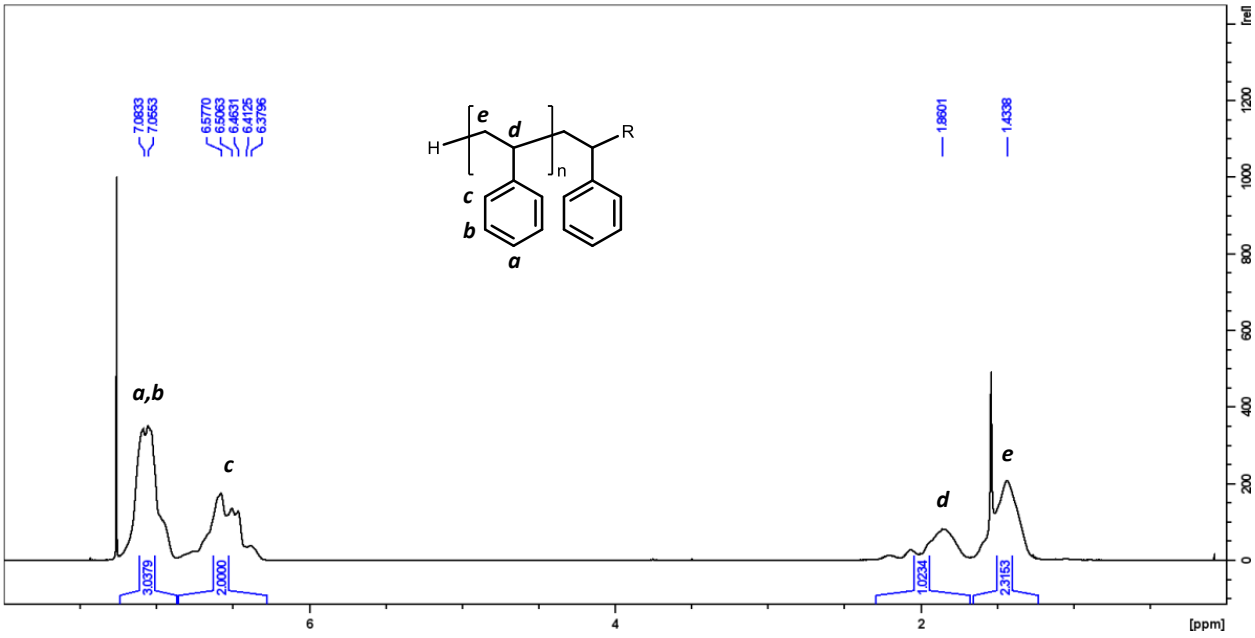
7. NMR Spectroscopy

The copolymer ratios (B/A, *n*:*m*) was determined by ^{1}H NMR integrated according to the following equation:

$$B/A = (I_B/H_B) \times (H_A/I_A)$$

where I_A and I_B correspond to the integrated intensities of monomers A and B, respectively, and H_A and H_B denote the number of protons associated with each signal.

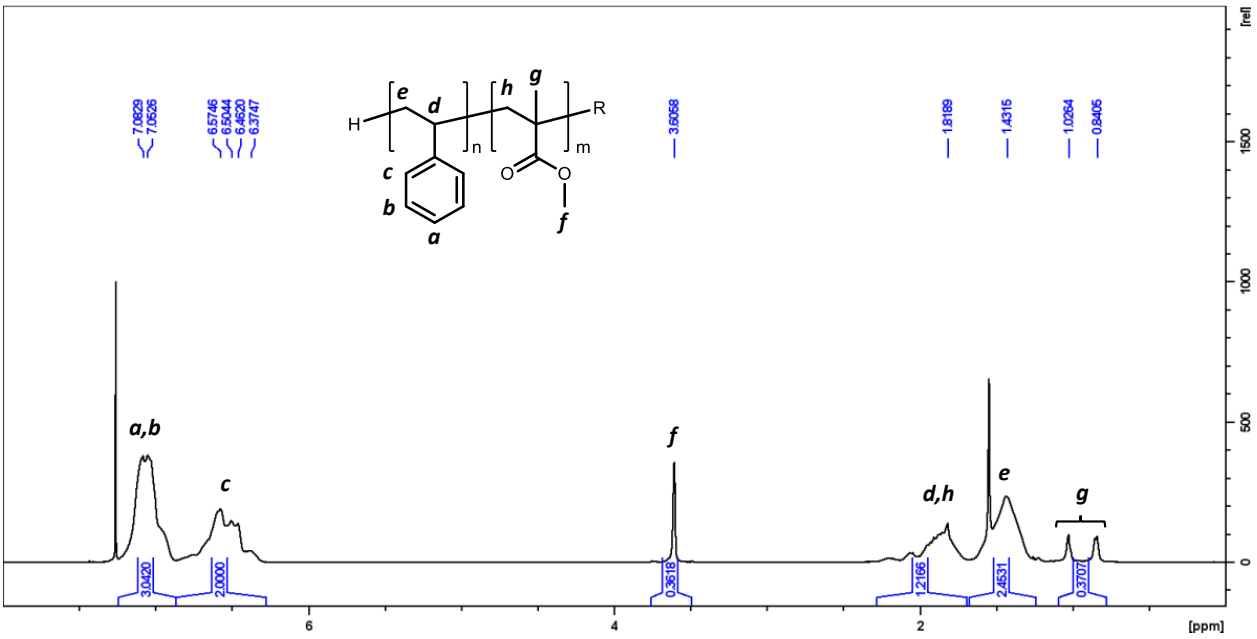
^{1}H NMR of poly(styrene) (4a)



Supplementary Figure 6. ^{1}H NMR of **4a**.

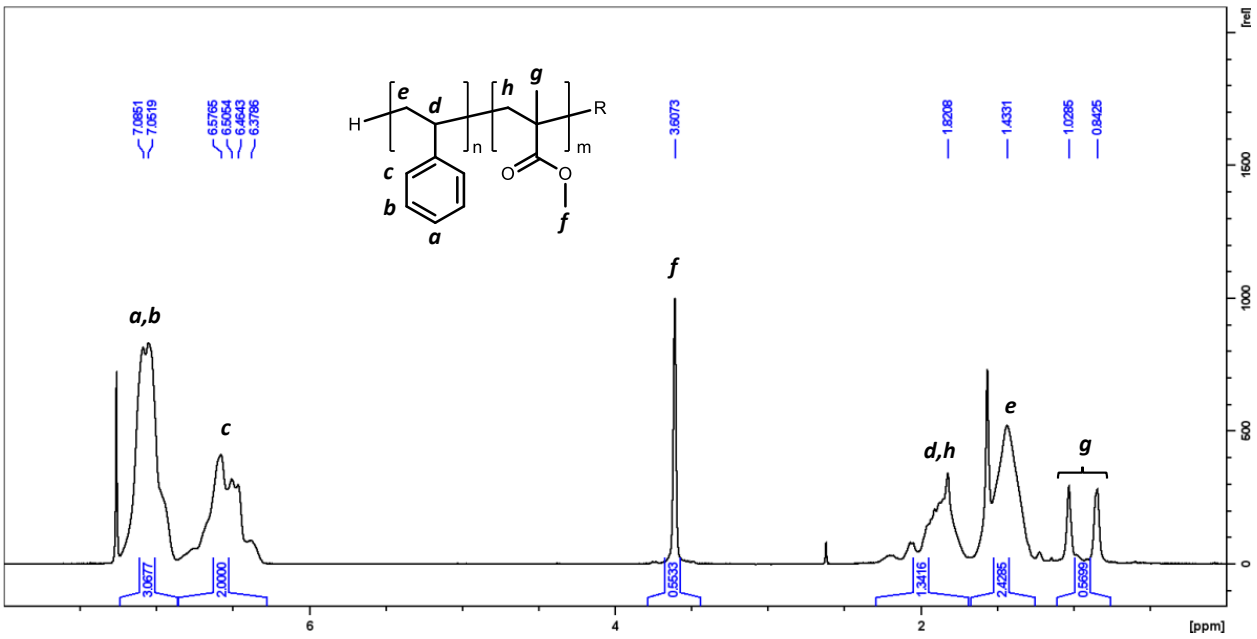
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24-6.87 (m, 3H, Ar*H*), 6.87-6.27 (m, 2H, Ar*H*), 2.30-1.68 (m, 1H, ArC*H*), and 1.68-1.25 (m, 2H, ArCHCH_2).

^{1}H NMR of poly(St-*b*-MMA) block copolymers (6)



Supplementary Figure 7. ^{1}H NMR of A-B block copolymer **6**. A and B represent St and MMA, respectively.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24-6.87 (m, 3H, Ar*H*), 6.87-6.27 (m, 2H, Ar*H*), 3.61 (s, 3H, OCH_3), 2.30-1.68 (m, 3H, ArC*H* and CH_2CCH$_3$CO$_2$CH$_3$), 1.68-1.25 (m, 2H, ArCHCH_2), 1.03 (s, 3H, COCCH_3), and 0.84 (s, 3H, COCCH_3). A:B = 1: 0.12.



Supplementary Figure 8. ^{1}H NMR of A-B-B block copolymer **6**. A and B represent St and MMA, respectively.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24-6.87 (m, 3H, Ar*H*), 6.87-6.27 (m, 2H, Ar*H*), 3.61 (s, 3H, OCH_3), 2.30-1.68 (m, 3H, Ar*CH* and $CH_2CCH_3CO_2CH_3$), 1.68-1.25 (m, 2H, $ArCHCH_2$), 1.03 (s, 3H, $COCCH_3$), and 0.84 (s, 3H, $COCCH_3$). A:B = 1:0.18.

8. GPC Results of Block Copolymers 6

Supplementary Table 6. GPC results of copolymerization via HAP (see Fig. 3e). A and B represent St and MMA, respectively.

copolymer	$\mathbf{M_w}$	$\mathbf{M_n}$	$\boldsymbol{Đ}$
A-B	27900	15800	1.8
A-B-B	29800	16700	1.8

9. Reactions on Large-Scale Polymerization

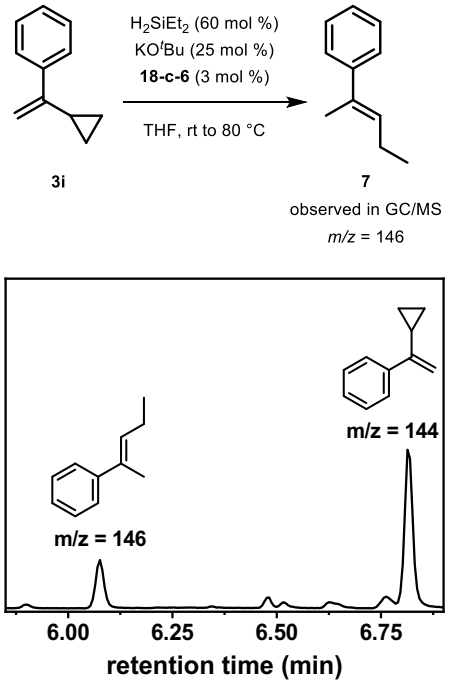
Supplementary Table 7. GPC results of scale-up polymerization via HAP.[a]

entry	hydrosilane	polymer	M_w	M_n	$Đ$
1[a]	TMDS	**4a**	91000	49000	1.9
2	H_2SiEt_2	**6**	21000	16000	1.4

[a][**3a**]$_o$:[hydrosilane]$_o$:[KO^{t}Bu]$_o$:[**18-c-6**]$_o$ = 267:167:67:7 mM in THF at 25 °C.

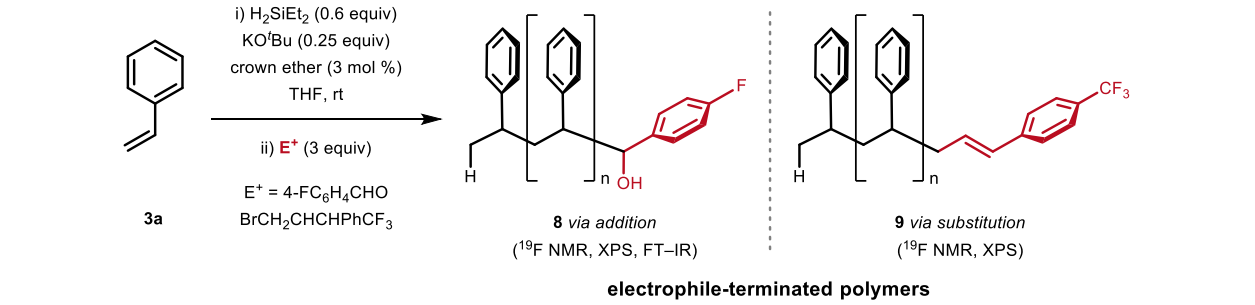
10. Mechanistic Studies

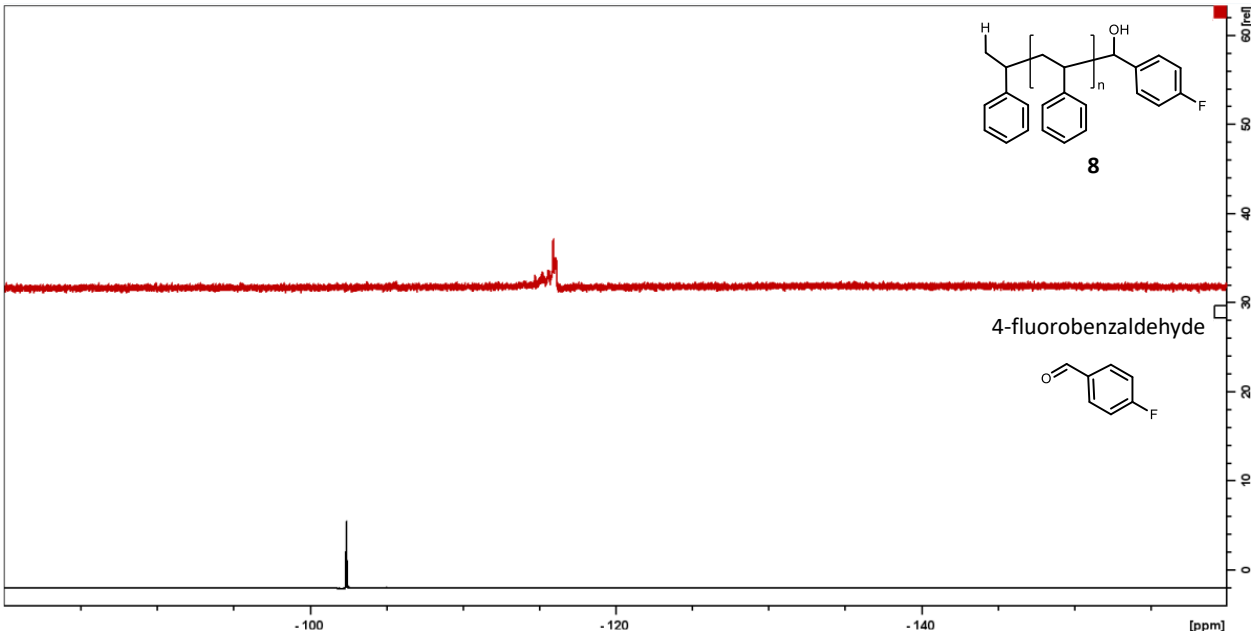
3i (120 µL, 0.8 mmol), **18-c-6** (4.9 mg, 0.02 mmol, 3 mol %), and THF (3 mL, 0.3 M,) were added to a screw cap vial. KO^{t}Bu (200 µL, 25 mol %) and H_2SiEt_2 (70 µL, 0.5 mmol, 60 mol %) were then added to the solution. The septum was replaced by a screw cap with a Teflon liner, and the reaction mixture was stirred 16 h at 80 °C. The reaction mixture was purified by medium-pressure liquid chromatography (MPLC). The resulting product **7** was confirmed by gas chromatography-mass spectrometry (GC-MS) and ^{1}H NMR.[4]



Supplementary Figure 9. GC-MS spectrometry of the radical clock reaction.

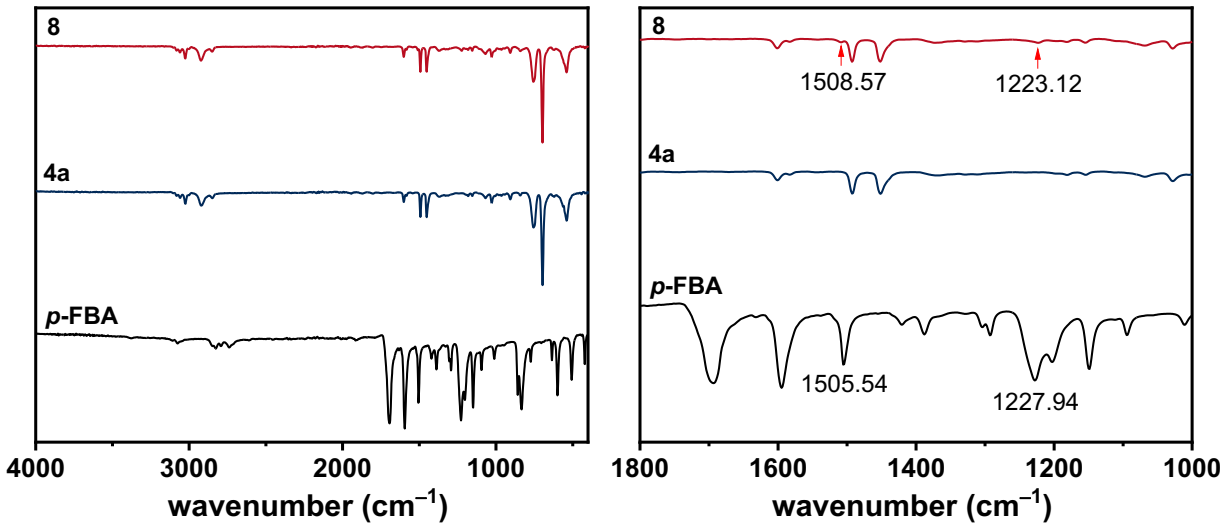
Styrene **3a** (92 μL, 0.8 mmol), **18-c-6** (4.9 mg, 0.02 mmol, 3 mol %), and THF (3 mL, 0.3 M) were added to a screw cap vial. H_2SiEt_2 (70 μL, 0.5 mmol, 60 mol %) was then added to the solution, and the mixture was gently swirled at room temperature. KO^{t}Bu (200 μL, 25 mol %) was subsequently introduced to the solution. The septum was replaced by a screw cap with a Teflon liner. Upon completion of polymerization, a carbanion trapping agent–either 4-fluorobenzaldehyde (*p*-FBA) (3 equiv) or 1-[(1*E*)-3-bromo-1-propen-1-yl]-4-(trifluoromethyl)benzene (3 equiv)–was added, and the reaction mixture was stirred 16 h at 80 °C. After completion, the reaction mixture was precipitated in cold methanol and hexanes. This precipitation process was repeated once or twice to purify the polymer. The structure of the resulting polymer was analyzed by ^{19}F NMR, FT-IR, and X-ray photoelectron spectroscopy (XPS).



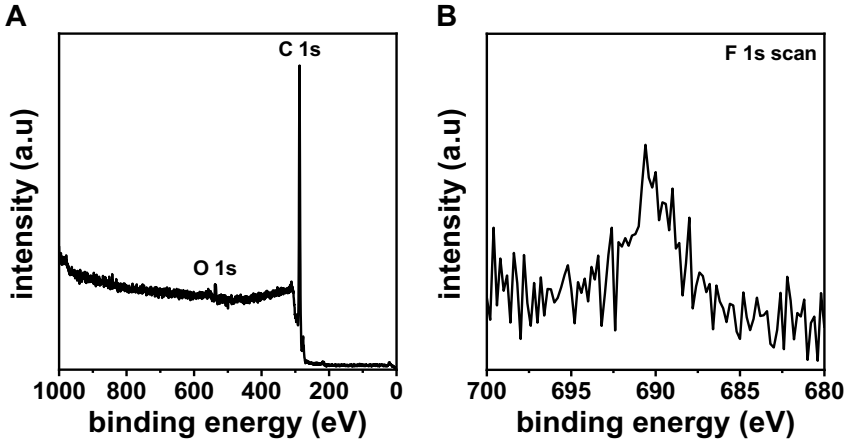


Supplementary Figure 10. ^{19}F NMR of **8**.

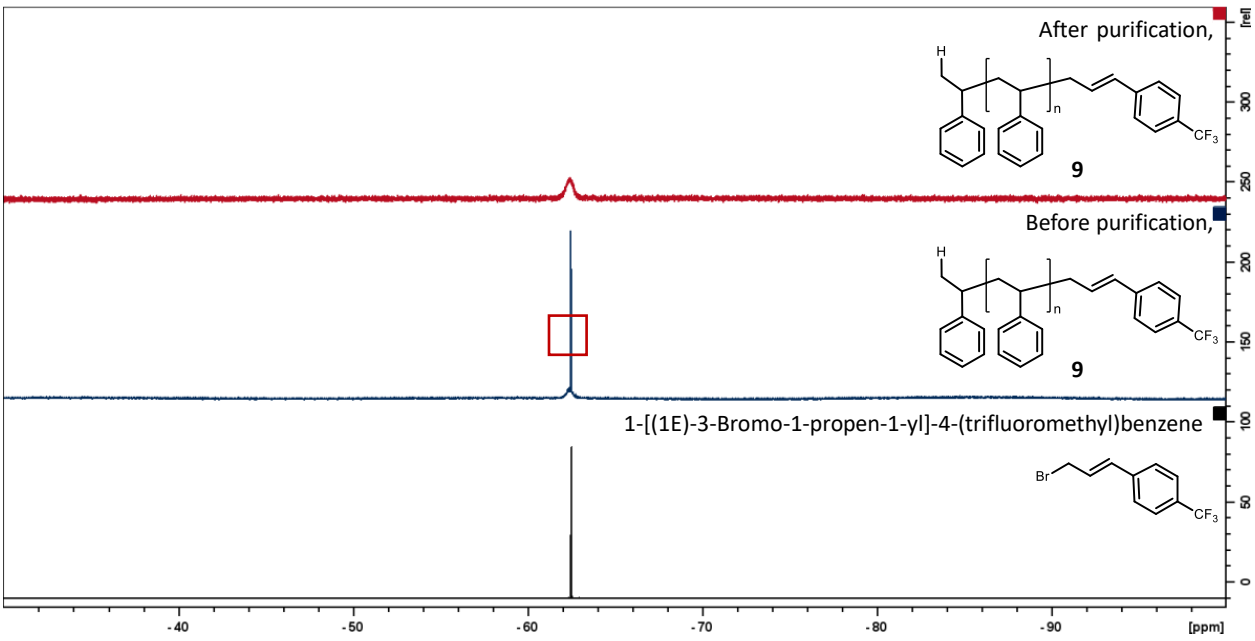
^{19}F NMR ($CDCl_3$, 470 MHz): δ −115.86 (m) ppm.



Supplementary Figure 11. FT-IR of **8**.

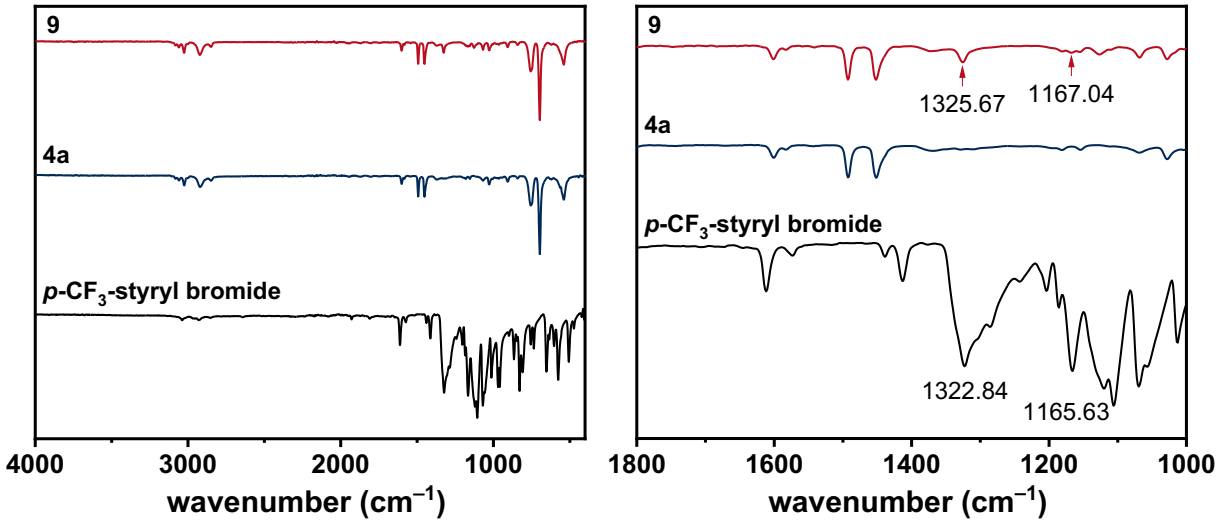


Supplementary Figure 12. XPS survey spectrum of surface **8**: (A) survey scan and (B) F 1s scan.

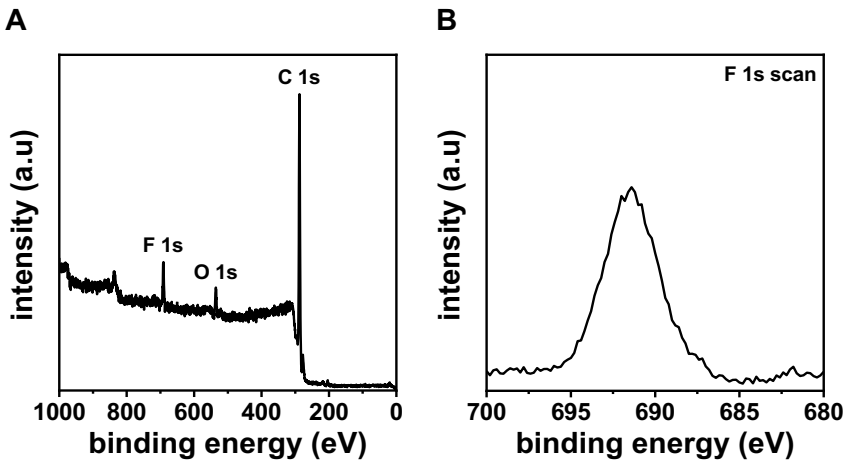


Supplementary Figure 13. ^{19}F NMR of **9**.

^{19}F NMR ($CDCl_3$, 470 MHz): δ −62.49 ppm.



Supplementary Figure 14. FT-IR of **9**.



Supplementary Figure 15. XPS survey spectrum of surface **9**: (A) survey scan and (B) F 1s scan.

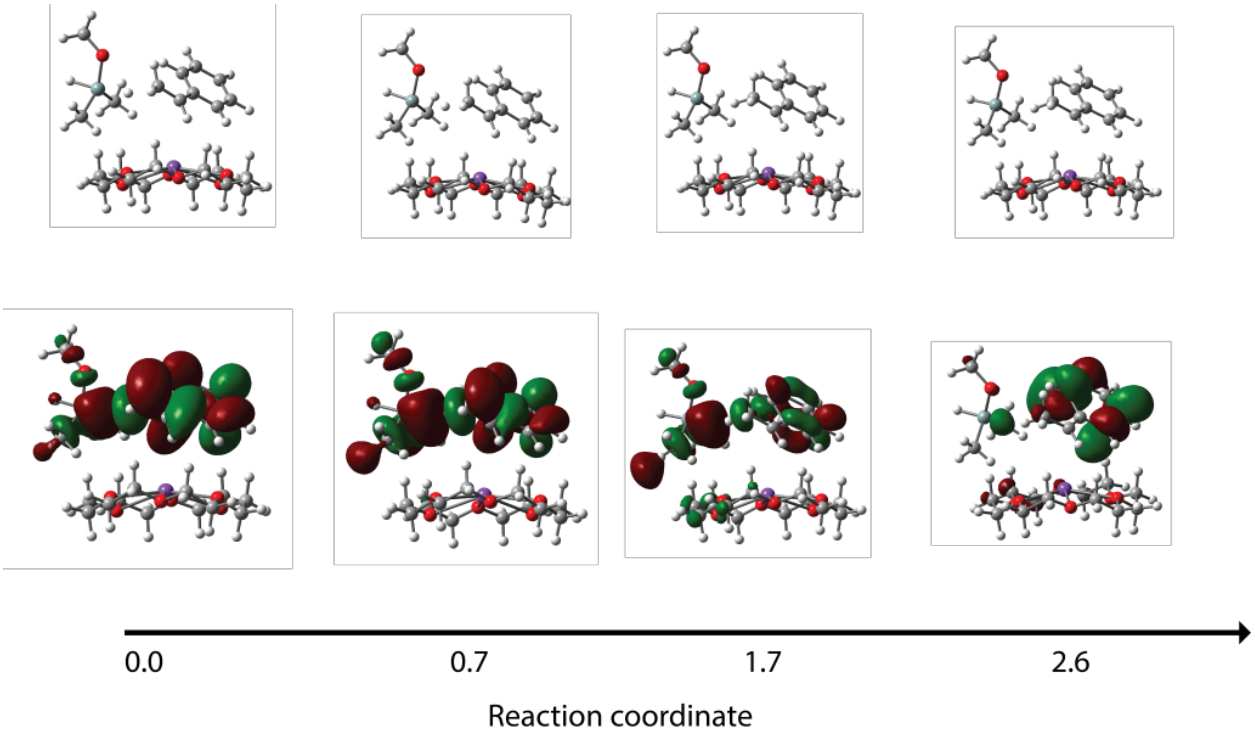
11. Initial Rate Kinetic Studies and Linear Free-Energy (Hammett) Analysis

Para-substituted styrene monomer (0.8 mmol), **18-c-6** (4.9 mg, 0.02 mmol, 3 mol %), and THF (3 mL, 0.3 M) were added to a screw cap vial. H_2SiEt_2 (70 μL, 0.5 mmol, 60 mol %) was then added to the solution, and the mixture was gently swirled at room temperature. KO^{t}Bu (100 μL, 10 mol %) was subsequently added to the solution. Upon completion, the reaction mixture was precipitated in cold methanol. This precipitation process was repeated once or twice to purify the polymer. The final product was dried in a vacuum oven. The conversion of monomer and kinetics were determined by real-time FT-NIR monitoring.

Supplementary Table 8. Apparent polymerization rate constant of *p*-substituted styrenes.

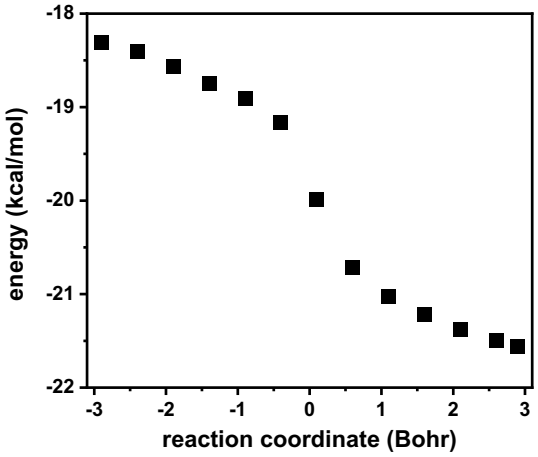
p-substituent	σ_p	K_p^{app} (mol^{-1} L s^{-1})	Log (k_{pX}/k_{pH})
Cl	0.23	0.73	0.20
F	0.06	0.52	0.05
H	0	0.46	0
CH_3	−0.17	0.30	−0.19
$C(CH_3)_3$	−0.20	0.28	−0.22

12. Evolution of Highest Singly Occupied Molecular Orbital (SOMO) Following HAT



Supplementary Figure 16. Evolution of the singly occupied molecular orbital (SOMO) along the IRC reaction coordinate following hydrogen atom transfer (HAT). Starting from the transition state (TS; IRC = 0.0 Bohr), the SOMO evolves through the charge-crossing region, where the silane and styrene fragments bear comparable charges (Fig. 4G), and ultimately reaches the product state. For example, in IRC = 2.6 Bohr state, the SOMO electron density is predominantly localized on the styrene anionic fragment.

13. Binding Energy of K^+(18-c-6) Complex with Substrates



Supplementary Figure 17. Binding energy of K^+(**18-c-6**) complex with styrene and silane along the IRC reaction pathway. The transition state is indicated as 0 Bohr.

14. Cartesian Coordinates and Energies

10

Charge = 0 Multiplicity = 1

ATOM	X	Y	Z
K	-0.17328	-1.20774	0.49899
C	-3.46453	-0.05939	0.09287
Si	-2.41711	1.34800	-0.72717
C	-1.32200	0.73925	-2.20204
O	-2.45029	3.02896	-0.18279
H	-1.24751	1.23489	0.32933
H	-3.61044	1.68799	-1.71755
H	-3.94704	-0.68299	-0.67162
H	-2.91299	-0.70481	0.78561
H	-4.26853	0.41087	0.67628
H	-0.37593	0.27006	-1.90998
H	-1.88567	0.04900	-2.84381
H	-1.06336	1.61021	-2.82031
C	-3.35570	3.98144	-0.70870
H	-3.15749	4.94585	-0.22326
H	-3.24377	4.11485	-1.79474
H	-4.40562	3.71289	-0.52012
O	1.30746	0.53610	2.23210
O	-0.99647	-0.88529	3.18472
O	-1.80760	-3.21156	1.80513
O	-1.18256	-3.44000	-0.96316
O	1.25694	-2.22495	-1.80350
O	2.12438	0.11624	-0.48972
C	-2.49860	-2.72351	2.95267

H	-3.28796	-2.02369	2.64639
H	-2.96369	-3.55851	3.49680
C	-1.51450	-2.02420	3.86045
H	-0.69527	-2.70458	4.13685
H	-2.03574	-1.71895	4.77959
C	-0.16902	-0.07122	4.00987
H	-0.75750	0.33953	4.84322
H	0.65393	-0.66999	4.42735
C	0.38353	1.06491	3.18219
H	0.89383	1.77839	3.84588
H	-0.43049	1.58498	2.65928
C	1.88100	1.54908	1.40733
H	1.08832	2.07141	0.85473
H	2.42111	2.27875	2.02849
C	2.85228	0.90471	0.44675
H	3.56538	0.27397	0.99787
H	3.41624	1.68832	-0.07996
C	2.96166	-0.59995	-1.38898
H	3.66057	0.08608	-1.88953
H	3.54818	-1.35200	-0.84056
C	2.09816	-1.26328	-2.43589
H	2.74232	-1.75589	-3.17882
H	1.48702	-0.50912	-2.94957
C	0.34485	-2.83809	-2.71163
H	-0.37567	-2.09393	-3.07812
H	0.88847	-3.25080	-3.57385
C	-0.36904	-3.96658	-2.00714
H	0.36535	-4.67056	-1.58923
H	-0.99179	-4.50676	-2.73528
C	-1.84937	-4.46423	-0.23141
H	-2.51214	-5.03509	-0.89824

H	-1.11085	-5.15658	0.19838
C	-2.67668	-3.84466	0.86907
H	-3.25324	-4.63903	1.36499
H	-3.38093	-3.11012	0.45496

HF=-2008.8397776

3a

Charge = 0 Multiplicity = 1

ATOM	X	Y	Z
C	3.40785	2.72935	-3.55279
C	2.05000	2.49075	-3.30612
C	1.47083	2.89013	-2.10358
C	2.23563	3.53952	-1.11546
C	3.59761	3.77161	-1.37778
C	4.17989	3.37206	-2.58246
C	1.67558	3.98324	0.17220
C	0.40829	3.85816	0.59498
H	4.20338	4.27138	-0.62662
H	5.23377	3.56272	-2.76146
H	3.85582	2.41658	-4.49091
H	1.44229	1.99128	-4.05478
H	0.41721	2.69493	-1.93252
H	2.39303	4.46411	0.83603
H	0.11222	4.22691	1.57158
H	-0.36895	3.39276	-0.00411

HF=-309.7043607

11

Charge = 0 Multiplicity = 1

ATOM	X	Y	Z
C	-0.92334	4.50847	0.44102
C	0.09179	3.55362	0.29562
C	0.33885	2.95807	-0.93962
C	-0.43081	3.31196	-2.06653
C	-1.44772	4.27030	-1.90848
C	-1.69345	4.86508	-0.66826
C	-0.20710	2.71813	-3.39462
C	0.75015	1.83647	-3.72369
K	-0.48186	-1.07551	0.58028
C	4.06356	-1.56695	-0.02552
Si	3.18467	0.14384	0.06046
C	2.42612	0.44118	1.82072
O	3.02833	1.18578	-1.37284
H	1.81623	-0.41699	-0.48262
H	4.49953	0.94736	0.41597
H	4.92423	-1.62203	0.65400
H	3.36285	-2.37770	0.20747
H	4.43924	-1.73721	-1.04465
H	1.81150	-0.41091	2.13916
H	3.19431	0.61237	2.58564
H	1.77081	1.32323	1.81159
H	-2.05077	4.55053	-2.76850
H	-2.48495	5.60220	-0.56983
H	-1.11070	4.96547	1.40808
H	0.69395	3.26959	1.15370
H	1.13435	2.22365	-1.03330

H	-0.90038	3.05268	-4.16638
H	0.82144	1.46568	-4.74226
H	1.47531	1.46361	-3.00309
C	3.93120	2.22974	-1.67772
H	4.06089	2.93003	-0.84062
H	4.92866	1.85482	-1.95086
H	3.52909	2.78843	-2.53349
O	-0.28259	-2.52302	-1.94964
O	0.95947	-3.50181	0.42742
O	0.01912	-2.71340	2.95395
O	-1.44680	-0.29216	3.18263
O	-2.87919	0.56892	0.85480
O	-1.81959	-0.13831	-1.66894
C	1.20601	-3.48625	2.79439
H	2.07637	-2.82310	2.69185
H	1.35924	-4.13123	3.67183
C	1.06591	-4.34867	1.56190
H	0.17751	-4.99269	1.64231
H	1.95423	-4.99197	1.47655
C	0.99052	-4.19966	-0.81163
H	1.90908	-4.80070	-0.88209
H	0.12612	-4.87595	-0.88833
C	0.97735	-3.19212	-1.93662
H	1.13572	-3.71503	-2.89169
H	1.78215	-2.46083	-1.78986
C	-0.33811	-1.50520	-2.94691
H	0.45100	-0.76380	-2.76818
H	-0.18863	-1.94444	-3.94473
C	-1.69148	-0.83848	-2.90047
H	-2.49069	-1.58881	-2.99343
H	-1.77044	-0.13371	-3.74015

C	-3.06443	0.53402	-1.53655
H	-3.23892	1.18264	-2.40761
H	-3.88410	-0.19774	-1.47828
C	-3.02721	1.39674	-0.29903
H	-3.96310	1.97126	-0.23256
H	-2.19196	2.10002	-0.36156
C	-2.78933	1.33633	2.05179
H	-1.91331	1.99829	2.00944
H	-3.68681	1.96201	2.16807
C	-2.68833	0.40396	3.23399
H	-3.52148	-0.31378	3.21975
H	-2.75320	0.99173	4.16156
C	-1.29666	-1.21066	4.26043
H	-1.32984	-0.67606	5.22121
H	-2.11596	-1.94413	4.24336
C	0.03119	-1.91796	4.13544
H	0.17999	-2.55444	5.01996
H	0.85100	-1.18728	4.09200

HF=-2318.5631571

TS

Charge = 0 Multiplicity = 1

ATOM	X	Y	Z
C	3.08308	-0.81281	-3.12429
C	1.94796	-0.10339	-2.70922
C	1.74102	0.19431	-1.36412
C	2.67354	-0.19896	-0.36966
C	3.80830	-0.92864	-0.80900

C	4.00872	-1.22363	-2.15626
C	2.49326	0.10700	1.03413
C	1.51076	0.93016	1.54507
K	2.46886	-3.46349	1.50449
C	-1.82993	-0.61625	3.23799
Si	-1.61888	-0.00869	1.42337
C	-1.17085	-1.33793	0.10475
O	-1.56065	1.69767	1.03573
H	-0.00756	0.24710	1.69788
H	-3.15376	-0.05312	1.10187
H	-2.65090	-1.33981	3.33360
H	-0.90795	-1.05443	3.63167
H	-2.08543	0.25192	3.86111
H	-0.17878	-1.77673	0.25167
H	-1.92710	-2.13252	0.06538
H	-1.16239	-0.84702	-0.87681
H	4.53746	-1.25222	-0.06960
H	4.89651	-1.77285	-2.45998
H	3.23955	-1.04398	-4.17349
H	1.21001	0.21203	-3.44264
H	0.84127	0.72229	-1.06787
H	3.14285	-0.42301	1.72717
H	1.52925	1.17759	2.60234
H	1.02057	1.66924	0.92139
C	-2.69879	2.41268	0.58856
H	-3.09044	2.01967	-0.36080
H	-3.52029	2.39011	1.31894
H	-2.40545	3.45818	0.43216
O	3.56092	-2.42420	3.95162
O	0.80576	-2.96452	3.71255
O	-0.01693	-4.85980	1.76479

O	1.58409	-5.18401	-0.56062
O	4.37150	-4.80406	-0.17501
O	5.33134	-3.01247	1.81917
C	-0.93930	-4.15382	2.59534
H	-1.24289	-3.21950	2.11071
H	-1.83562	-4.76743	2.76768
C	-0.28559	-3.85549	3.92231
H	0.07314	-4.78159	4.39483
H	-1.03004	-3.39153	4.58419
C	1.38756	-2.50879	4.92810
H	0.65247	-1.92874	5.50489
H	1.70995	-3.36635	5.53637
C	2.57331	-1.63047	4.60701
H	2.97671	-1.21904	5.54295
H	2.26843	-0.79648	3.96075
C	4.80778	-1.75590	3.78720
H	4.68237	-0.85649	3.16853
H	5.20542	-1.44873	4.76522
C	5.78085	-2.70969	3.13676
H	5.85140	-3.63316	3.72969
H	6.77622	-2.24384	3.09946
C	6.16353	-3.96830	1.16856
H	7.19836	-3.59930	1.11979
H	6.15906	-4.91301	1.73174
C	5.65857	-4.19643	-0.23565
H	6.36138	-4.85475	-0.76692
H	5.60262	-3.24340	-0.77554
C	3.79332	-5.00676	-1.46436
H	3.52940	-4.03938	-1.91259
H	4.51071	-5.51456	-2.12480
C	2.56977	-5.87873	-1.31784

H	2.83842	-6.81672	-0.81057
H	2.17773	-6.12299	-2.31594
C	0.43521	-5.98451	-0.29728
H	-0.02643	-6.30677	-1.24199
H	0.72749	-6.88034	0.26975
C	-0.56762	-5.17437	0.48720
H	-1.48655	-5.76658	0.60742
H	-0.81722	-4.25139	-0.05181

HF=-2318.5367707

12

Charge = 0 Multiplicity = 1

ATOM	X	Y	Z
C	-0.25892	3.52222	0.66973
C	0.90610	2.73498	0.71229
C	1.23451	1.83845	-0.29845
C	0.39567	1.65832	-1.47362
C	-0.80448	2.47973	-1.47653
C	-1.10336	3.36263	-0.45360
C	0.71214	0.77025	-2.49848
C	1.98628	-0.03346	-2.51380
K	-1.36368	-0.61459	-0.06964
C	4.78945	-1.30706	0.23373
Si	5.14366	0.39538	0.92937
C	3.96580	0.88706	2.30896
O	5.03006	1.44700	-0.37088
H	2.05187	-0.76643	-1.68961
H	6.53563	0.45066	1.47322
H	4.78416	-2.06024	1.02946

H	3.81630	-1.32150	-0.26722
H	5.55016	-1.59188	-0.50049
H	2.93608	0.95107	1.94798
H	3.99973	0.14730	3.11704
H	4.23638	1.85950	2.73408
H	-1.48154	2.39303	-2.32551
H	-2.01649	3.95340	-0.52294
H	-0.50496	4.21467	1.46863
H	1.58081	2.83240	1.56252
H	2.16036	1.27638	-0.23207
H	0.05266	0.71390	-3.36272
H	2.07815	-0.60491	-3.44561
H	2.89720	0.58451	-2.42875
C	4.96338	2.86276	-0.21214
H	4.00942	3.16056	0.23747
H	5.78915	3.23905	0.40671
H	5.03545	3.31716	-1.20351
O	-1.56839	-2.57915	-2.22851
O	0.57486	-2.63783	-0.34868
O	0.19708	-1.54655	2.24878
O	-1.83694	0.40836	2.52945
O	-3.93154	0.60253	0.62980
O	-3.45738	-0.44375	-1.97673
C	1.47078	-1.92765	1.73863
H	1.92781	-1.08230	1.20881
H	2.13819	-2.22542	2.56079
C	1.29271	-3.08986	0.79187
H	0.74698	-3.90557	1.28837
H	2.28191	-3.46536	0.49183
C	0.37692	-3.65066	-1.32744
H	1.34230	-4.09347	-1.61366

H	-0.26347	-4.44788	-0.92176
C	-0.25549	-3.03362	-2.55186
H	-0.30491	-3.79036	-3.34912
H	0.35154	-2.18932	-2.90097
C	-2.20116	-1.94929	-3.33951
H	-1.60065	-1.09012	-3.66931
H	-2.29063	-2.65881	-4.17557
C	-3.58043	-1.48988	-2.93334
H	-4.15122	-2.32728	-2.50562
H	-4.11327	-1.12665	-3.82460
C	-4.71395	0.08276	-1.56634
H	-5.24992	0.50067	-2.43139
H	-5.33183	-0.71443	-1.12743
C	-4.48129	1.17726	-0.55261
H	-5.44070	1.66543	-0.32582
H	-3.79080	1.92928	-0.95805
C	-3.72641	1.56744	1.65977
H	-3.04252	2.35111	1.30760
H	-4.68476	2.02955	1.93990
C	-3.13509	0.87939	2.86694
H	-3.77252	0.04143	3.18607
H	-3.07277	1.60312	3.69294
C	-1.11161	-0.10992	3.63623
H	-1.04269	0.64604	4.43227
H	-1.61714	-0.99839	4.04270
C	0.28037	-0.46114	3.16923
H	0.89787	-0.74437	4.03428
H	0.73601	0.41086	2.68109

HF=-2318.5906791

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