Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Gradient Copolymers of Styrene-Methyl Acrylate and Styrene-Acrylic Acid by Organostibine-mediated Controlled/Living Radical Polymerization and Their Glass Transition Behaviors

Jinping Zhang,[a] Jun Li,[a] Liyan Huang, Zhengping Liu*

[a] Institute of Polymer Chemistry and Physics, Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China. Fax: 86-10-58802075; Tel: 86-10-58806896; E-mail: jun@bnu.edu.cn

Table of Contents

1. Preparation and characterization of poly(St-grad-MA) copolymer with high molecular weight

Table S1. Copolymerization data for the semi-batch SBRP poly(St-grad-MA)[a]

Reaction Time (h)	M_n[b]	PDI[b]	DP[c]	$F_{cum,St}$[d]	$F_{cum,MA}$[d]
12	11500	1.43	115	0.785	0.215
24	21800	1.25	220	0.729	0.271
30	28300	1.23	288	0.684	0.316
36	34000	1.19	348	0.647	0.353
47.2	39700	1.25	413	0.563	0.437

[a] The initial feeding molar ratio of St to St and MA ($f(St)_0$) was 50%; Total feeding amount of St and MA was 250 mmol; AIBN was 0.025 mmol; ethyl 2-dimethylstibanyl -2-methylpropionate was 0.5 mmol; MA adding rate was 0.004 mLmin^{-1}. [b] Measured by GPC (THF, 40 °C, flow rate 1 mL min^{-1}) against polystyrene standards. [c] calculated by Mn, $F_{cum,St}$, $F_{cum,MA}$ and the molecule weight of St and MA. [d] $F_{cum,St}$: St cumulative amount of the final polymer, calculated by ^{1}H NMR (please refer to the ESI, section (2)); $F_{cum,MA}=1-F_{cum,St}$.

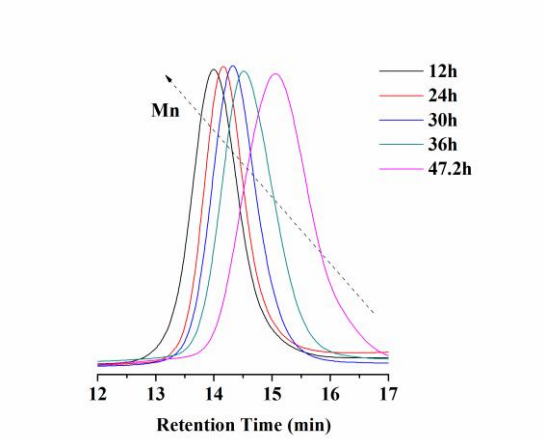


Figure S1-1. GPC curves of poly(St-grad-MA) copolymers at different reaction time.

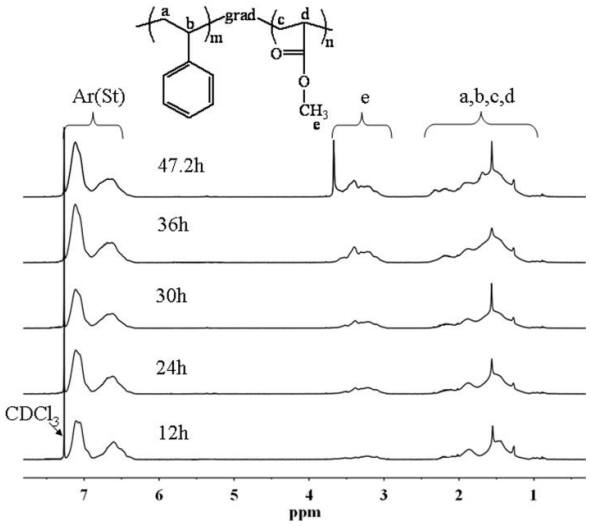


Figure S1-2. ^{1}H NMR spectra of poly(St-grad-MA) copolymers at different reaction time.

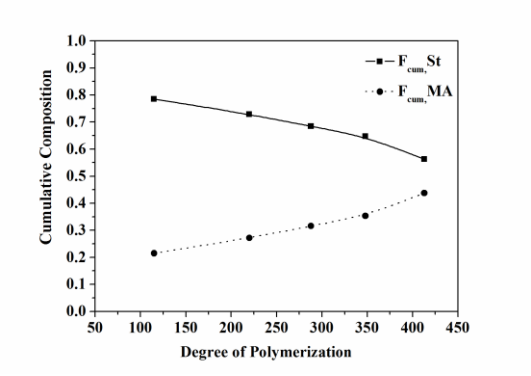


Figure S1-3. Cumulative composition of poly(St-grad-MA) versus the degree of polymerization.

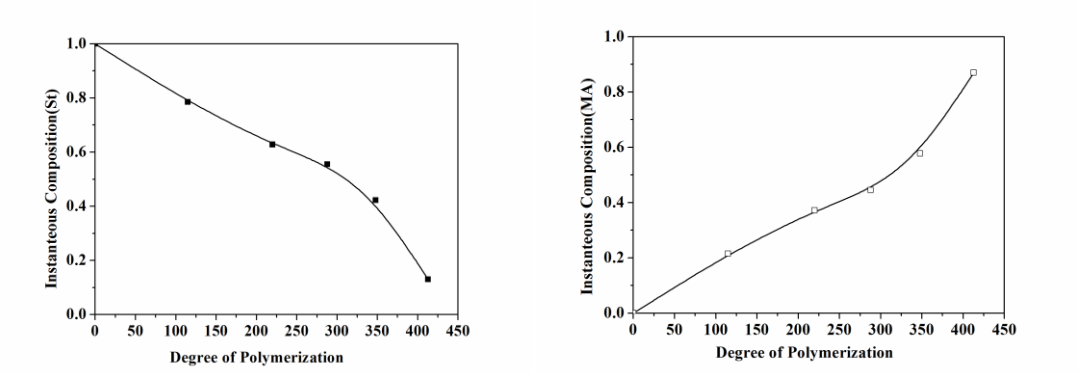


Figure S1-4. Instantaneous composition of poly(St-grad-MA) versus the degree of polymerization.

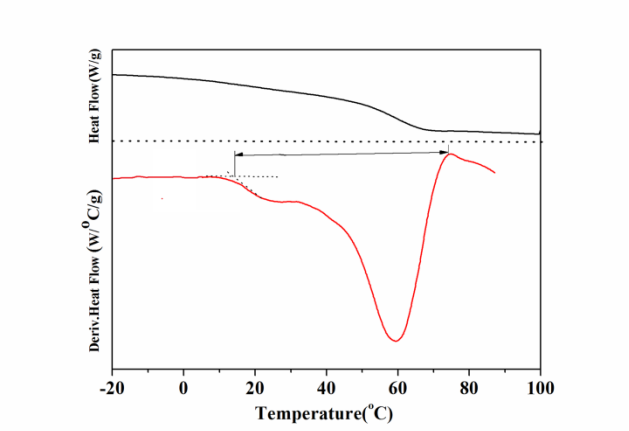


Figure S1-5. DSC curves for poly(St-grad-MA) (heating method: 10k min^{-1}).

T_g: 59.3 °C; T_g Breadth: 60.7 °C (onset: 15.1 °C, endset: 75.8 °C)

2. Derivation of equation (1) $F_{cum},St=\frac{6A_1}{3A_1+5A_2}$

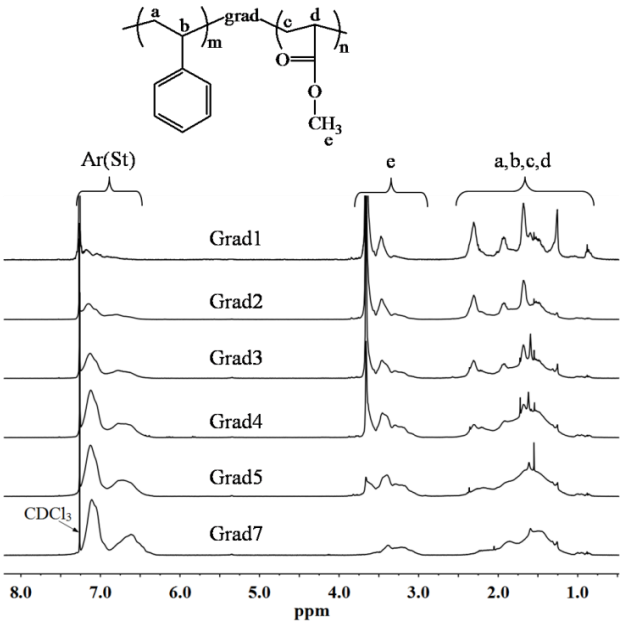


Figure S2. ^{1}H NMR spectra of poly(St-grad-MA) copolymers.

In the ^{1}H NMR spectra:

(1) Signals of 6.6~7.3 ppm assign to the 5 aromatic protons from St units. The peak area is A_1;

(2) Signals of 0.8~3.7 ppm assign to the 9 aliphatic protons, 3 from St units and 6 from MA units. The peak area is A_2.

Thus, the molar ratio of St/MA incorporated in the resulting copolymer is:

$$\frac{m}{n}=\frac{\frac{A_1}{5}}{\frac{(A_2-3\times\frac{A_1}{5})}{6}}=\frac{6A_1}{5A_2-3A_1}$$

And then, the cumulative composition of St (F_{cum},St) can be calculated as:

$$F_{cum},St=\frac{m}{m+n}=\frac{6A_1}{3A_1+5A_2}$$

3. Proportion of MAMAMA sequence in MA units of gradient copolymers calculated by ^{1}H NMR spectra

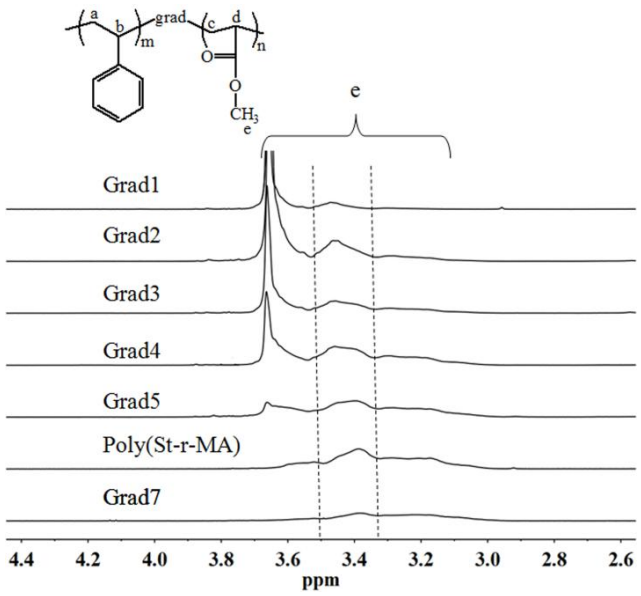


Figure S3. ^{1}H NMR spectra of poly(St-grad-MA) and Poly(St-r-MA) copolymers.

The signals of $-CH_3$ at 3.66~3.52, 3.49~3.38 and 3.30~3.18 ppm can respectively be assigned to the MA-centered triads of MAMAMA, MAMASt and StMASt. Thus, the proportion of MAMAMA sequences in the whole MA units ($\overline{F}(MAMAMA)$) were calculated by the ratio of the peak areas of MAMAMA sequences at 3.66~3.52 ppm to the whole peak areas of MA units at 3.66~3.18 ppm. The calculated data is listed in Table S3. The proportion of MAMAMA in Grad5 is much higher than that in the poly(St-r-MA) with similar F_{cum},MA. The ^{1}H NMR spectra comparisons of the copolymers with other compositions give the same result.

Table S3. Calculated $\overline{F}(MAMAMA)$.

Sample	F_{cum},MA[a]	$\overline{F}(MAMAMA)$[b]
Grad1	0.895	0.787
Grad2	0.805	0.694
Grad3	0.699	0.571
Grad4	0.579	0.398
Grad5	**0.486**	**0.278**
Poly(St-r-MA)	**0.479**	**0.150**
Grad7	0.292	0.096

[a] See Table 2 in the article. [b] ^{1}H NMR spectra for different compositions of poly(St-r-MA) were reported in: *(a) M. A. Semsarzadeh and M. Abdollahi,* ***J. Appl. Polym. Sci****., 2009, 114, 2509-2521. (b) (K. karaky, E.Pere, C.Pouchan, H. Garay, A. Khoukh, J. Francois, J. Desbrieres, L. Billon,* ***New J. Chem****., 2006, 30, 698-705).* (c) *G. Van Doremaele, A. L. German, N. De Vries and G. Van der Velden,* ***Macromolecules****, 1990, 23, 4206-4215.*

4. ^{1}H NMR spectra of gradient copolymers at different reaction time

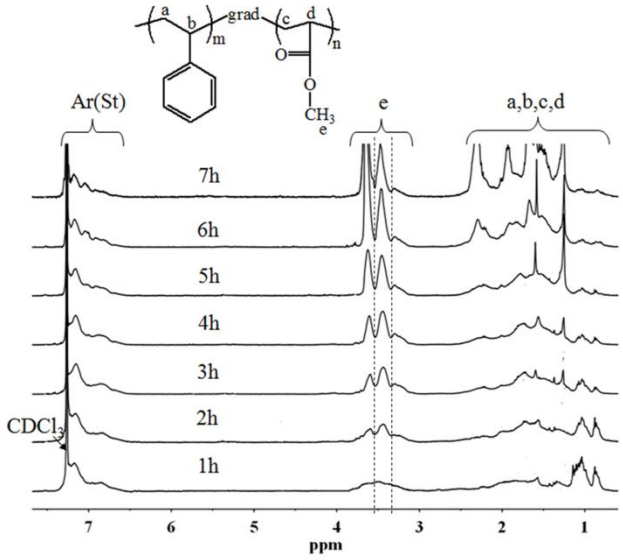


Figure S4-1. ^{1}H NMR spectra of Grad1 at different reaction time

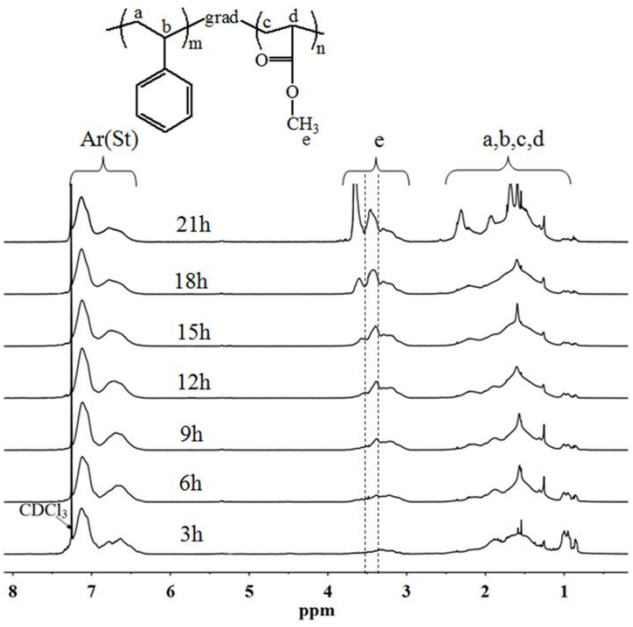


Figure S4-2. ^{1}H NMR spectra of Grad3 at different reaction time

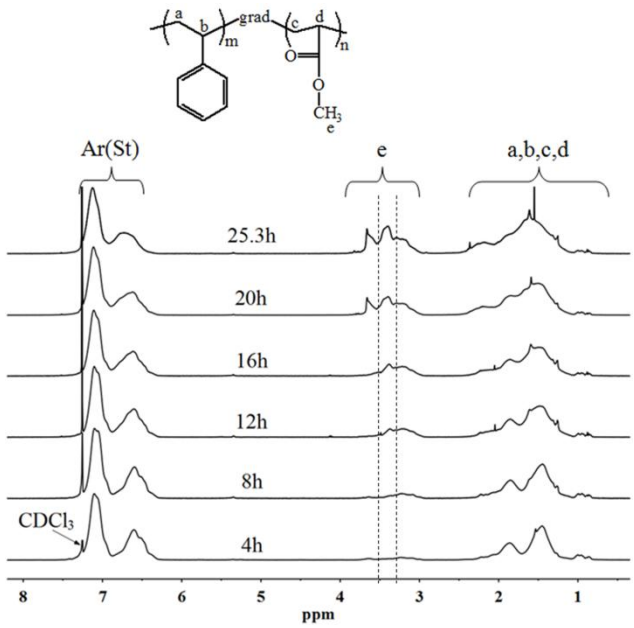


Figure S4-3. ^{1}H NMR spectra of Grad5 at different reaction time

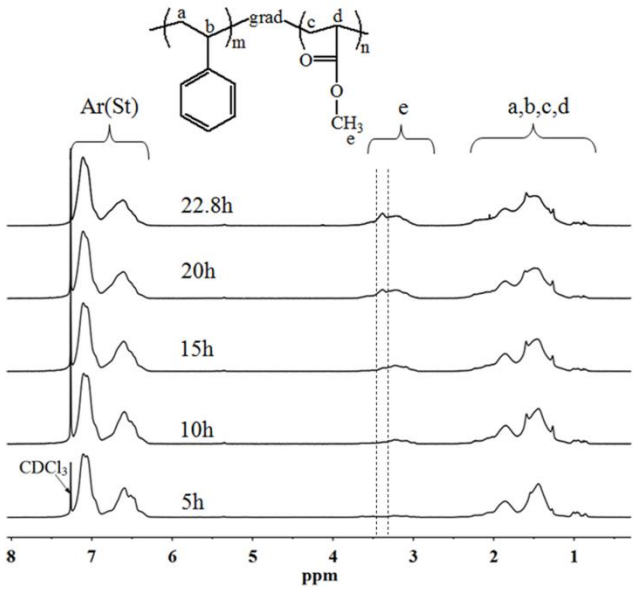


Figure S4-4. ^{1}H NMR spectra of Grad7 at different reaction time

5 . ^{1}H NMR spectra of hydrolysates and calculation of F_{cum}

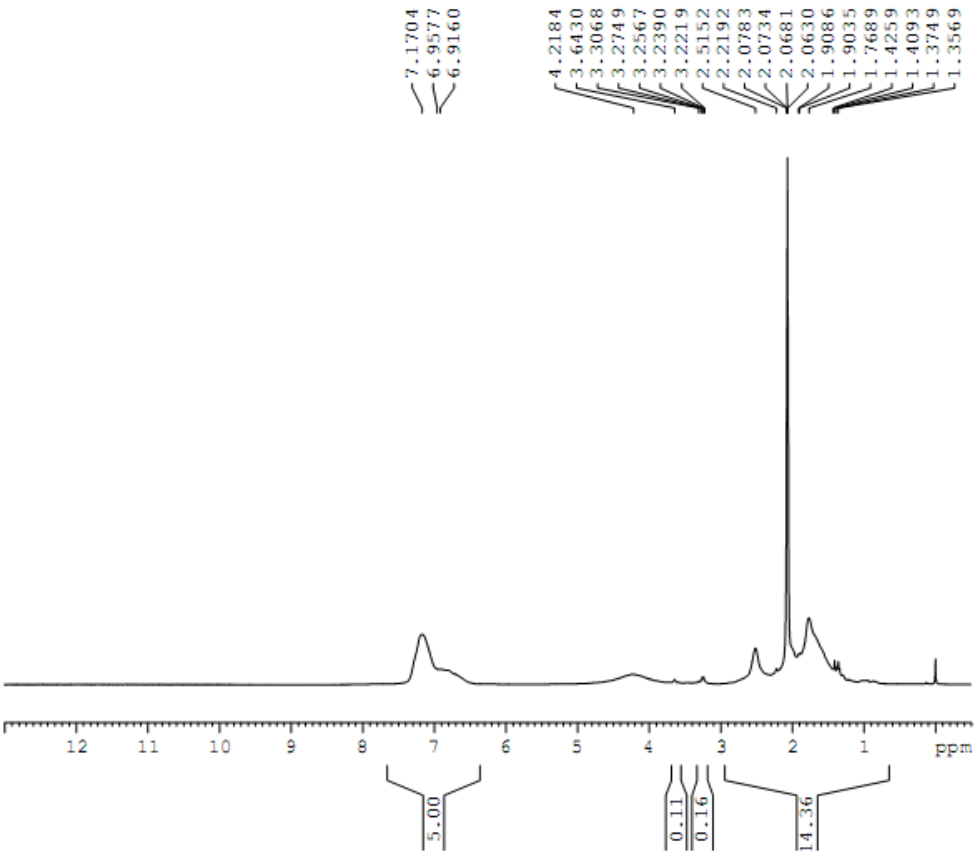


Figure S5-1. Original ^{1}H NMR spectra of hydrolysates **(Grad3′** in acetone-d6)

Take Grad3′ for the example: the signals of 3.0~3.7 ppm assign to the protons of $-CH_3$, the peak area is A_1. The signals of 6.6~7.3 ppm assign to the protons of benzene rings , the peak area is A_2, then：

$$\frac{F_{cum},MA}{F_{cum},St}=\frac{A_1/3}{A_2/5}=\frac{5A_1}{3A_2}$$

Then, $F_{cum},MA=\frac{5A_1}{3A_2}\times F_{cum},St$

$$F_{cum},AA=1-F_{cum},St-F_{cum},MA$$

For Grad3′, F_{cum},St=0.301, A_1=0.27, A_2=5

Then, $F_{cum},MA=\frac{5\times 0.27}{3\times 5}\times 0.301=0.027$; and $F_{cum},AA=1-0.301-0.027=0.672$

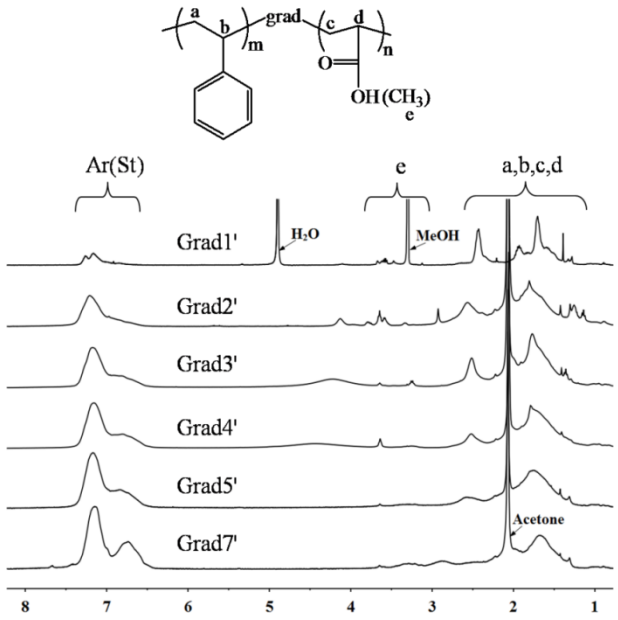


Figure S5-2. ^{1}H NMR spectra of all hydrolysates

Table S5. Calculated F_{cum} of hydrolysates

	$F_{cum,}$St	$F_{cum,}$MA	$F_{cum,}$AA
Grad1'	0.105	0.041	0.854
Grad2'	0.195	0.057	0.748
Grad3'	0.301	0.027	0.672
Grad4'	0.421	0.038	0.541
Grad5'	0.514	0.033	0.453
Grad7'	0.708	0.057	0.235

6. DSC curves of copolymers

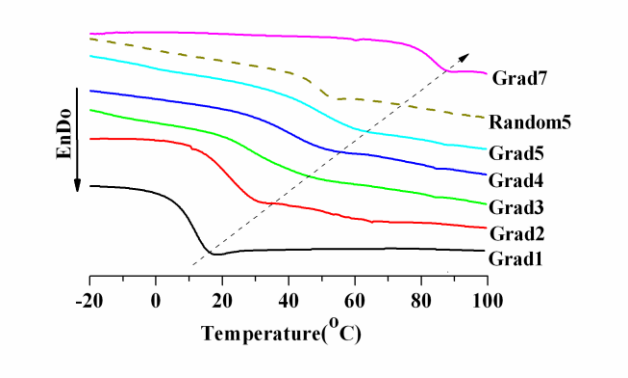


Figure S6-1. DSC curves of poly(St-grad-MA) and poly(St-r-MA) (heating method: 10k min^{-1}).

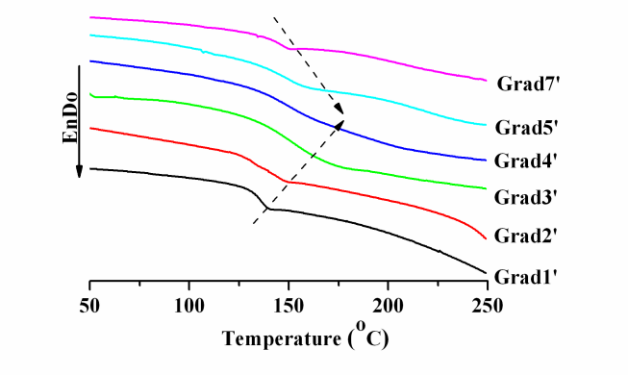


Figure S6-2. DSC curves of poly(St-grad-AA) (heating method: 10k min^{-1}).

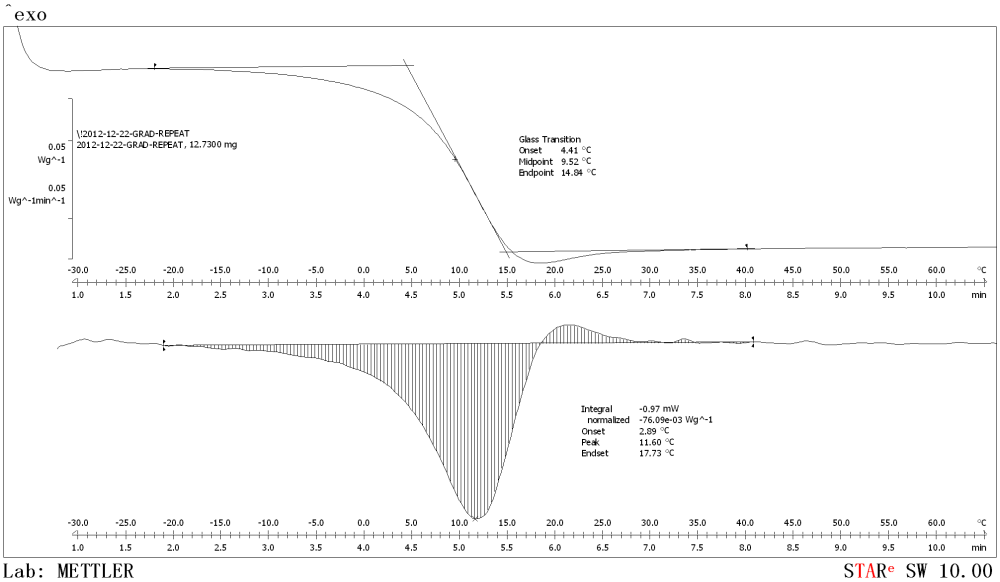
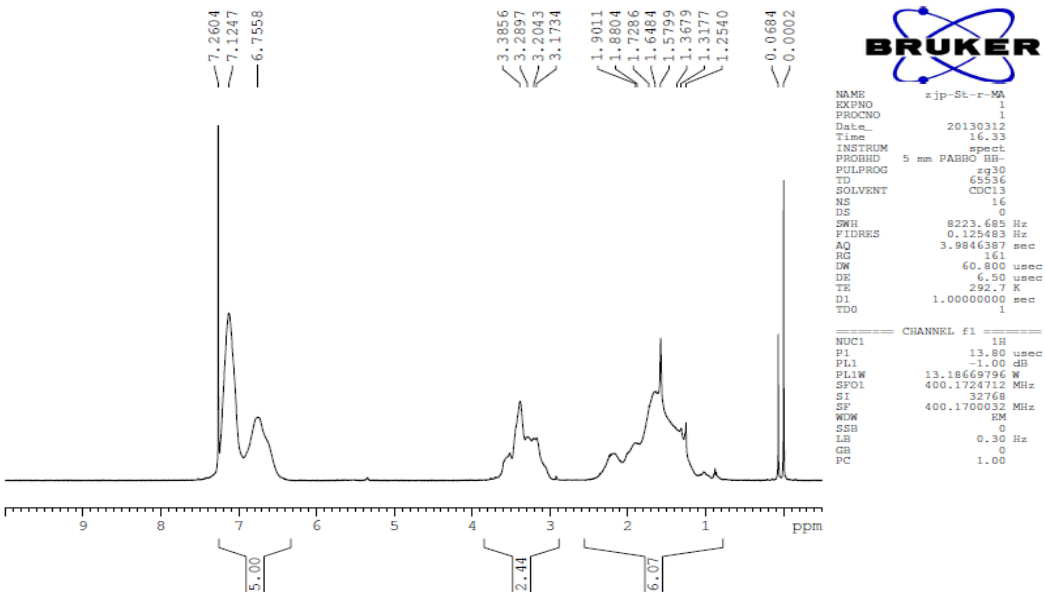


Figure S6-3. Example of original Spectrum **(Grad1)**

7. ^{1}H NMR spectrum of Poly(St-r-MA)



F_{cum},St=0.521, F_{cum},MA=0.479, T_g=49.4 ^{o}C, T_g breadth=14.6 ^{o}C