Supporting information for:

RAFT solution copolymerization of styrene and 1,3-butadiene and its application as a tool for block copolymer preparation

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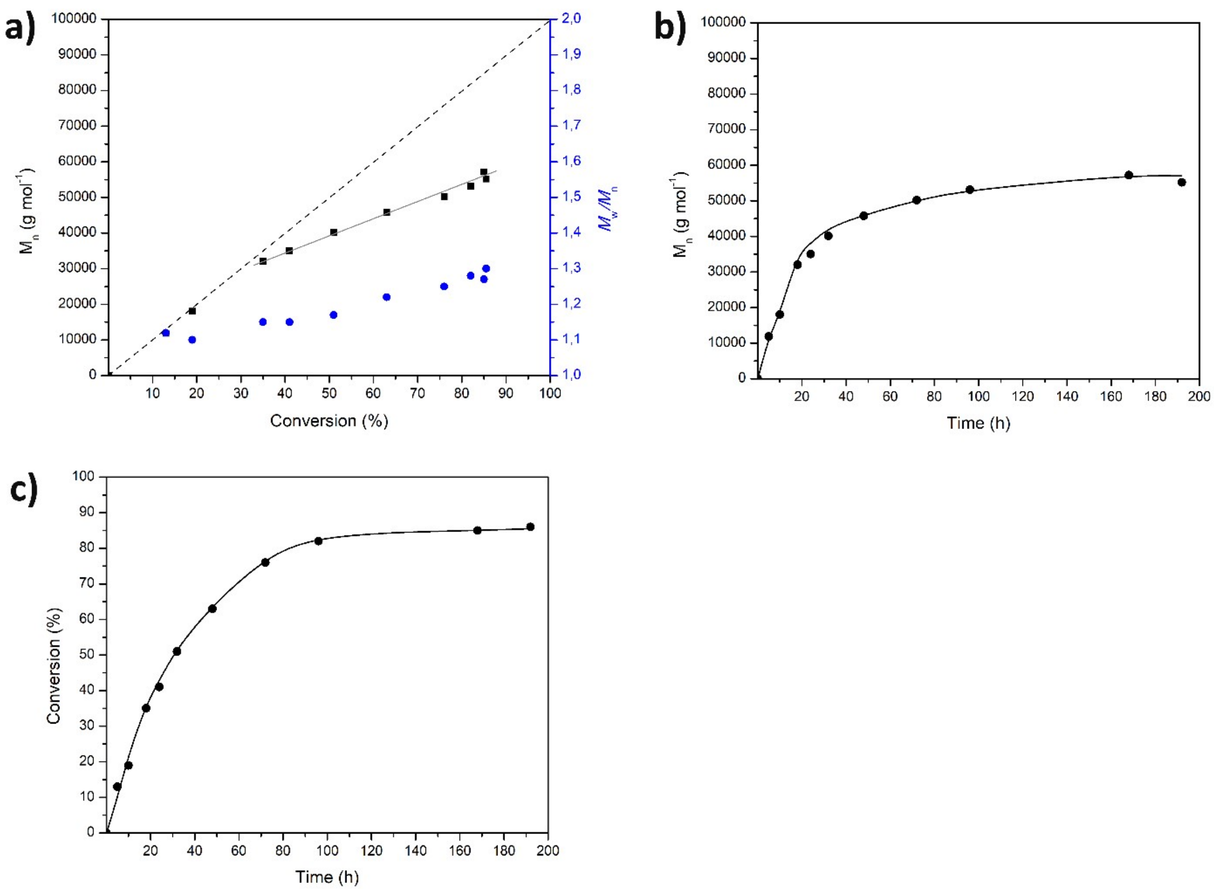


Figure S1. M_n vs. conversion (a), M_n vs. time (b) and conversion vs. time (c) kinetic plots for styrene RAFT polymerization (DMAc as a solvent, 100°C, CDTPA:VAm-110 = 5:1 by mol, [St] = 1.44 g ml^{-1} or 50 wt%, M_n theor = 100000 g mol^{-1}).

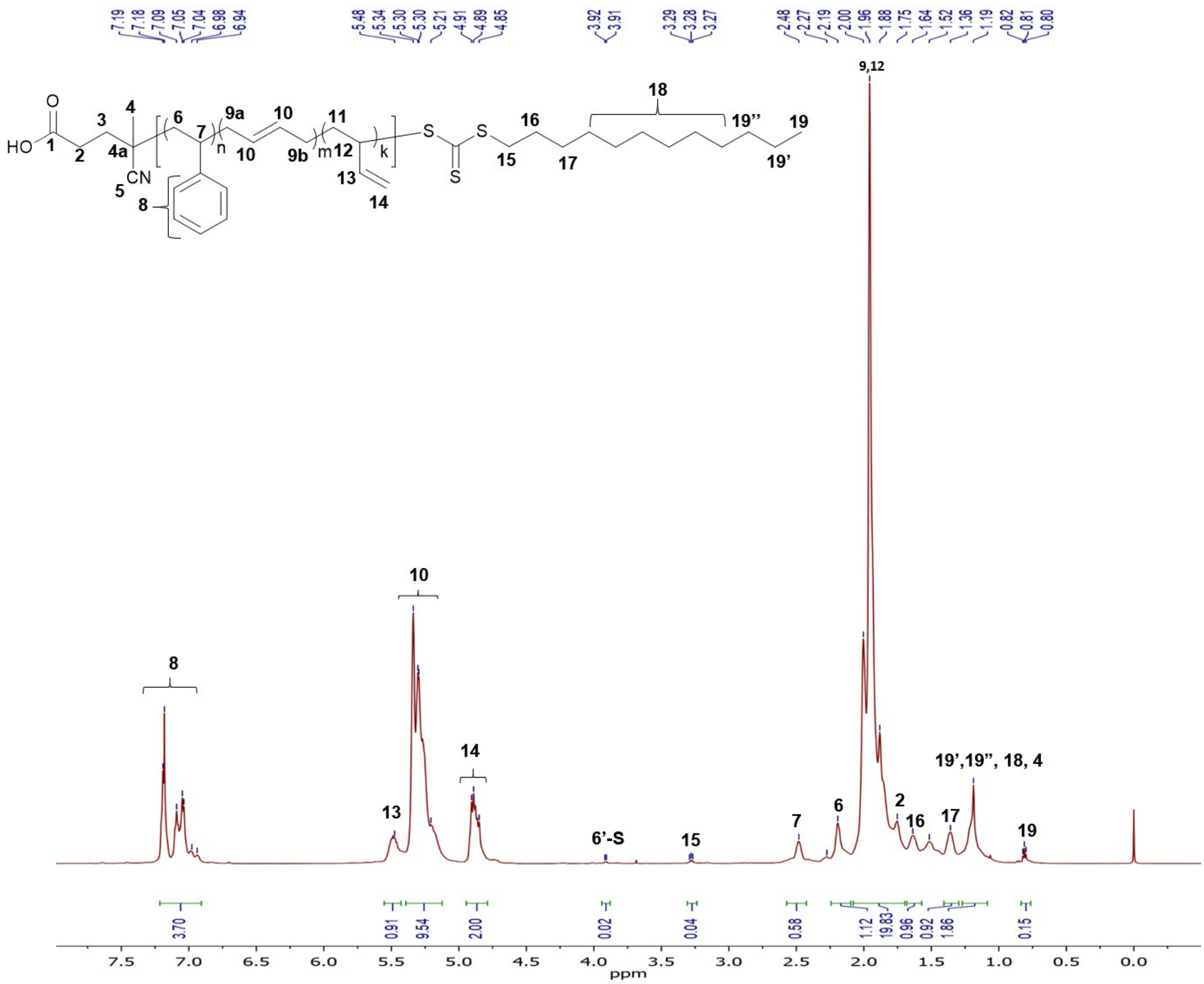


Figure S2. ^{1}H NMR of poly(St_n-*r*-Bd_m) copolymer (Table 1, entry 11, $M_{n\,SEC}$ = 15500 g mol^{-1}, M_w/M_n = 1.3).

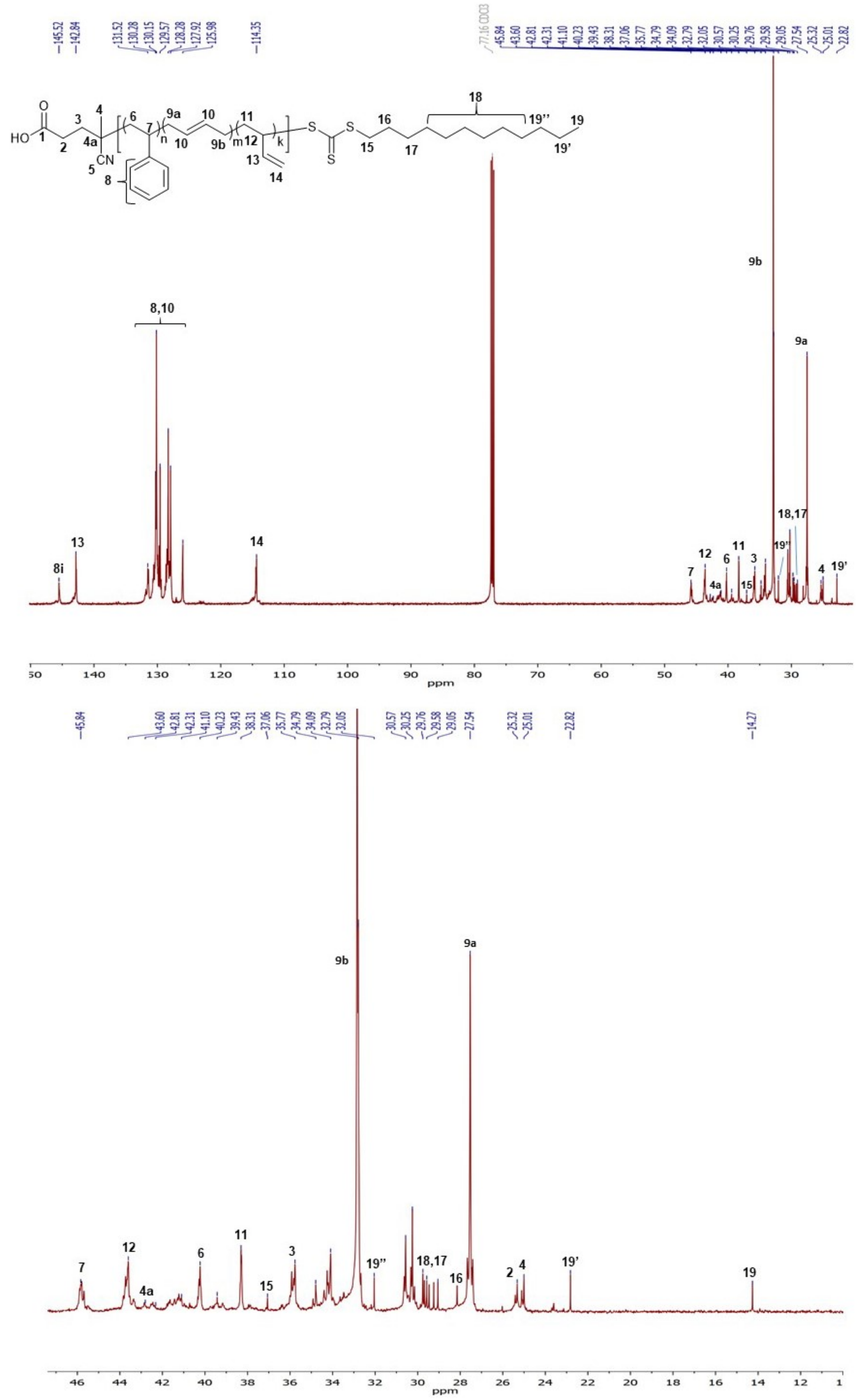


Figure S3. ^{13}C NMR of poly(St$_n$-*r*-Bd$_m$) copolymer (Table 1, entry 11, $M_{n\,SEC}$ = 15500 g mol^{-1}, M_w/M_n = 1.3).

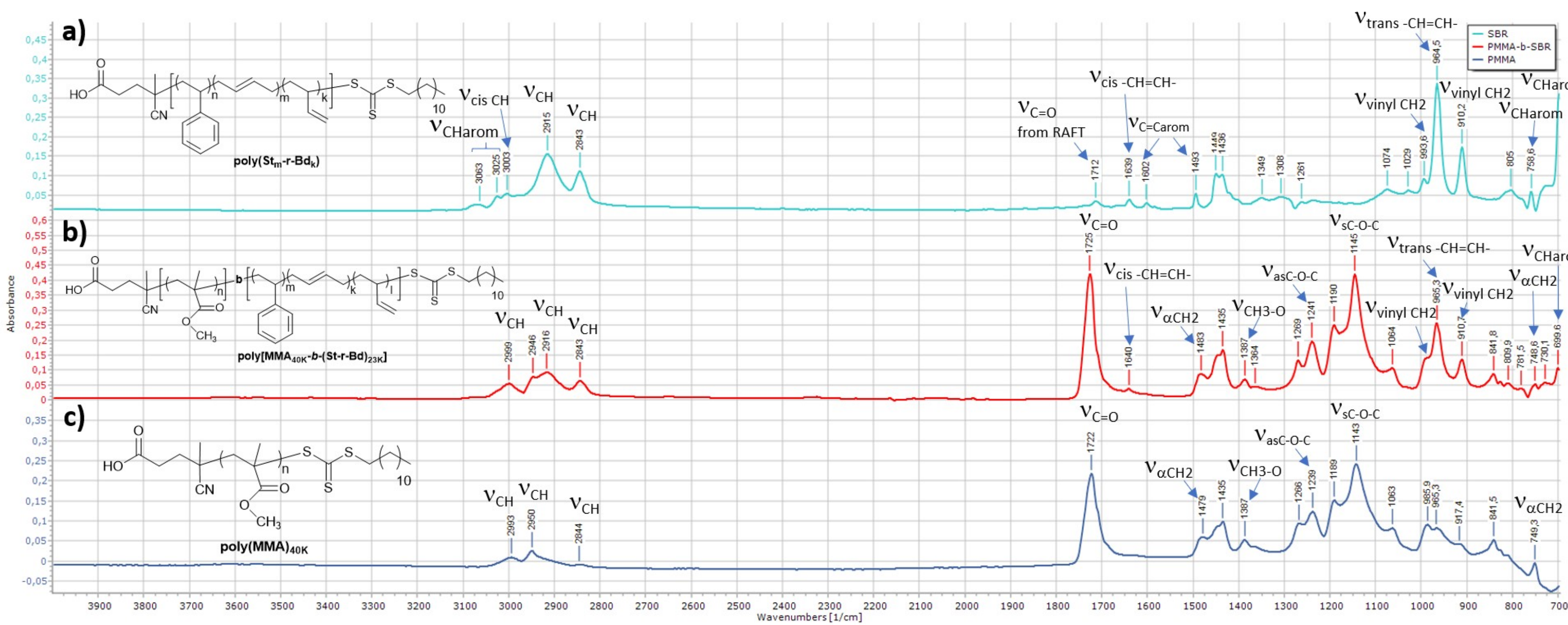


Figure S4. FT-IR spectra of poly(St$_n$-*r*-Bd$_m$) (**a**), poly[MMA$_n$-*b*-(St$_m$-*r*-Bd$_k$)] (**b**) and poly(MMA)$_n$ (**c**).

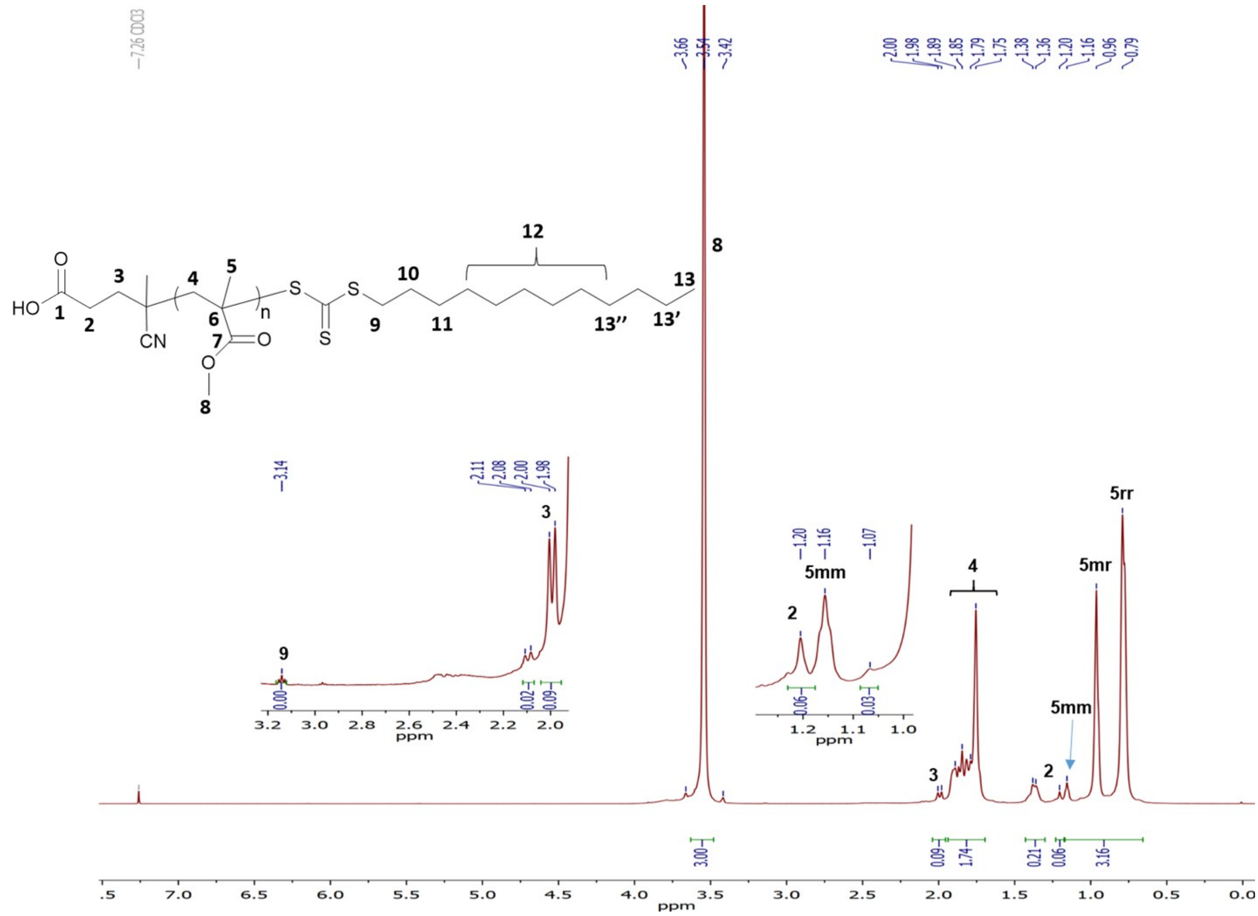


Figure S5. ^{1}H NMR of poly(MMA)$_n$ macro-CTA ($M_{n\,SEC}$ = 40300 g mol^{-1}, M_w/M_n = 1.1).

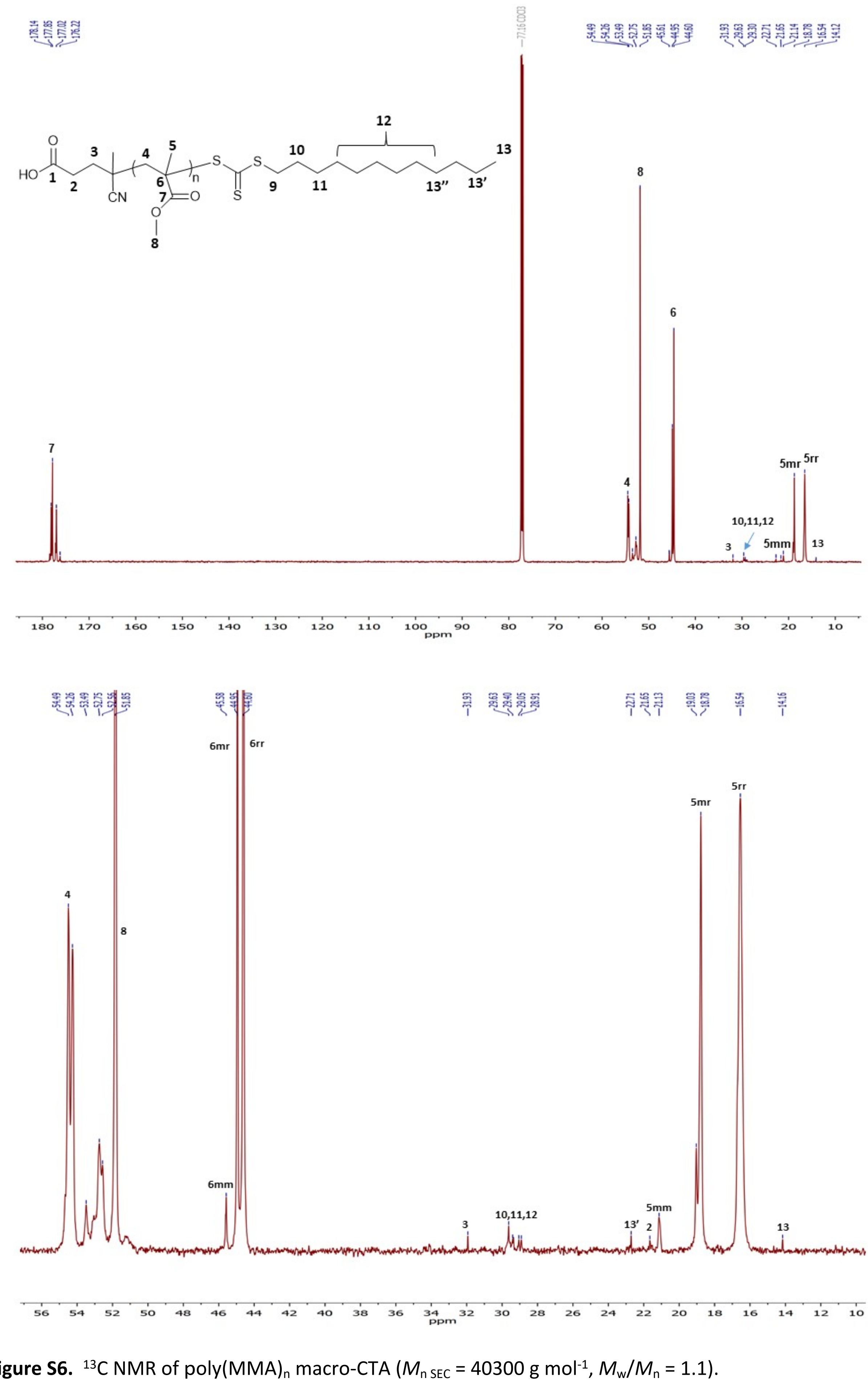


Figure S6. ^{13}C NMR of poly(MMA)$_n$ macro-CTA ($M_{n\ SEC}$ = 40300 g mol^{-1}, M_w/M_n = 1.1).

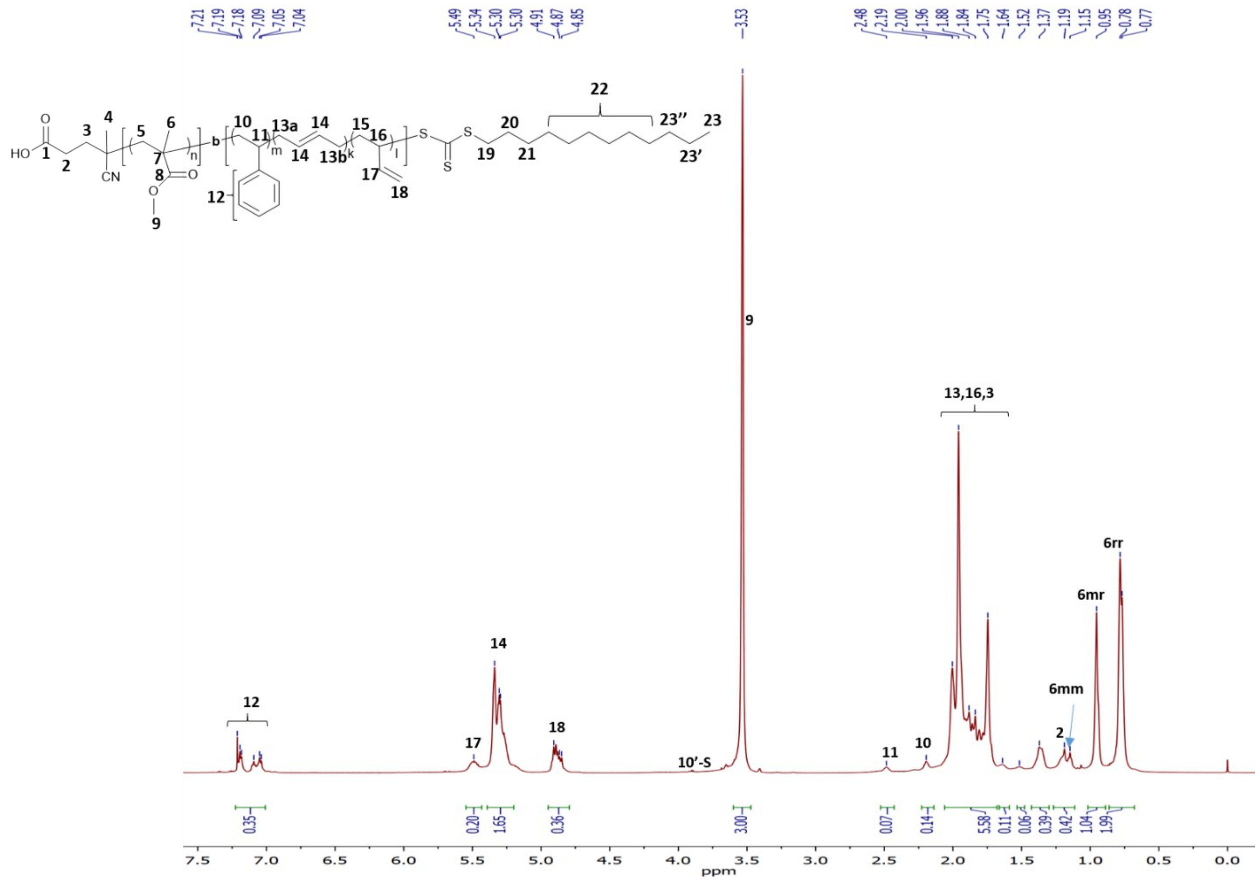


Figure S7. ^{1}H NMR of poly[MMA_{40K}-*b*-(St-*r*-Bd)$_{23K}$] ($M_{n\ SEC}$ = 63800 g mol^{-1}, M_w/M_n = 1.4).

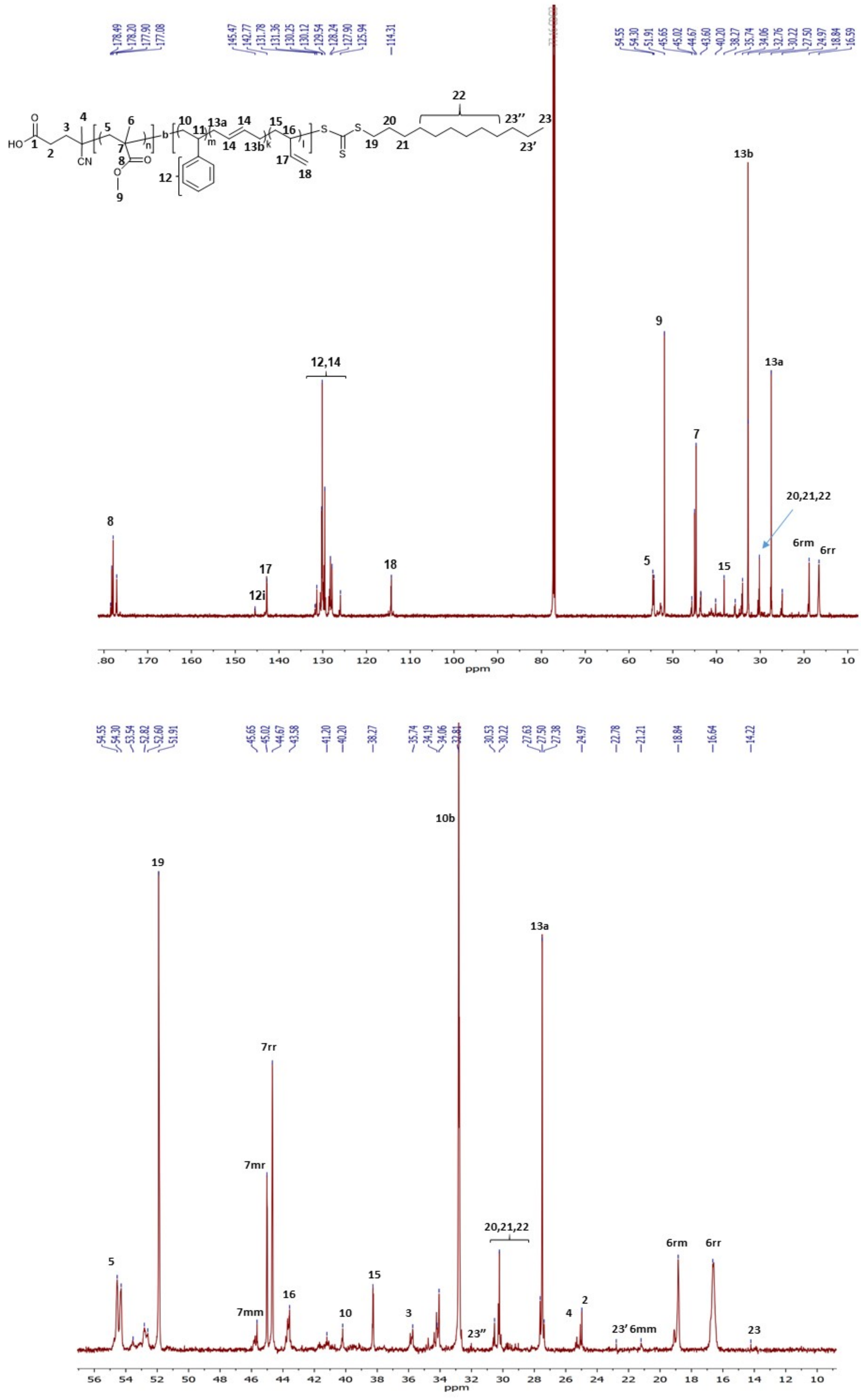


Figure S8. ^{13}C NMR of poly[MMA$_{40K}$-*b*-(St-*r*-Bd)$_{23K}$] ($M_{n\ SEC}$ = 63800 g mol^{-1}, M_w/M_n = 1.4).

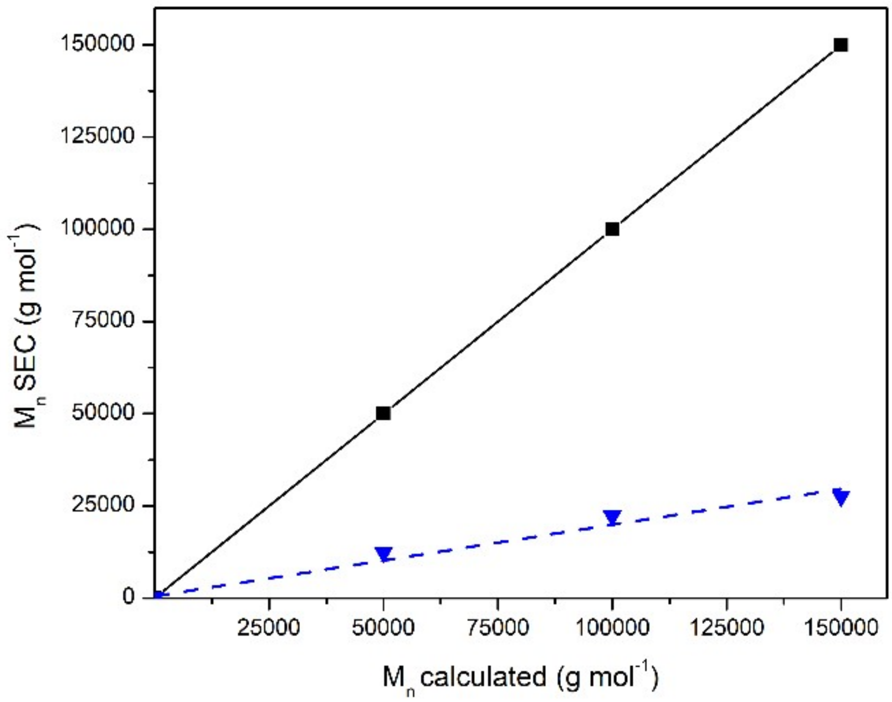


Fig. S9 Correlation of experimental poly(St_n-*r*-Bd_m) copolymer $M_{n(SEC)}$ (□ values from RI-detection, SEC in $CHCl_3$ at 40 °C) with calculated theoretical M_n (■).

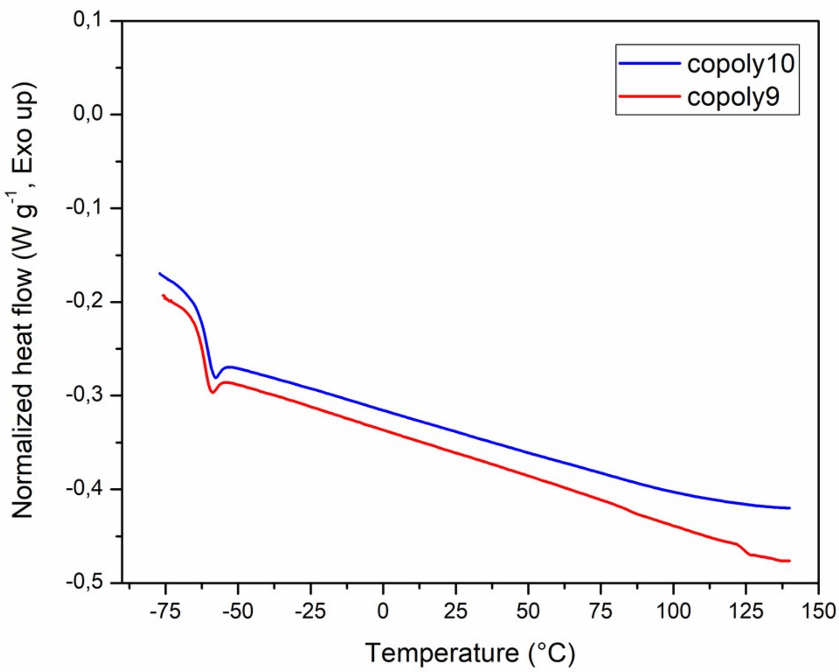


Figure S10. DSC curves of poly(St_n-*r*-Bd_m) obtained by RAFT method (Table 1, entries 9 and 10).

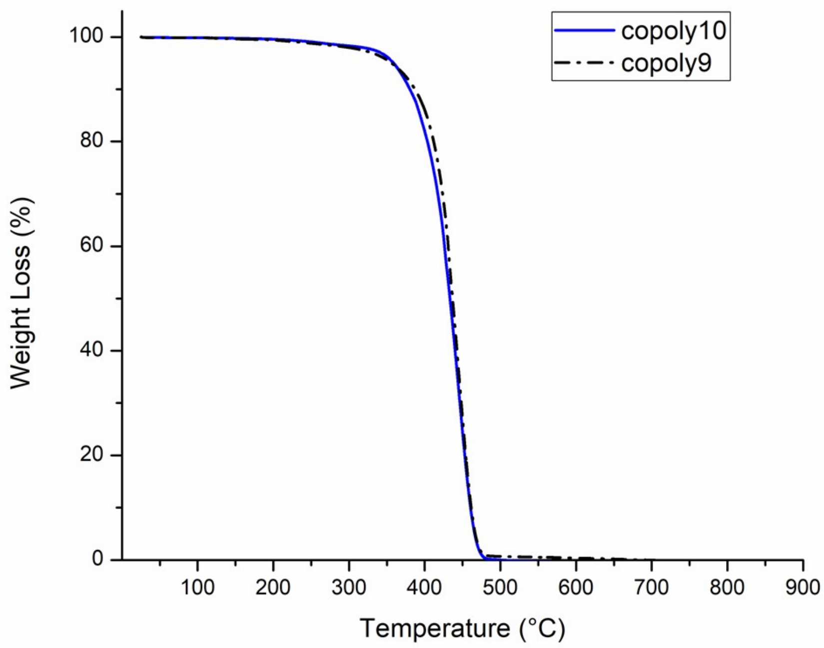


Figure S11. TGA curves of poly(St_n-*r*-Bd_m) synthesized by RAFT method (Table 1, entries 9 and 10) (TGA performed under inert atmosphere).

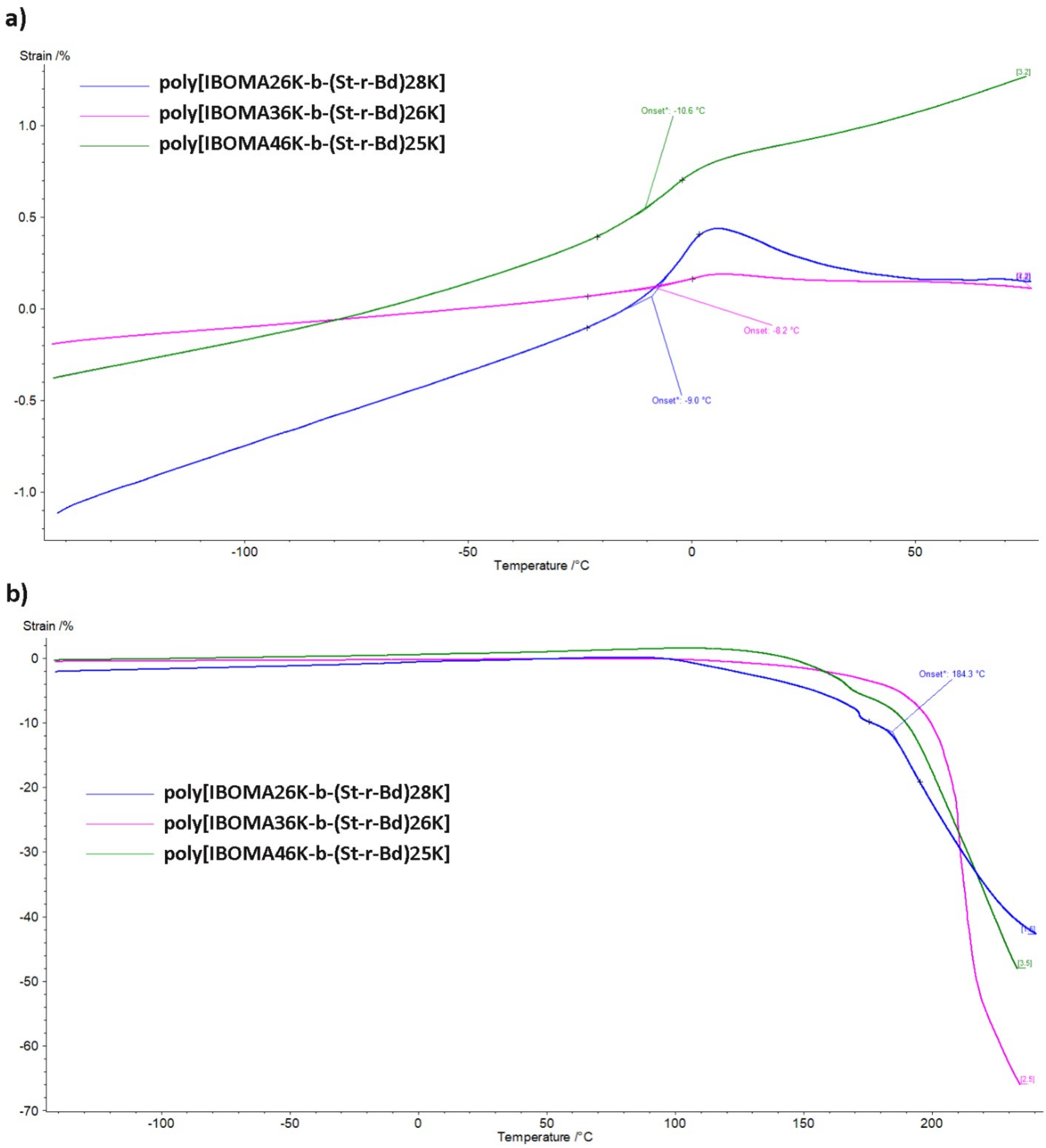
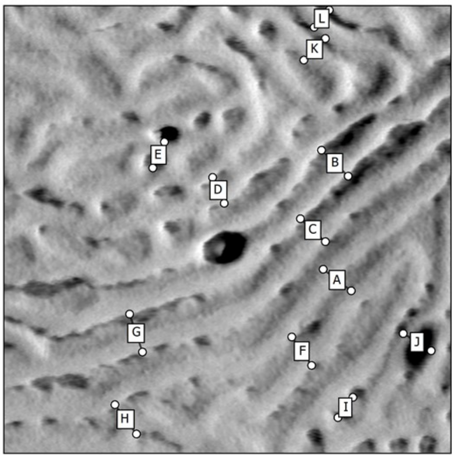


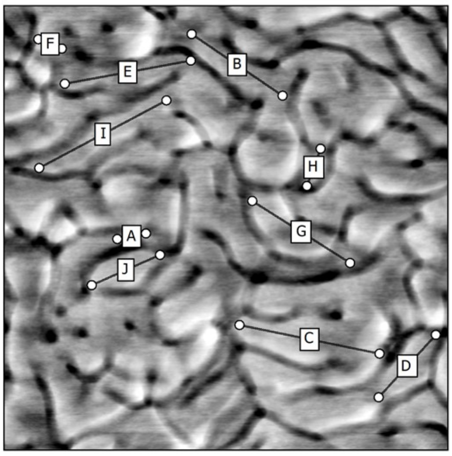
Figure S12. TMA curves of poly[IBOMA$_{26K}$-*b*-(St-*r*-Bd)$_{28K}$], poly[IBOMA$_{36K}$-*b*-(St-*r*-Bd)$_{26K}$] and poly[IBOMA$_{46K}$-*b*-(St-*r*-Bd)$_{25K}$] block copolymers (1st heating curve at 3^{o}C min^{-1}(***a***) and 2nd heating curve at 5^{o}C min^{-1}(***b***)).

a) *Size A (domains length for lamellar morphology)*



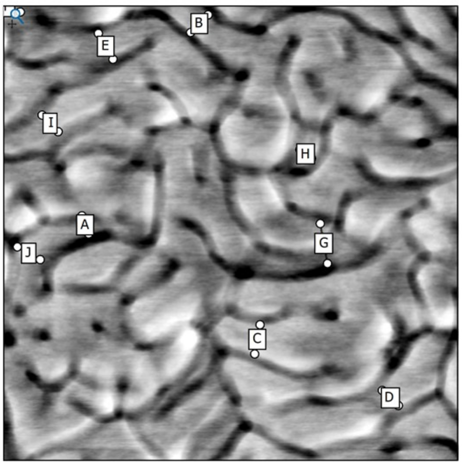
Distances	Unit	A	B	C	D	E	F	G	H	I	J	K	L
HDist	nm	78.96	83.08	75.65	63.38	63.38	77.48	89.56	81.29	56.44	73.48	68.09	51.18

b) *Size A (ribbons length for modulated lamellar morphology)*



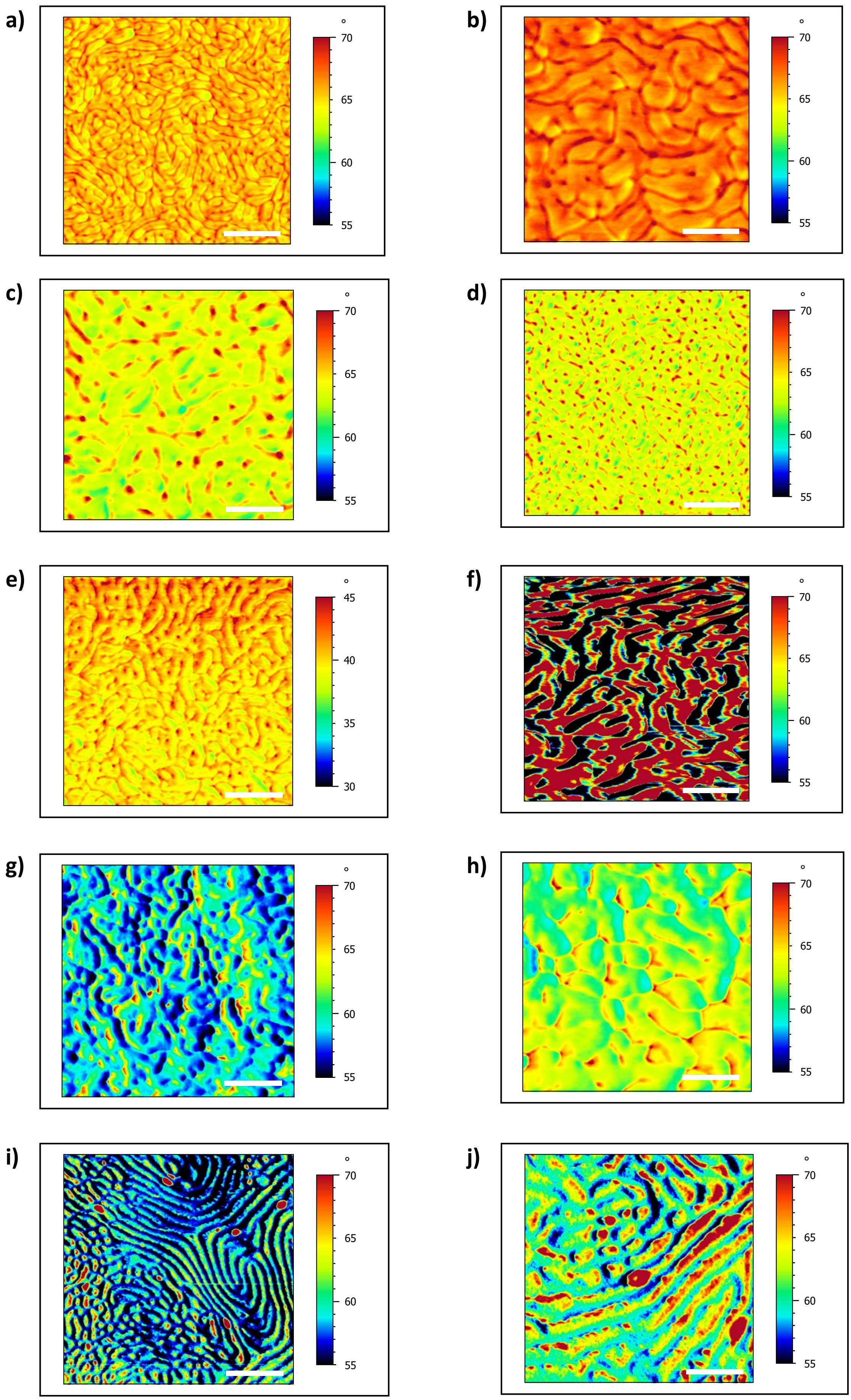
Distances	Unit	A	B	C	D	E	F	G	H	I	J
HDist	nm	65.69	247.5	322.2	190.8	288.7	57.02	260.9	89.29	324.7	168.5

c) *Size B (ribbons diameter for modulated lamellar morphology)*



Distances	Unit	A	B	C	D	E	F	G	H	I	J
HDist	nm	38.11	49.02	58.77	43.60	58.66	57.02	80.31	28.88	45.63	51.71

Figure S13. Determination of the domains sizes from AFM images as represented by an example of poly[MMA$_{40K}$-*b*-(St-*r*-Bd)$_{23K}$] (**a**) and poly[IBOMA$_{46K}$-*b*-(St-*r*-Bd)$_{25K}$] (**b**,**c**) block copolymers.



a)
°
70
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60
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b)
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c)
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d)
°
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e)
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f)
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g)
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h)
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60
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Figure S14. AFM topography of block copolymers coatings: poly[MMA_{40K}-*b*-(St-*r*-Bd)$_{23K}$] (a-b), poly[$IBOMA_{26K}$-*b*-(St-*r*-Bd)$_{28K}$] (c-d), poly[$IBOMA_{36K}$-*b*-(St-*r*-Bd)$_{26K}$] (e-f), poly[$IBOMA_{46K}$-*b*-(St-*r*-Bd)$_{25K}$] (g-h) and poly[St_{43K}-*b*-(St-*r*-Bd)$_{15K}$] (i-j).

Determination of composition of poly(St_n-*r*-Bd_m)

The composition of poly(St_n-*r*-Bd_m) and microstructure of polybutadiene (Pbd) were calculated using ^{1}H-NMR in accordance to the published procedure [1].

Table 1. Composition of poly(St_n-r-Bd_m) including styrene sequences and isomers of butadiene with their chemical shift location.

Sequence, Isomer	Integral	Chemical Shift, ppm
St (1St)	[A]	~ 7.60-7.07
St (2St-4St)	[B]	~ 7.07-6.75
St (>=5St)	[C]	~ 6.75-6.30
1,4+ 1,2-Pbd (=CH)	[E]	~ 5.7-5.1
1,2-Pbd (=CH_2)	[F]	~ 5.1-4.5

The following equations were used to determine the composition of **poly(St_n-*r*-Bd_m)** in moles:

St content = ([A] + [B] + [C]) /5

1,2-Pbd (vinyl content) = [F] /2

1,4-Pbd (cis + trans content) = ([E]- ([F]) /2) /2

The copolymer composition was provided in a weight percentage (wt%). Thus, first, the determined microstructure in the mole has to be converted to weight (wt). This was attained by multiplying the calculated St and Bd content ((1,2)-Bd and (1,4)-Bd) by 104.152 and 54.092, respectively.

Finally, the composition of St and Bd segments in wt% was calculated using the formulas below:

Total weight = St (wt) + 1,2-Pbd (wt) + 1,4-Pbd (wt)

St (wt%) = (St (wt)* 100) / total weight

1,2-Pbd (wt%) = (1,2-Pbd (wt)* 100) / total weight

1,4-Pbd (wt%) = (1,4-Pbd (wt)* 100) / total weight

References

[1] A. F. Halasa, C. Jasiunas, B. Hsu, S. Henning and K. S. Seo, J. Appl. Polym. Sci., 2013, 127, 2116-2120.