Electronic Supplementary Information

Comprehensive Studies of Continuous Flow Reversible Addition-Fragmentation Chain Transfer Copolymerization and Its Application for Photoimaging Materials

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ACOST-St		
Conversion	f_{ACOST}	F_{ACOST}
0.1257	0.1062	0.1072
0.1009	0.2102	0.2039
0.0913	0.2964	0.3190
0.0649	0.4043	0.4196
0.0752	0.5152	0.5105
0.0933	0.6034	0.6136
0.1310	0.7018	0.7182
0.1202	0.7997	0.7981
0.1226	0.8893	0.8639

Styrene-*t*BA		
Conversion	f_{ST}	F_{ST}
0.1279	0.1070	0.1512
0.1400	0.2010	0.2804
0.1482	0.2990	0.3684
0.0725	0.4116	0.4127
0.1467	0.5007	0.4922
0.1088	0.5970	0.5217
0.1424	0.6993	0.6188
0.1378	0.7995	0.6902
0.1410	0.9069	0.7811

ACOST-*t*BA		
Conversion	f_{ACOST}	F_{ACOST}
0.1333	0.1115	0.0278
0.1482	0.2073	0.0497
0.1161	0.3004	0.0670
0.1280	0.4085	0.1111
0.1246	0.5050	0.1551
0.1196	0.6012	0.2233
0.1288	0.6980	0.3241
0.0959	0.7911	0.4665
0.0711	0.8971	0.7381

ACOST-MAMA		
Conversion (%)	f_{ACOST}	F_{ACOST}
0.1055	0.1009	0.4356
0.0915	0.2004	0.4881
0.1035	0.3038	0.5358
0.1037	0.3984	0.5580
0.1228	0.4979	0.6028
0.0694	0.5970	0.6351
0.0698	0.7000	0.6807
0.1145	0.7963	0.7455
0.1048	0.8985	0.8567

ACOST-Maleimide		
Conversion (%)	f_{ACOST}	F_{ACOST}
0.1041	0.1021	0.3618
0.0486	0.2019	0.4127
0.0543	0.2999	0.4478
0.1128	0.4001	0.4733
0.1227	0.5001	0.4917
0.0943	0.5996	0.5274
0.0429	0.6992	0.5419
0.0755	0.7988	0.5683
0.0725	0.8999	0.5812

GBLMA-HAMA		
Conversion	f_{GBLMA}	F_{GBLMA}
0.1458	0.1013	0.1622
0.1235	0.2025	0.2802
0.1414	0.2980	0.3726
0.0870	0.4007	0.4566
0.1082	0.4997	0.5284
0.0927	0.6025	0.5925
0.0826	0.7003	0.6650
0.0992	0.8001	0.7563
0.0811	0.9011	0.8411

GBLMA-MAMA		
Conversion	f_{GBLMA}	F_{GBLMA}
0.0887	0.0997	0.2673
0.0685	0.2014	0.4062
0.0891	0.2978	0.4632
0.0811	0.4005	0.5245
0.0601	0.4987	0.5742
0.0344	0.5952	0.6250
0.0685	0.6920	0.6672
0.0882	0.7980	0.7253
0.1095	0.9011	0.8191

HAMA-MAMA		
Conversion	f_{HAMA}	F_{HAMA}
0.1277	0.1003	0.2088
0.0400	0.2007	0.3394
0.1098	0.2997	0.4427
0.1195	0.4010	0.5345
0.1098	0.5014	0.6208
0.0551	0.6000	0.7112
0.1324	0.6977	0.7841
0.0672	0.7990	0.8731
0.1151	0.8997	0.9397

Table S1. Monomer feed compositions actual copolymer compositions, and measured conversion values for copolymerization of different monomer pairs.

Determination of conversion and copolymer composition

(1) Conversions in copolymerization of St, ACOST, and *t*BA.

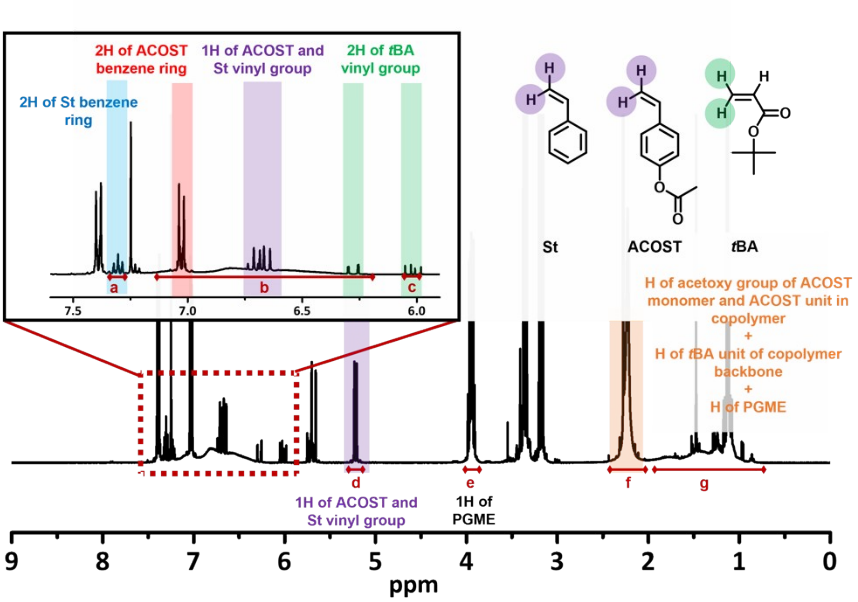

Figure S1. ^{1}H NMR spectrum of a copolymerization mixture of St, ACOST, and *t*BA to describe the estimation of conversion for each monomer (solvent: $CDCl_3$).

The conversion values for each monomer were estimated by quantitative analysis of a ^{1}H NMR spectrum of a crude copolymerization mixture acquired from the flow reactor, recorded in $CDCl_3$. The assignment of the characteristic peaks was shown in **Figure S3**. The integrated intensity of the peak *c*, assigned to one proton of a vinyl peak of *t*BA monomer, was set to the monomer concentration of *t*BA, and assumed to be unity, ($N_{t\mathrm{BA}} = 1$), as an internal reference value. The relative concentration of St monomer (N_{St}) was obtained by dividing the integrated intensity of the peak *a* (I_a) by two ($N_{\mathrm{St}} = I_a/2$). The relative concentration of ACOST monomer (N_{ACOST}) was obtained by subtracting N_{St} from the integrated intensity of the peak *d* (I_d) ($N_{\mathrm{ACOST}} = I_d - N_{\mathrm{St}}$). Then, the relative concentrations of reacted *t*BA, ACOST, and St, namely $P_{t\mathrm{BA}}$, P_{ACOST}, and P_{St}, were estimated by subtracting the integrated intensities from the monomers and solvent from the broad characteristic peaks including both unreacted and reacted units, using the formulated equations of (i) $P_{t\mathrm{BA}} = (I_g - 3I_e - 3N_{St} - 3N_{\mathrm{ACOST}} - 9N_{t\mathrm{BA}})/11$, (ii) $P_{\mathrm{ACOST}} = (I_f - P_{t\mathrm{BA}} - 3N_{\mathrm{ACOST}} - I_e)/3$, and (iii) $P_{\mathrm{St}} = (I_b - 3N_{\mathrm{ACOST}} - N_{St} - N_{t\mathrm{BA}} - 4N_{\mathrm{ACOST}})/5$. The conversion values were obtained by dividing the relative concentration of reacted unit (P_{X}) with the sum of the relative concentration values of reacted and unreacted monomer units ($P_{\mathrm{X}} + N_{\mathrm{X}}$).

(2) Estimation of conversion in copolymerization of GBLMA, HAMA, and MAMA, and in reactivity ratio determination.

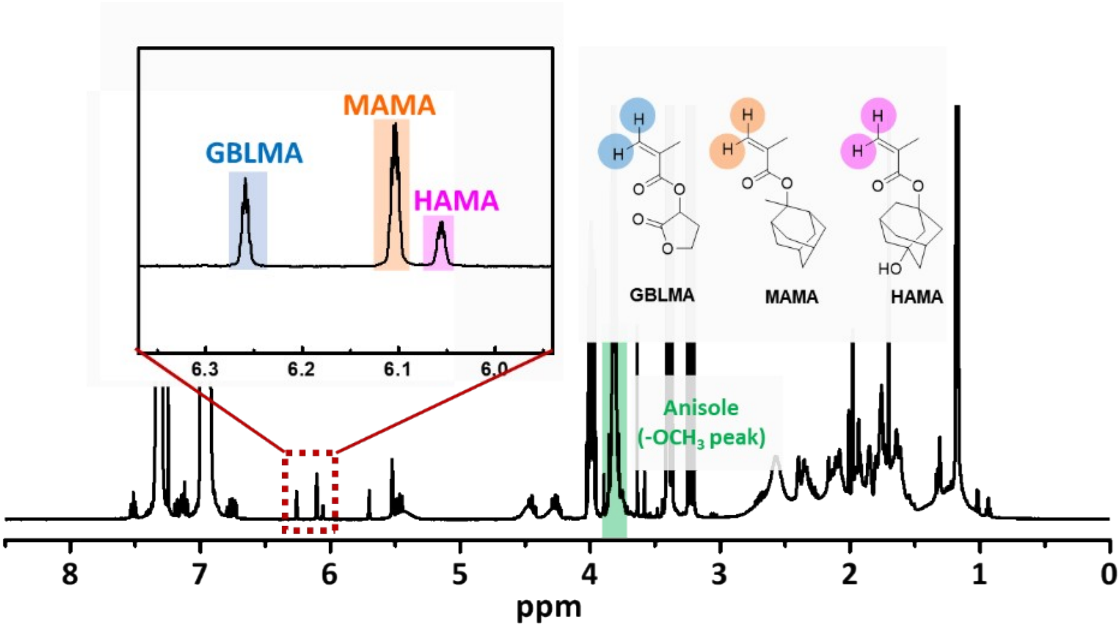

Figure S2. ^{1}H NMR spectrum of a copolymerization mixture of GBLMA, HAMA, and MAMA to describe the estimation of conversion for each monomer (solvent: $CDCl_3$).

Anisole was utilized as an internal reference to quantify the amounts of remaining monomers in the reaction mixture using ^{1}H NMR spectrum. A sample for ^{1}H NMR spectrum was prepared by mixing reaction mixture and anisole (carefully weighed for both) and $CDCl_3$. Fortunately, the vinyl peaks of these three monomers are well-separated and therefore, their integrated intensities were compared to the integrated intensities of a methoxy peak in anisole to obtain their molar ratio to the mole number of anisole, which is calculated from the weight of anisole added. Using the initial concentrations for each monomer, the amount of polymerized unit for each monomer was estimated and hence, the conversion also can be calculated. This method is employed for the reactivity determination. The amounts of polymerized monomers were converted to the actual composition of the copolymer with the equation of F_A = d[A]/(d[A] + d[B]), where A and B represent two different monomers in reactivity ratio determination experiments.

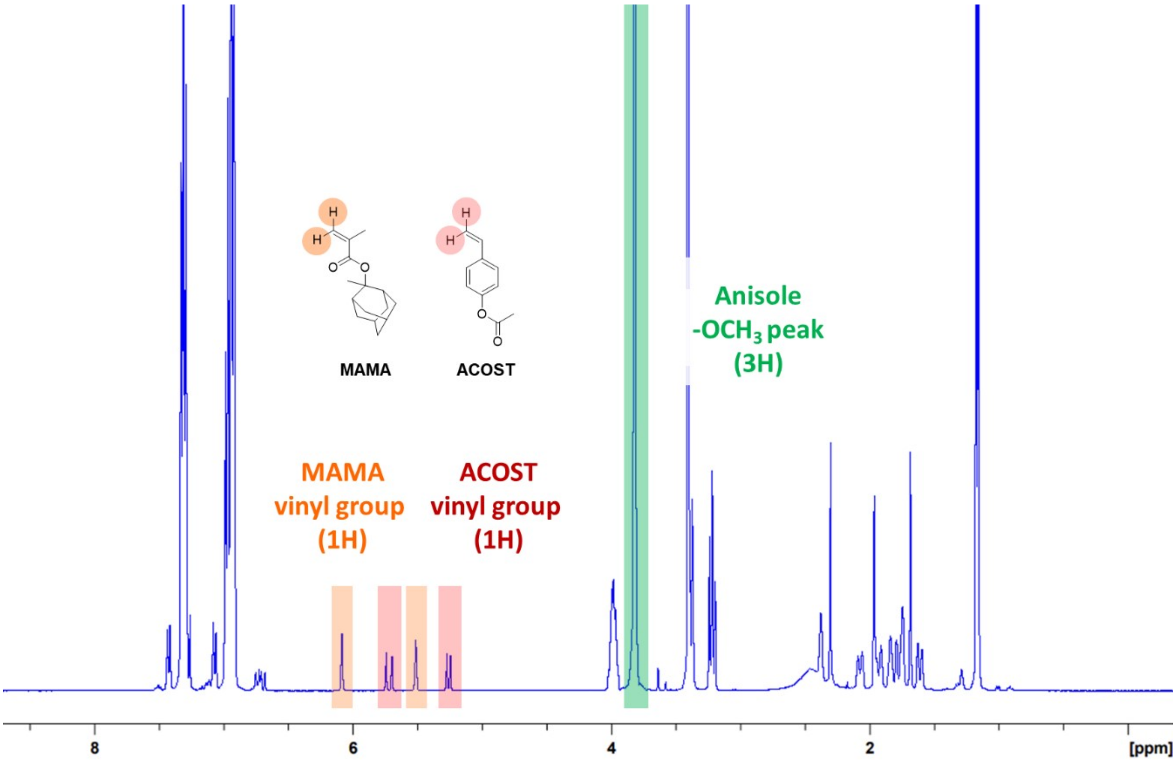

Figure S3. ^{1}H NMR spectrum of a copolymerization mixture of MAMA and ACOST to determine the conversion and actual composition with anisole as an internal reference (solvent: $CDCl_3$).

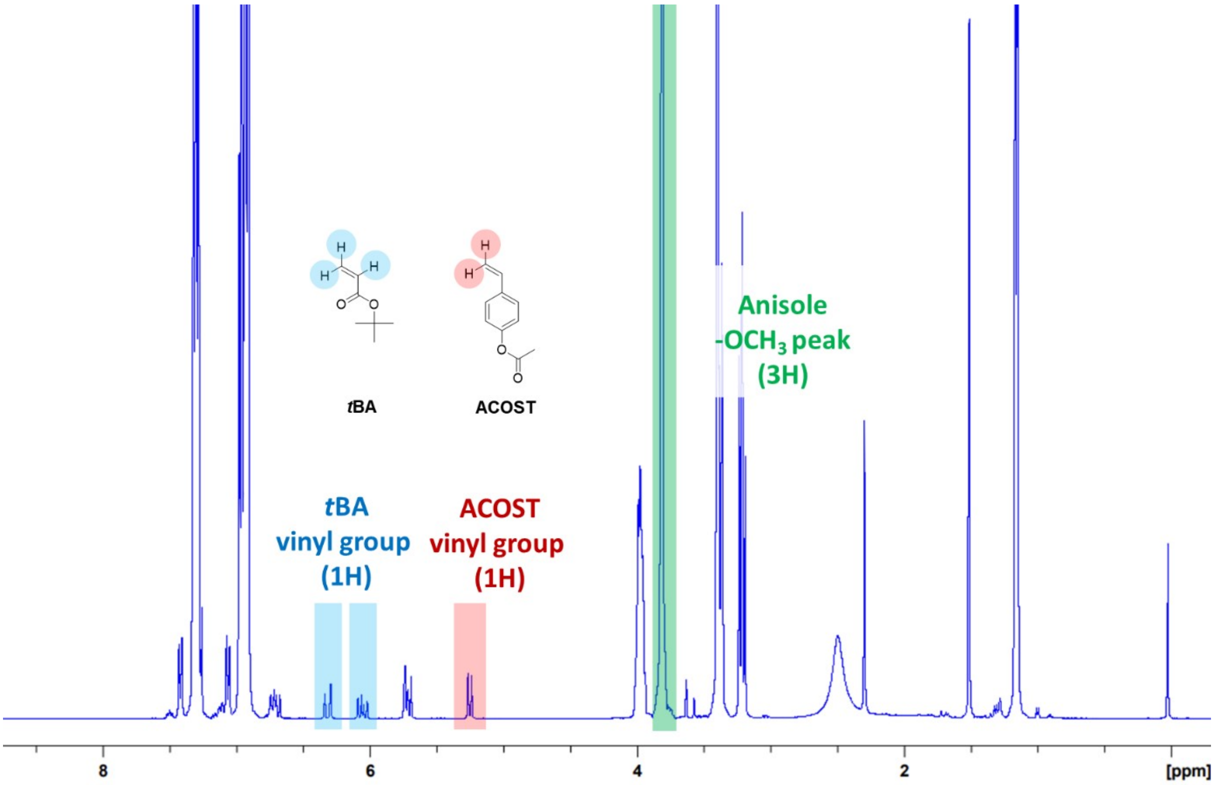

Figure S4. ^{1}H NMR spectrum of a copolymerization mixture of ACOST and *t*BA to determine the conversion and actual composition with anisole as an internal reference (solvent: $CDCl_3$).

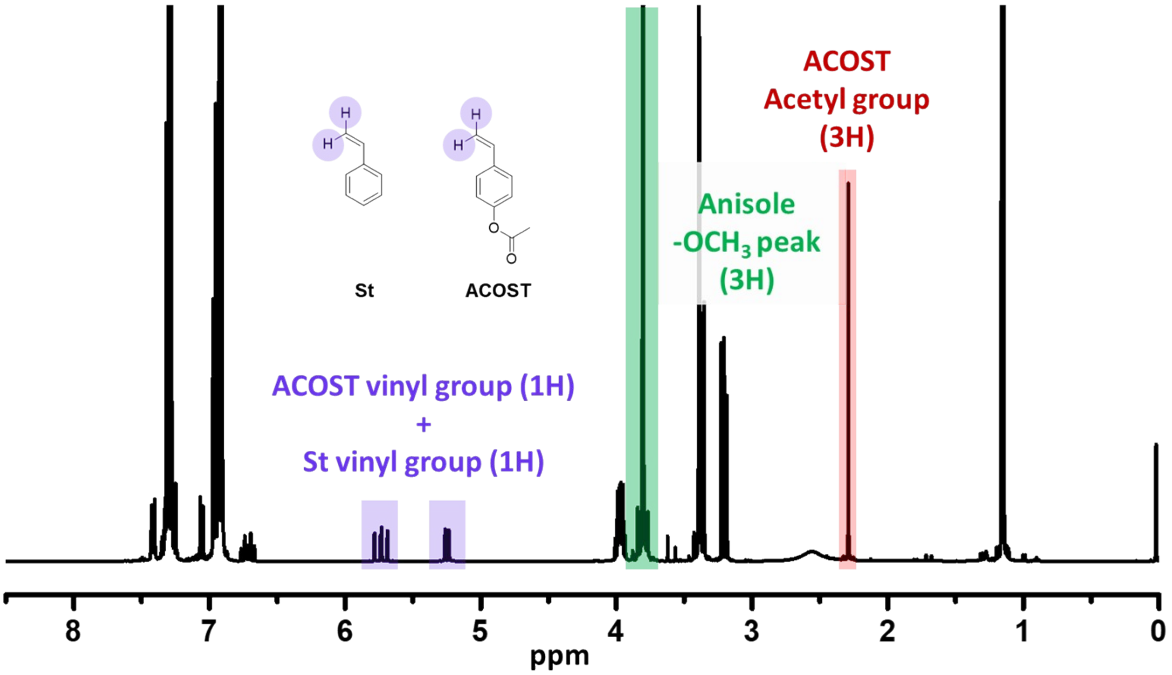

Figure S5. ^{1}H NMR spectrum of a copolymerization mixture of ACOST and St to determine the conversion and actual composition with anisole as an internal reference (solvent: CDCl$_3$). Because the proton signals from ACOST and St in 5-6 ppm are not well-separated, the number of ACOST calculated from the integrated intensity at ≈ 2.3 ppm was subtracted from the intensities in 5-6 ppm so that the integrated intensity of only St was isolated.

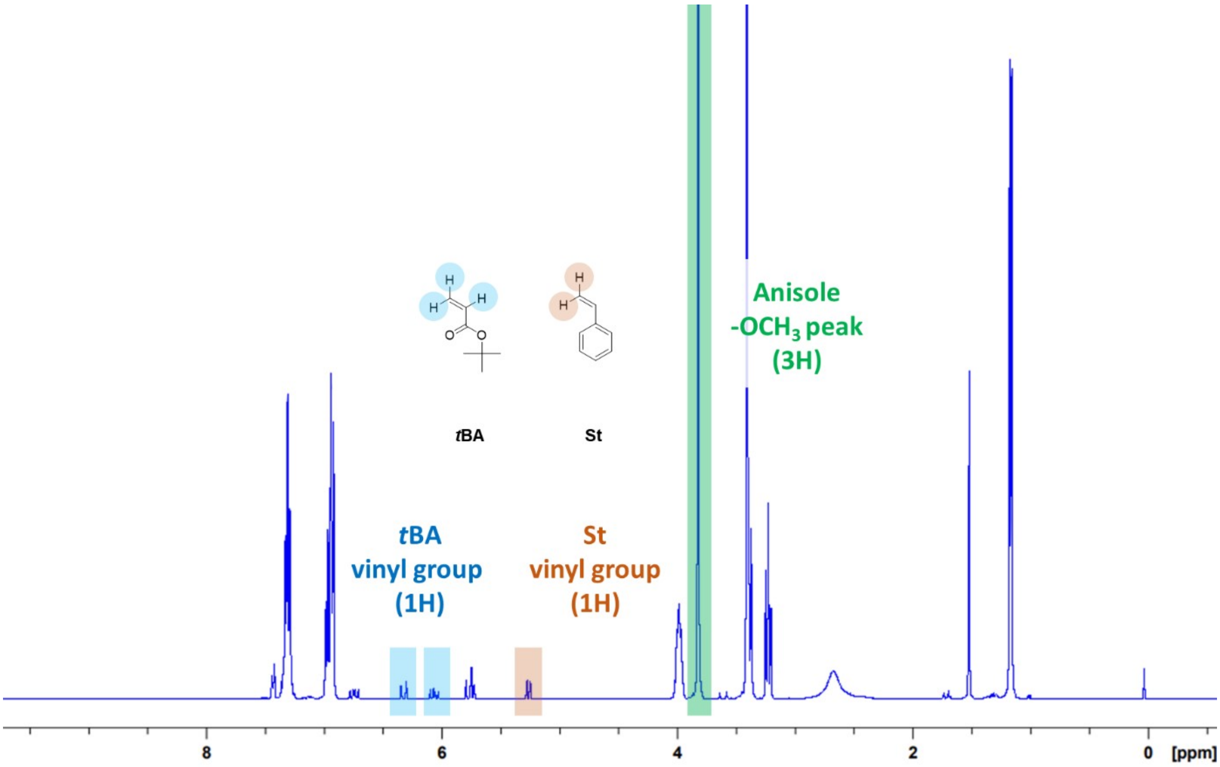

Figure S6. ^{1}H NMR spectrum of a copolymerization mixture of St and *t*BA to determine the conversion and actual composition with anisole as an internal reference (solvent: CDCl$_3$).

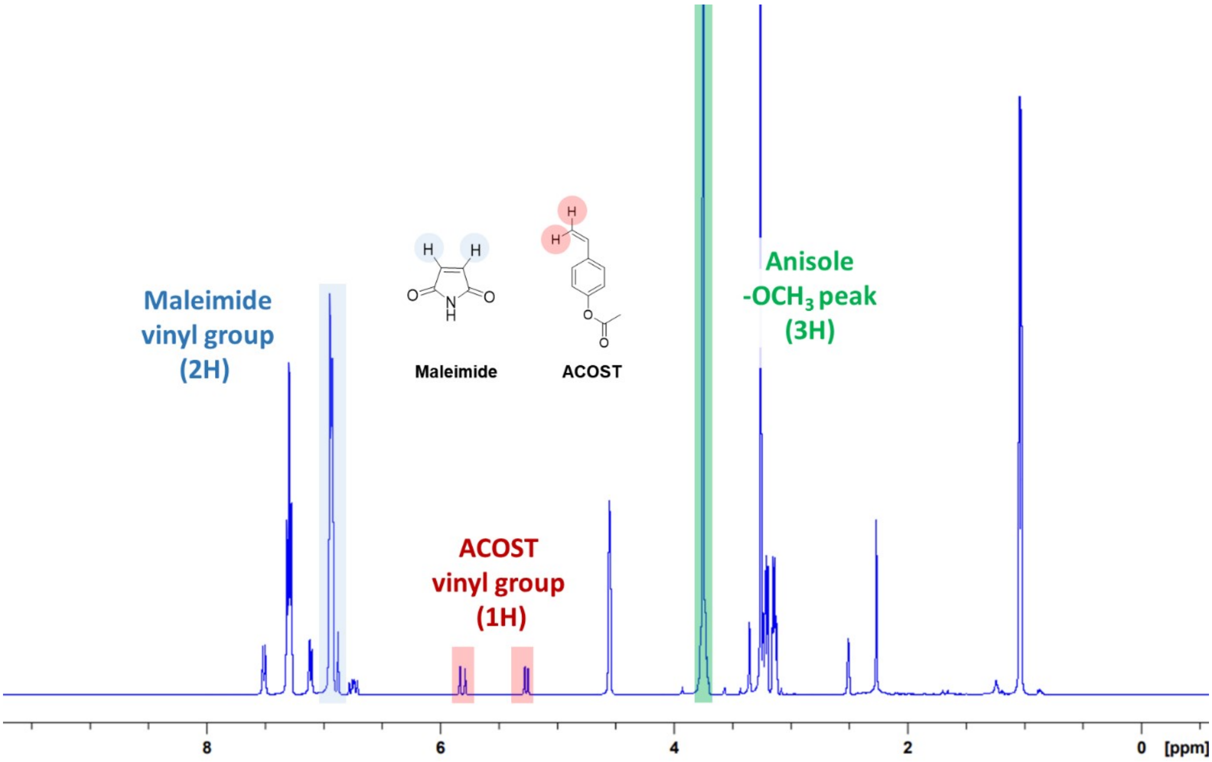

Figure S7. ^{1}H NMR spectrum of a copolymerization mixture of ACOST and MI to determine the conversion and actual composition with anisole as an internal reference (solvent: DMSO-d_6).

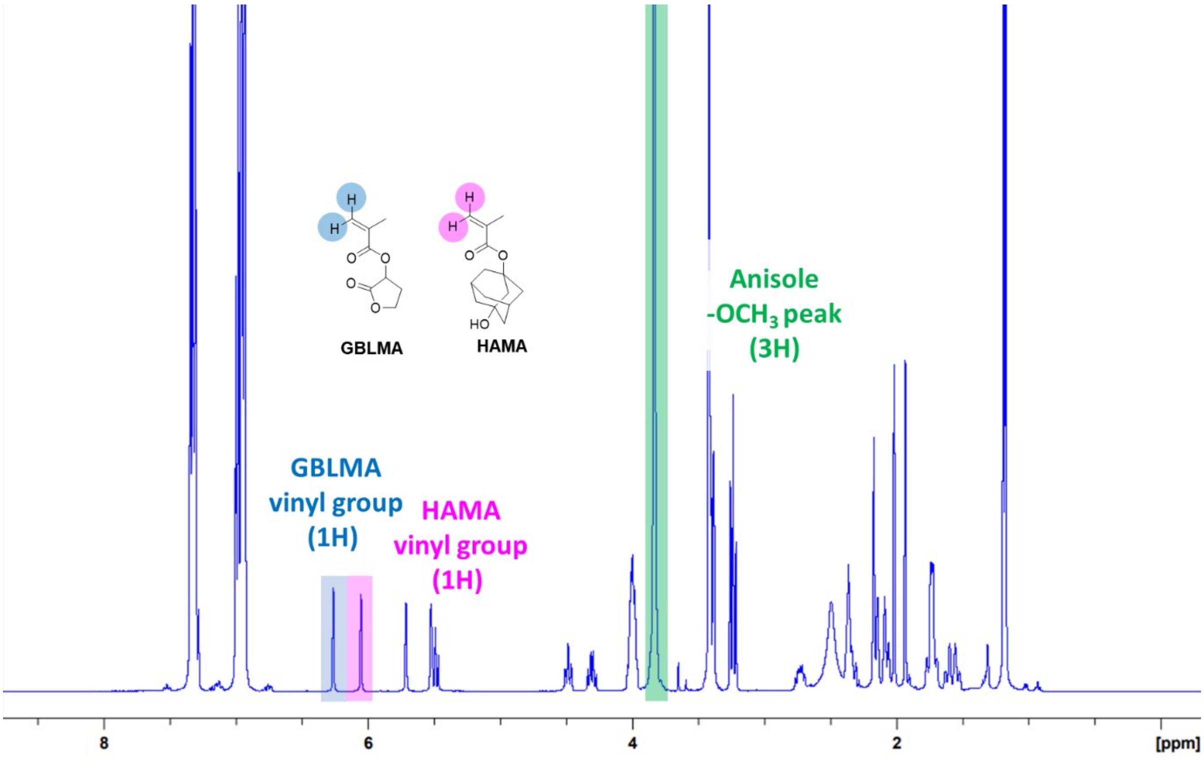

Figure S8. ^{1}H NMR spectrum of a copolymerization mixture of GBLMA and HAMA to determine the conversion and actual composition with anisole as an internal reference (solvent: $CDCl_3$).

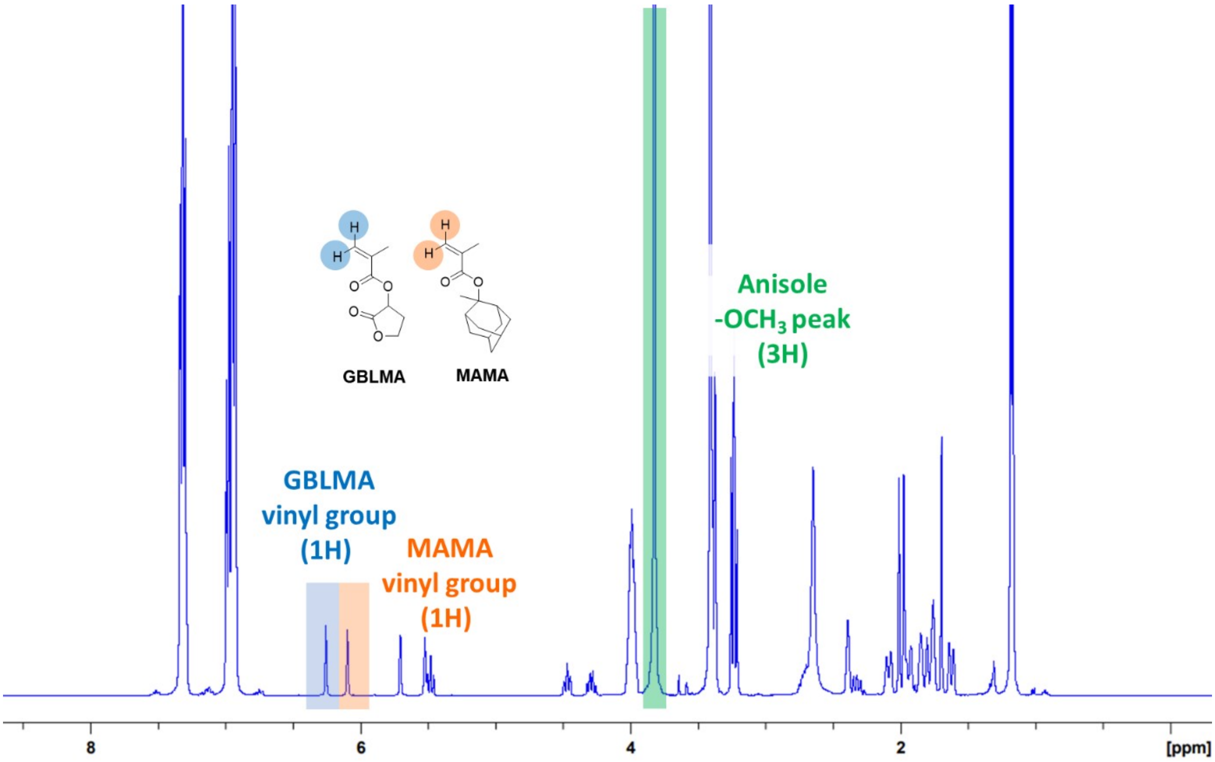

Figure S9. ^{1}H NMR spectrum of a copolymerization mixture of GBLMA and MAMA to determine the conversion and actual composition with anisole as an internal reference (solvent: $CDCl_3$).

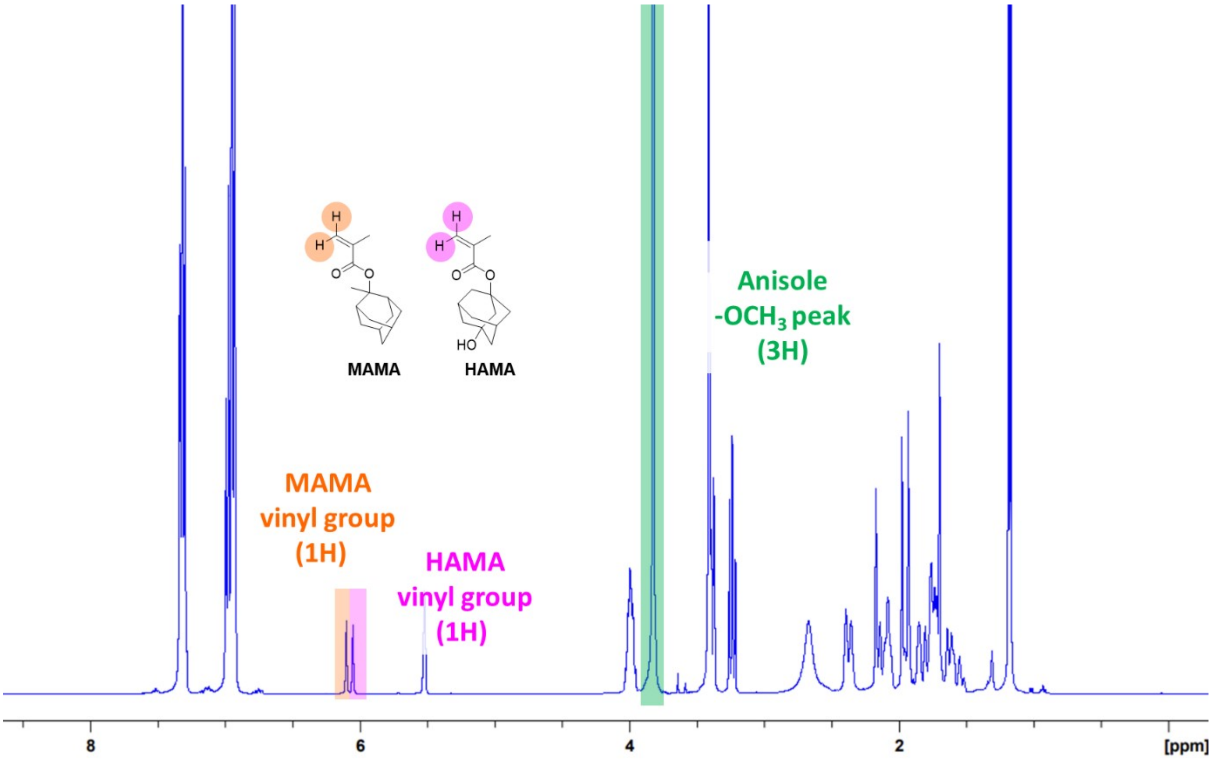

Figure S10. ^{1}H NMR spectrum of a copolymerization mixture of HAMA and MAMA to determine the conversion and actual composition with anisole as an internal reference (solvent: $CDCl_3$).

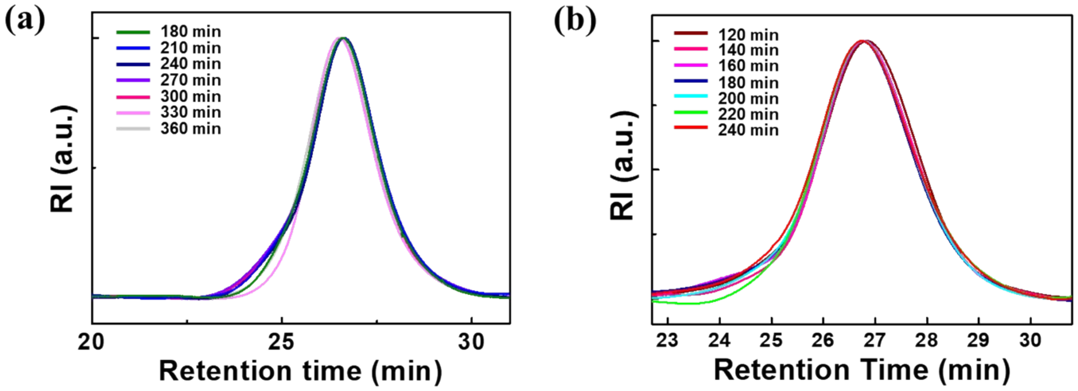

Figure S11. Representative SEC chromatograms acquired at different elution times for (a) poly(St-*r*-ACOST-*r*-*t*BA) and (b) poly(GBLMA-*r*-HAMA-*r*-MAMA). The residence time of the reaction system was 180 min.

Initiator	**Solvent**	**M_w (g/mol)**	**$Đ$**
ACVA	PGME 30 wt%	8,800	1.20
	PGME 20 wt%	9,700	1.19
	PGME 10 wt%	10,600	1.14
V-65	PGME 40 wt%	8,900	1.16
	PGME 34 wt%	9,800	1.17
	PGME 30 wt%	10,800	1.24

Table S2. M_w, and $Đ$ of the poly(St-*r*-ACOST-*r*-*t*BA)s synthesized under different conditions with the residence time of 180 min at 75 °C ($f_{St} : f_{ACOST} : f_{tBA} = 0.25 : 0.60 : 0.15$). The samples were collected for 30 min.

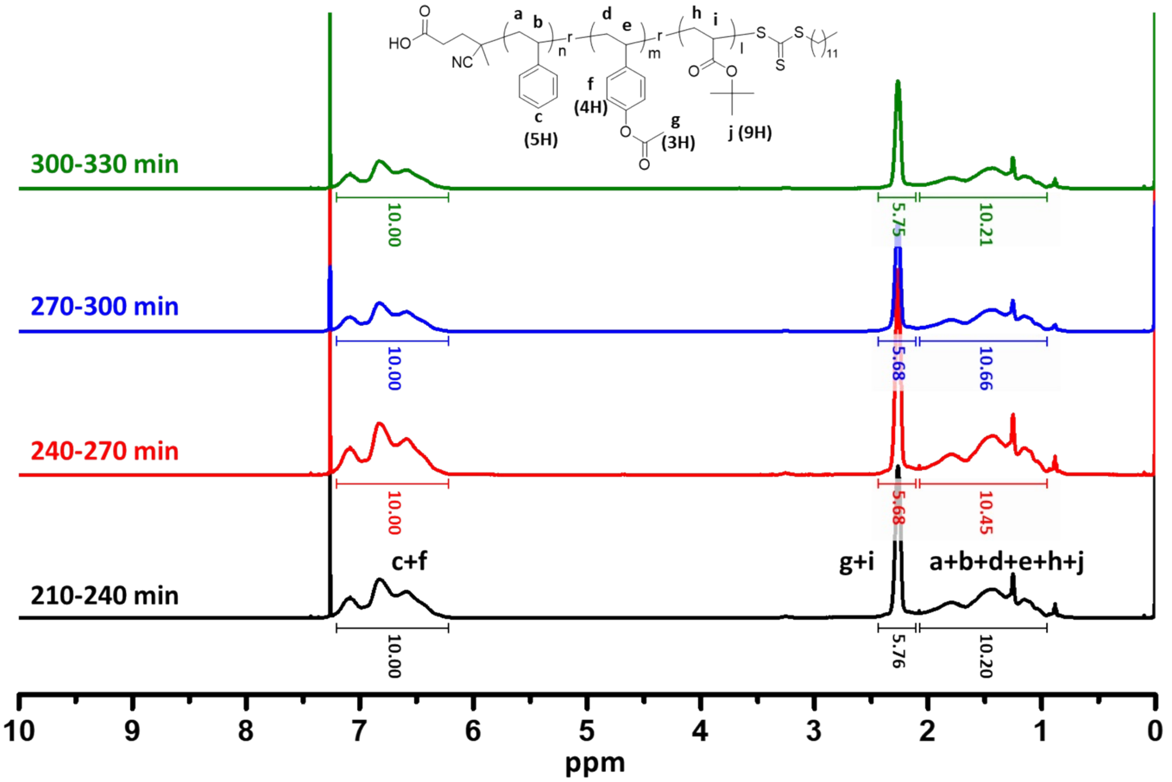

Figure S12. ^{1}H NMR spectra of four poly(St-*r*-ACOST-*r*-*t*BA) copolymers samples obtained at different time ranges. All samples were copolymerized in flow at 75 °C for 180 min (f_{St} : f_{ACOST} : $f_{t\mathrm{BA}}$ = 0.25 : 0.60 : 0.15; PGME: 30 wt%; initiator: V-65).

	M_w (g/mol)	$Đ$	F_{St} : F_{ACOST} : $F_{t\mathrm{BA}}$
210-240 min	10,400	1.31	0.240 : 0.644 : 0.116
240-270 min	10,600	1.30	0.227 : 0.654 : 0.119
270-300 min	10,800	1.24	0.228 : 0.651 : 0.121
300-330 min	10,500	1.31	0.229 : 0.665 : 0.106
Average	10,575	1.29	0.231 : 0.654 : 0.116
Standard deviation	171	0.03	0.006 : 0.009 : 0.007
Coefficient of variation × 100	1.61%	2.33%	3.24%

Table S3. M_w, $Đ$, and actual composition values of the poly(St-*r*-ACOST-*r*-*t*BA) samples obtained at different time ranges. All samples correspond to the samples of the spectra in **Figure S12**. The coefficient of variation for the compositions is the averaged value of the coefficients of variation from F_{St}, F_{ACOST}, and $F_{t\mathrm{BA}}$.

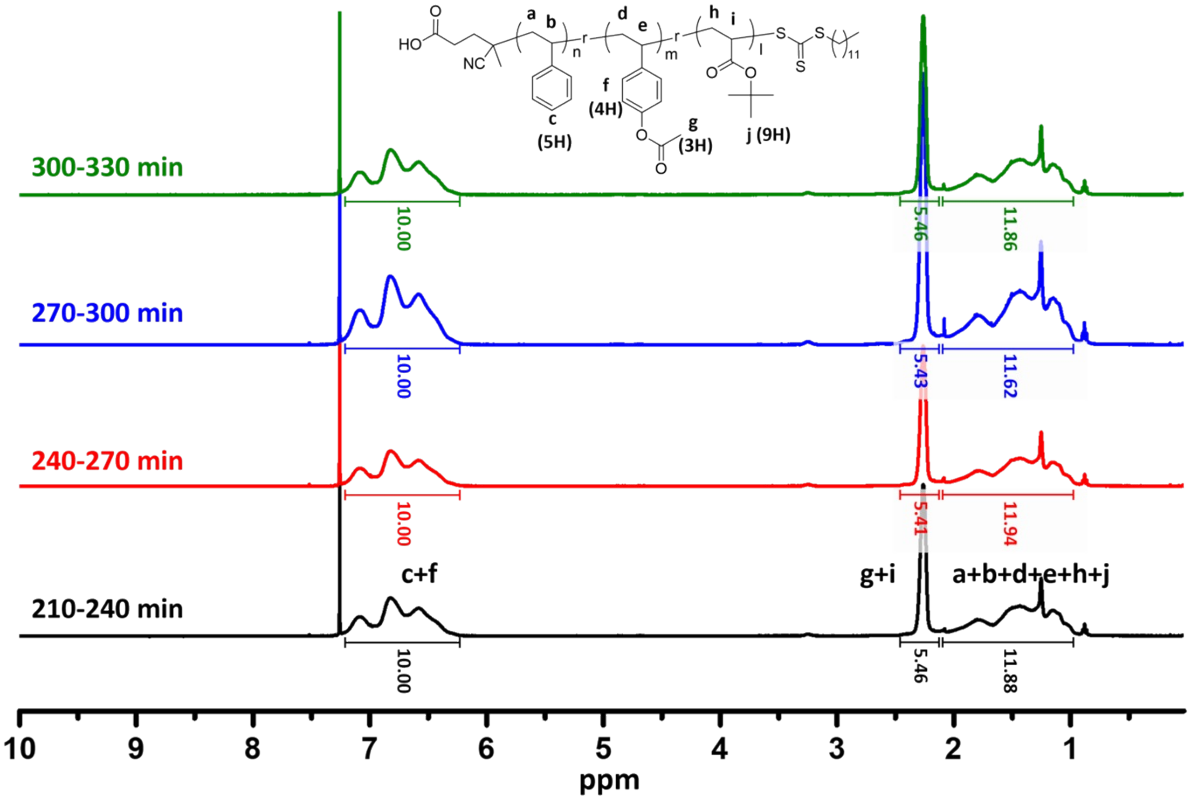

Figure S13. ^{1}H NMR spectra of four poly(St-*r*-ACOST-*r*-*t*BA) copolymers samples obtained at different time ranges. All samples were copolymerized in flow at 75 °C for 180 min ($f_{St} : f_{ACOST} : f_{tBA}$ = 0.25 : 0.60 : 0.15; PGME: 21 wt%; initiator: ACVA).

	M_w (g/mol)	**$Đ$**	**$F_{St} : F_{ACOST} : F_{tBA}$**
210-240 min	9,100	1.16	0.238 : 0.602 : 0.160
240-270 min	9,300	1.16	0.244 : 0.595 : 0.162
270-300 min	9,500	1.17	0.241 : 0.606 : 0.152
300-330 min	9,700	1.19	0.238 : 0.603 : 0.159
Average	9,400	1.17	0.240 : 0.601 : 0.158
Standard deviation	258	0.014	0.003 : 0.005 : 0.004
Coefficient of variation × 100	2.75%	1.21%	1.57%

Table S4. M_w, $Đ$, and actual composition values of the poly(St-*r*-ACOST-*r*-*t*BA) samples obtained at different time ranges. All samples correspond to the samples of the spectra in **Figure S13**. The coefficient of variation for the compositions is the averaged value of the coefficients of variation from F_{St}, F_{ACOST}, and F_{tBA}.

Determination of reactivity ratio[1-3]

The reactivity ratios, r_1 and r_2, can be empirically determined with Mayo-Lewis equation:

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \quad (1)$$

where f_1 and F_1 are initial feed ratio of monomer 1 and actual composition of monomer 1 in a resulting copolymer. r_1 and r_2 values are obtained by fitting the plot of f_1 and F_1 with nonlinear least square (NLS) fitting with the equation (1). Fineman-Ross (FR) method uses a rearranged form of the Mayo-Lewis equation,

$$G = Hr_1 - r_2 \quad (2)$$

where G and H are $[f_1(2F_1 - 1)]/[(1 - f_1)F_1]$ and $[f_1^2(1 - F_1)]/[(1 - f_1)^2F_1]$. the Kelen-Tüdös (KT) method is also utilized for the reactivity ratio determination, in which the biased results at low or high monomer concentration in the FR method are minimized. In the KT method, an arbitrary constant, α, is introduced to address the issue of unweighted compositional data in FR method the compositional data, as given in the equations:

$$\alpha = (H_{min}H_{max})^{0.5} \quad (3)$$

$$\eta = \left[r_1 + \frac{r_2}{\alpha}\right]\mu - \frac{r_2}{\alpha} \quad (4)$$

where H_{min} and H_{max} are the minimum and the maximum H values in equation (2), and η and μ are $G/(\alpha+H)$ and $H/(\alpha+H)$, respectively.

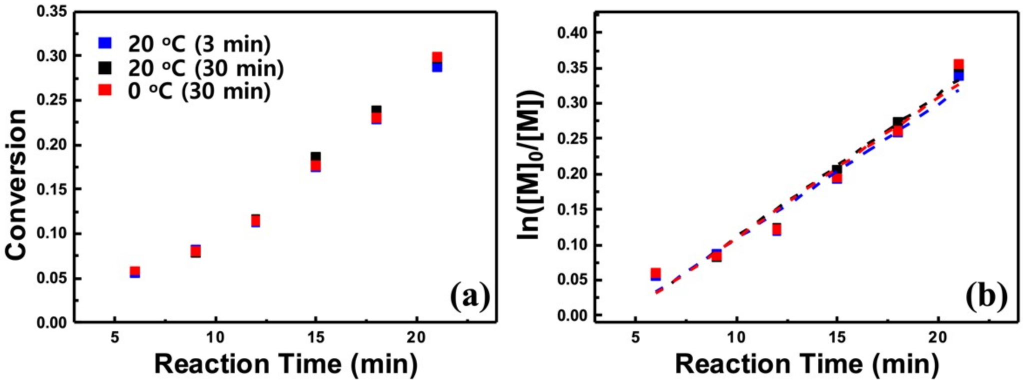

Figure S14. Plots showing (a) total conversion and (b) ln([M]$_0$/[M]) obtained from copolymerization of GBLMA and HAMA (f_{GBLMA} = 0.500) in flow as a function of time under different quenching conditions. Right after the flow of the reaction mixture exited the immersed section in heating oil bath, the tube was exposed to the cooling section at 20 °C for 3 min, or at 20 °C for 30 min, or 0 °C for 30 min. Extracted k_p^{app} values were 0.0190 ± 0.0017 (20°C for 3 min), 0.0201 ± 0.0017 (20°C for 30 min), and 0.0198 ± 0.0021 (0 °C for 30 min). F_{GBLMA} values at the conversion of ≈ 0.1 were 0.526 (20 °C for 3 min), 0.513 (20 °C for 30 min), and 0.528 (0 °C for 30 min).

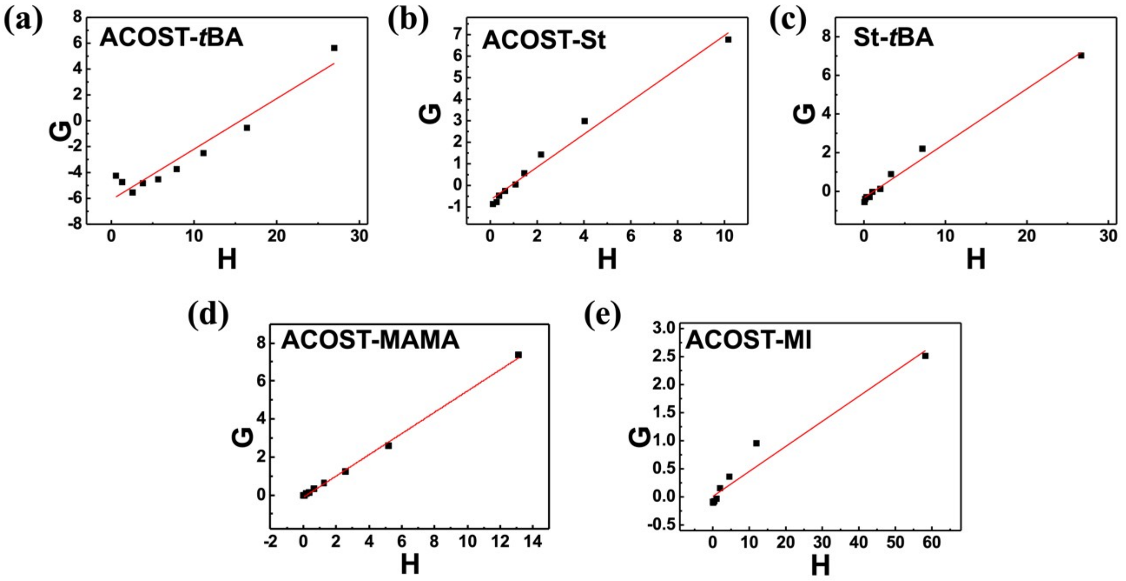

Figure S15. Plots showing reactivity ratio determination with Fineman-Ross method for the pairs of (a) ACOST/*t*BA, (b) ACOST/St, (c) St/*t*BA, (d) ACOST/MAMA, and (e) ACOST/MI.

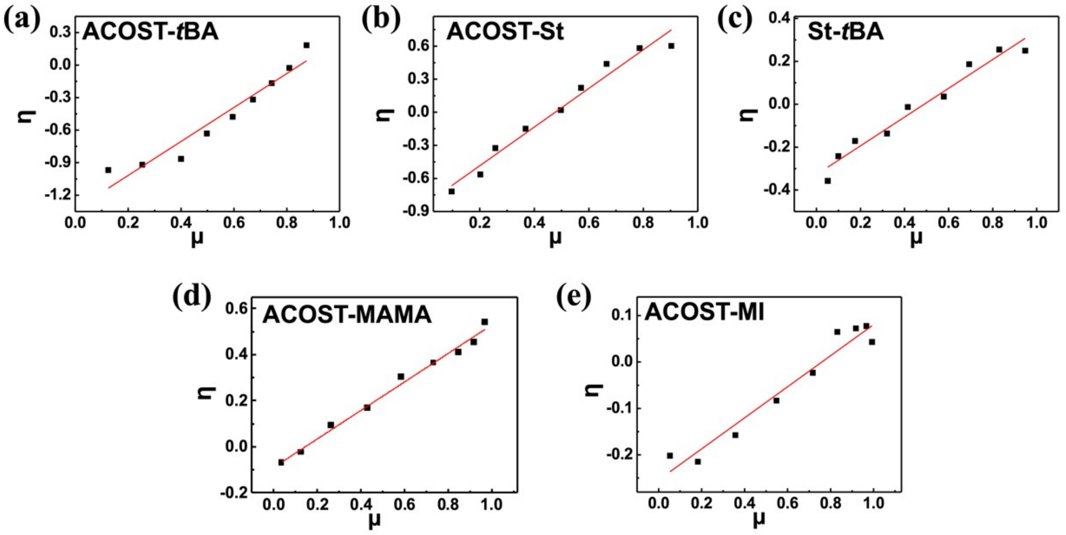

Figure S16. Plots showing reactivity ratio determination with Kelen-Tüdös method for the pairs of (a) ACOST/*t*BA, (b) ACOST/St, (c) St/*t*BA, (d) ACOST/MAMA, and (e) ACOST/MI.

Monomer A / Monomer B	**Fineman-Ross**		**Kelen-Tüdös**	
	r_{AB}	r_{BA}	r_{AB}	r_{BA}
ACOST / MAMA	0.56 ± 0.01	0.09 ± 0.05	0.53 ± 0.00	0.04 ± 0.01
ACOST / *t*BA	0.39 ± 0.04	6.10 ± 0.49	0.24 ± 0.02	5.12 ± 0.36
ACOST / St	0.76 ± 0.04	0.68 ± 0.15	0.92 ± 0.01	0.91 ± 0.09
St / *t*BA	0.28 ± 0.01	0.34 ± 0.10	0.34 ± 0.00	0.48 ± 0.04
ACOST / MI	0.04 ± 0.00	0.01 ± 0.07	0.08 ± 0.00	0.10 ± 0.01

Table S5. Reactivity ratio values in continuous flow RAFT copolymerization of five monomer pairs including styrenic monomers determined with Fineman-Ross and Kelen-Tüdös methods.

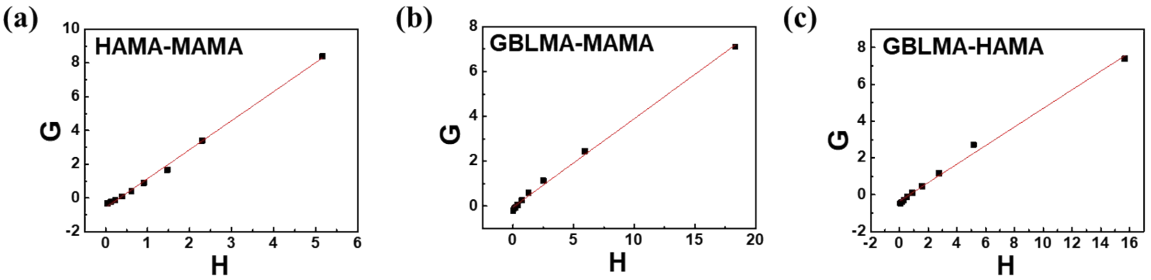

Figure S17. Plots showing reactivity ratio determination with Fineman-Ross method for the pairs of (a) HAMA/MAMA, (b), GBLMA/MAMA, and (c) GBLMA/HAMA.

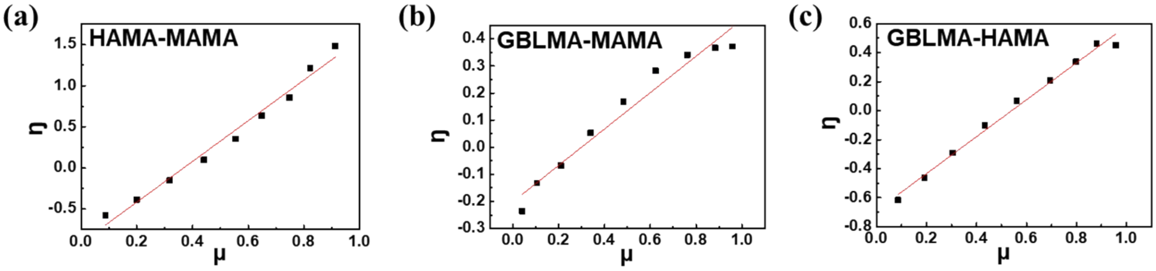

Figure S18. Plots showing reactivity ratio determination with Kelen-Tüdös method for the pairs of (a) HAMA/MAMA, (b), GBLMA/MAMA, and (c) GBLMA/HAMA.

Monomer A / Monomer B	**Fineman-Ross**		**Kelen-Tüdös**	
	r_{AB}	r_{BA}	r_{AB}	r_{BA}
GBLMA / HAMA	0.50 ± 0.01	0.35 ± 0.08	0.58 ± 0.00	0.47 ± 0.02
GBLMA / MAMA	0.39 ± 0.01	0.05 ± 0.05	0.47 ± 0.00	0.16 ± 0.02
HAMA / MAMA	1.72 ± 0.03	0.57 ± 0.06	1.56 ± 0.01	0.45 ± 0.04

Table S6. Reactivity ratio values in continuous flow RAFT copolymerization of three methacrylate monomer pairs determined with Fineman-Ross and Kelen-Tüdös methods.

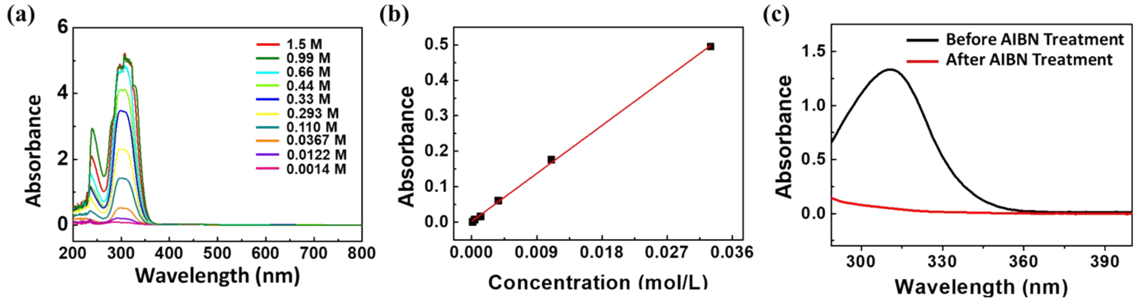

Figure S19. (a) UV/vis absorption spectra of CDSTSP with a concentration variation, and (b) the plot of absorbance at 306 nm versus the concentration of CDSTSP, and (c) UV/vis absorption spectra of poly(ACOST-*r*-MAMA) before (black) and after (red) AIBN treatment.

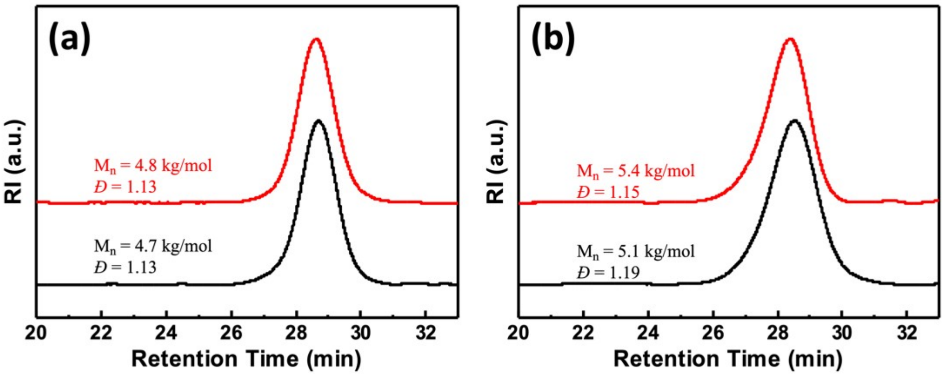

Figure S20. SEC traces of poly(ACOST-*r*-MAMA) copolymer samples synthesized by (a) batch reaction and (b) continuous flow reaction before (bottom; black) and after (top; red) AIBN treatment for the end group modification.

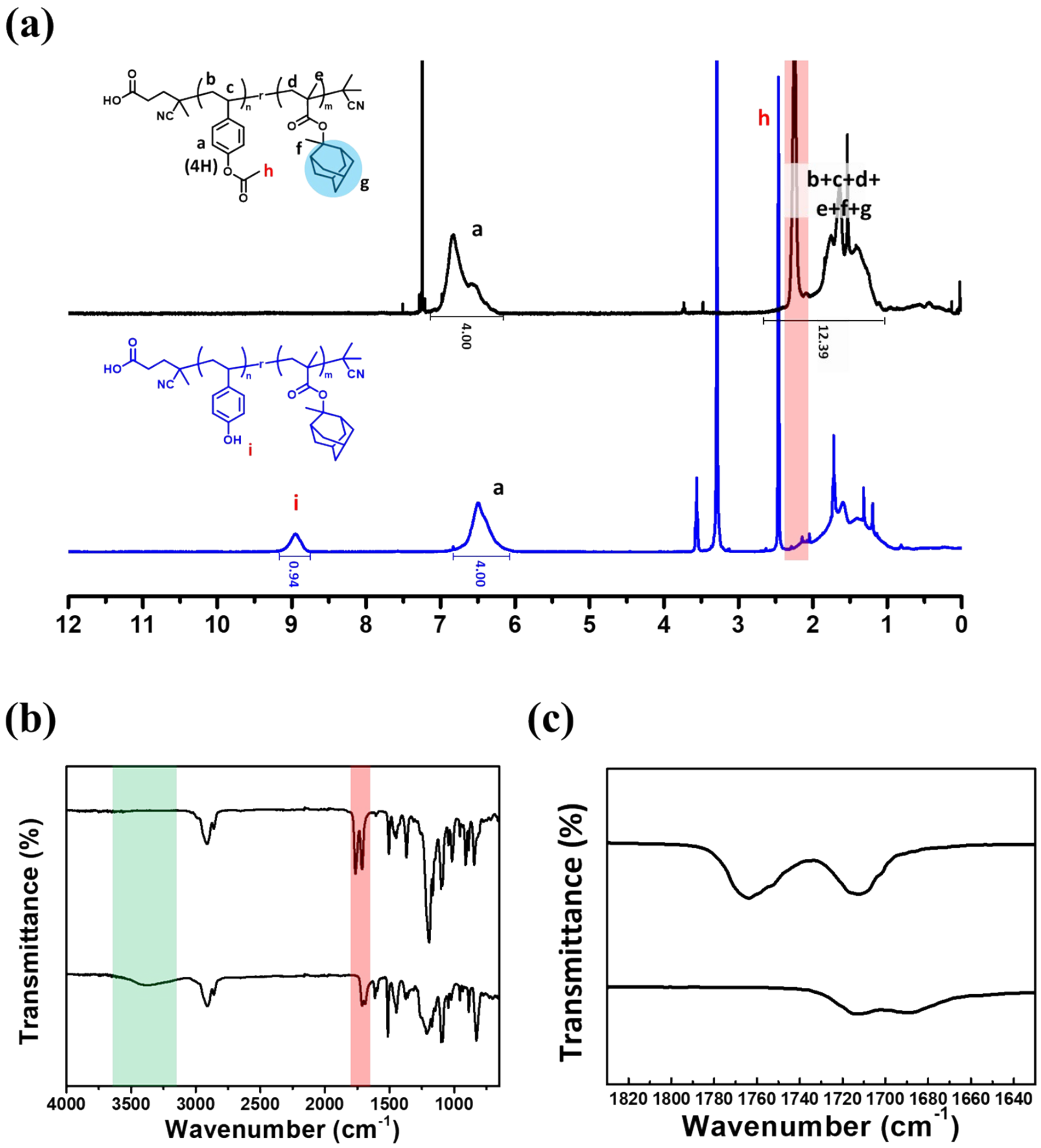

Figure S21. (a) ^{1}H NMR spectra of poly(ACOST-*r*-MAMA) (top; solvent: CDCl$_3$) and poly(HSt-*r*-MAMA) (bottom; solvent: DMSO-d$_6$), and (b) FT-IR spectrum of poly(ACOST-*r*-MAMA) (top) and poly(HSt-*r*-MAMA) (bottom) and (c) zoomed-in spectrum in 1810-1630 cm^{-1}. In ^{1}H NMR spectrum, the peak at ≈ 2.2 ppm disappeared after deacetylation (blue-shaded region). In FT-IR spectrum, the peak at ≈ 1760 cm^{-1} (assigned to carbonyl in acetyl group; red-shaded region) disappeared, and the peak at ≈ 3450 cm^{-1} (assigned to phenol group; green-shaded region) emerged, confirming successful deacetylation.

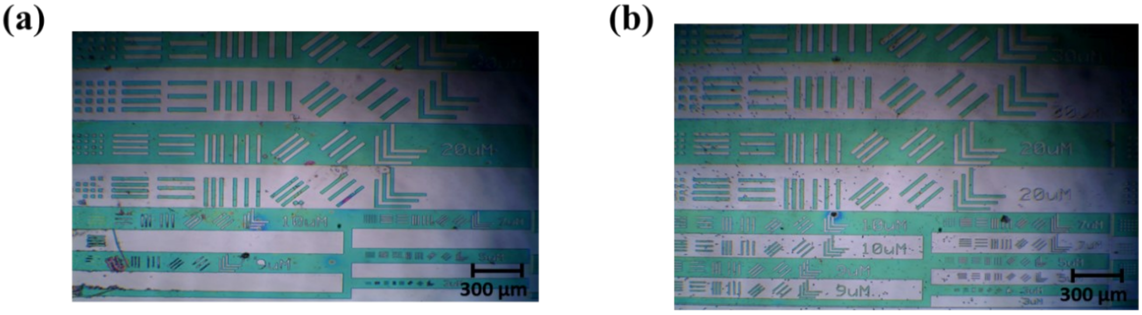

Figure S22. Optical microscopic images of patterns fabricated with the CAR formulated with the poly(HSt-*r*-MAMA) (a) before and (b) after the removal of trithiocarbonate end group.

References

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