

Supporting Information

Tapered Multiblock Copolymers Based on Isoprene and 4-Methyl Styrene: Influence of the Tapered Interface on the Self-assembly and Thermomechanical Properties

Eftyxis Galanos,¹ Eduard Grune,^{2,3} Christian Wahlen,² Axel H.E. Müller,² Michael Appold,⁵ Markus Gallei,⁵ Holger Frey,^{*,2} George Floudas^{*,1,4}

¹ Department of Physics, University of Ioannina, P.O. Box 1186, 45110 Ioannina (Greece)

² Institute of Organic Chemistry, Johannes Gutenberg – University, Duesbergweg 10-14, 55128 Mainz (Germany)

³ Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany

⁴ Max Planck Institute for Polymer Research, 55128 Mainz (Germany)

⁵ Macromolecular Chemistry Department, Technische Universität Darmstadt, Alarich-Weiss Str. 4, 64287 Darmstadt, Germany

Preparation of multiblock copolymers

In a previous short account we described a synthetic approach for $(AB)_n$ multiblock copolymers, based on the highly disparate reactivity ratios of isoprene (I) and 4-methylstyrene (4MS) ($r_I = 25.4$; $r_{4MS} = 0.007$).¹ Due to the highly favoured incorporation of I, the statistical copolymerization of I/4MS yields tapered block copolymer in one step.² The living chain end permits further addition of I/4MS monomer mixtures, providing rapid access to linear tapered $(AB)_n$ multiblock copolymers (Figure S1 a). This general synthetic approach was used in our recent study to generate tapered multiblock copolymers based on isoprene and styrene.³ The resulting $(AB)_n$ multiblocks showed ordered structures for up to ten blocks ($n=5$) and extraordinary toughness. To examine whether multiblock properties like state of order and mechanical response are affected by length and shape of the tapered interface, three series of $(AB)_n$ multiblock copolymers with varying block number, but constant molecular weights of 80 kg/mol; 240 kg/mol and 400 kg/mol were prepared based on isoprene and 4-methylstyrene (Figure S1 b).

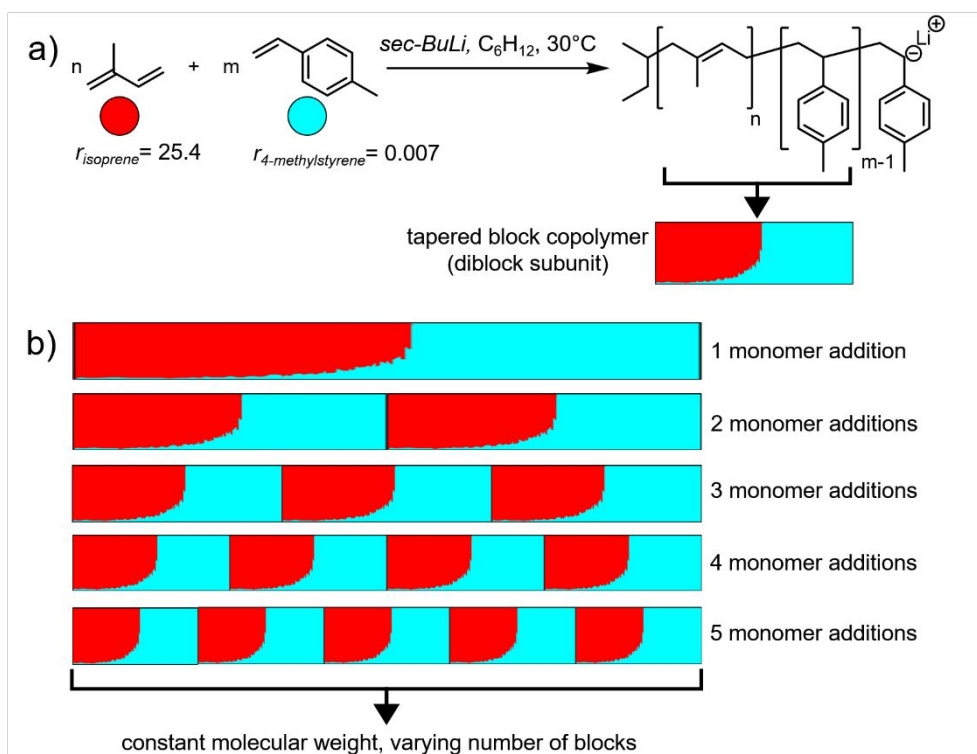


Figure S1: a) one-step tapered block copolymer formation; b) composition profile of multiblock copolymers with constant molecular weights and varied block numbers.

For a better comparison of the samples, we aimed for a constant isoprene content of 50 mol% for all copolymers. The discrepancies between the targeted molecular weights and the molecular weights determined by SEC are, mainly caused by the calibration with polystyrene

standards. However, the SEC results provide a sufficient estimation of the actual molecular weights (Table S1). The dispersities of the multiblock samples showed a broadening of the molecular weight distributions and the appearance of small shoulders at low molecular weights for increasing molecular weights and an increasing number of monomer additions (Supp. Inf. Figure S3). Both effects can be explained by a small percentage of termination during every monomer addition step. However, considering the high molecular weights and the high number of blocks, the dispersities are still very narrow and demonstrate the potential and applicability of this synthetic approach for well-defined linear multiblock copolymers.

¹H NMR Analysis

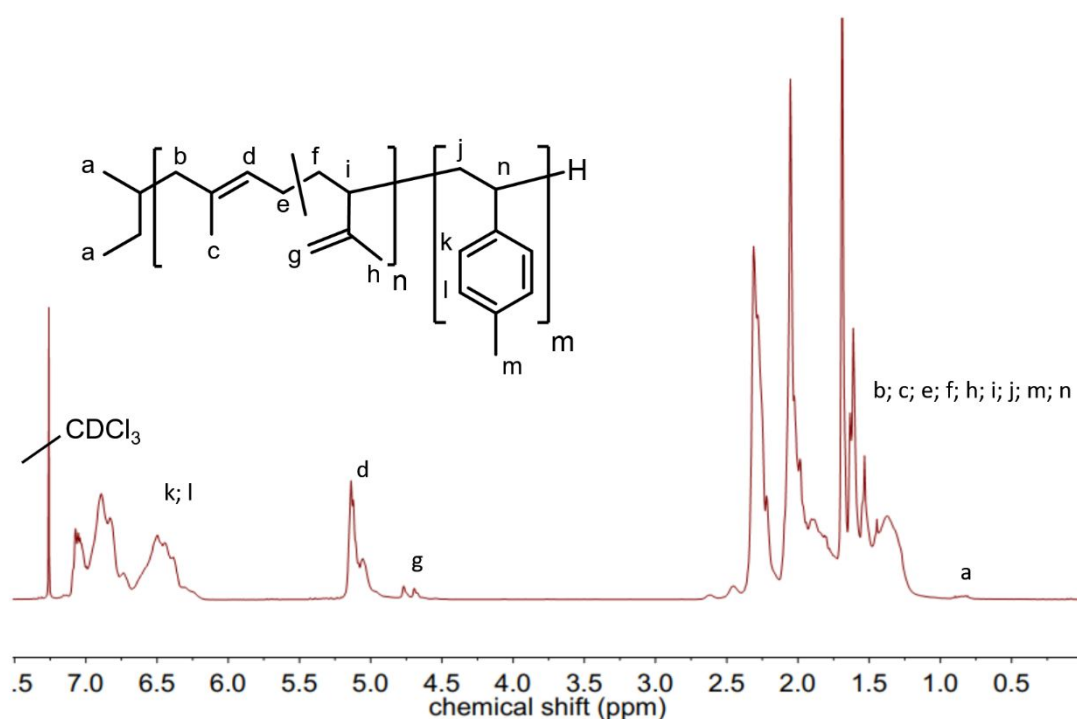


Figure S2. ¹H-NMR spectrum (400 MHz) of 400K10B in CDCl₃ (Table S1 Entry 15).

SEC

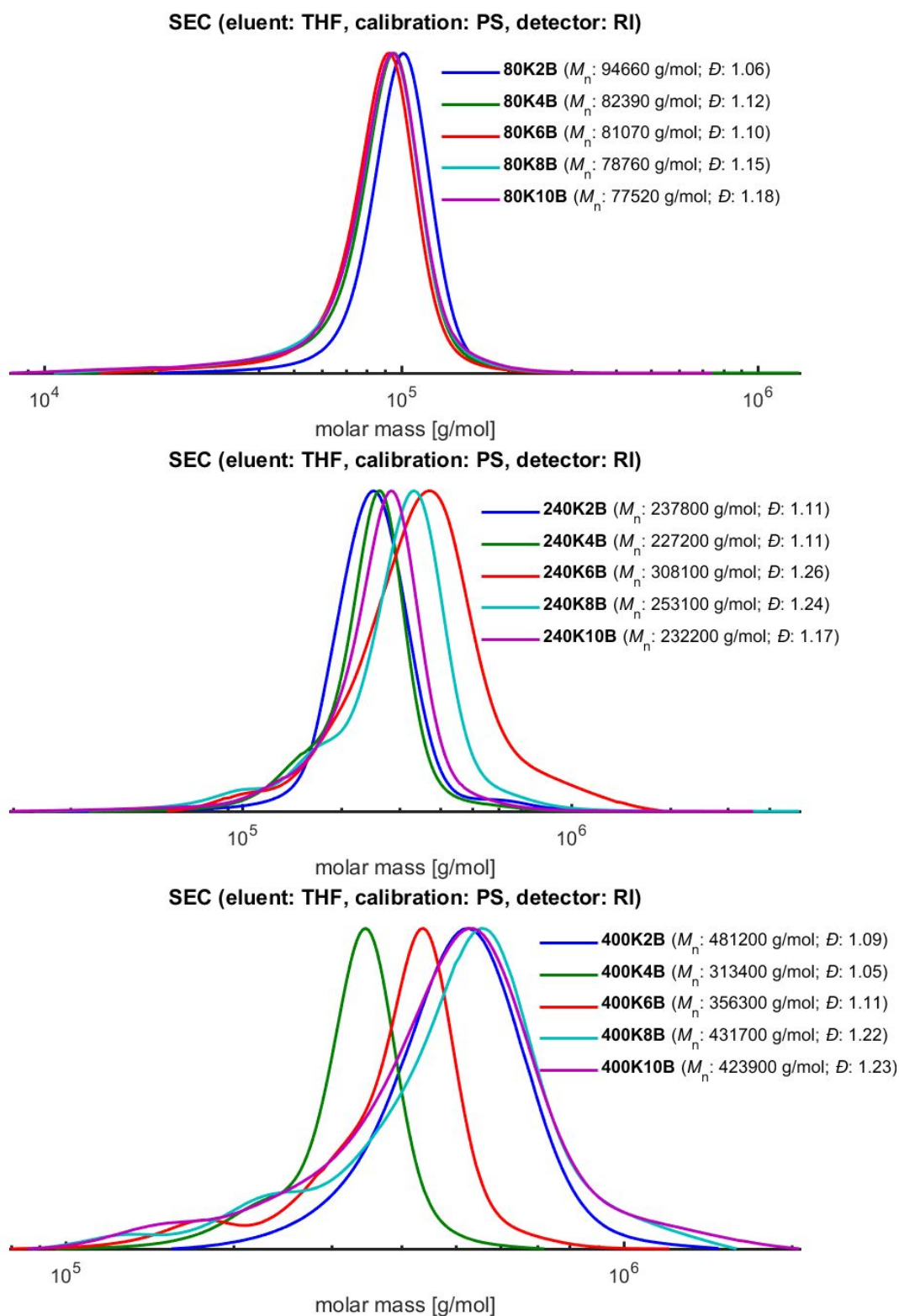


Figure S3. SEC elugrams of I/4MS multiblock copolymers.

Rheology

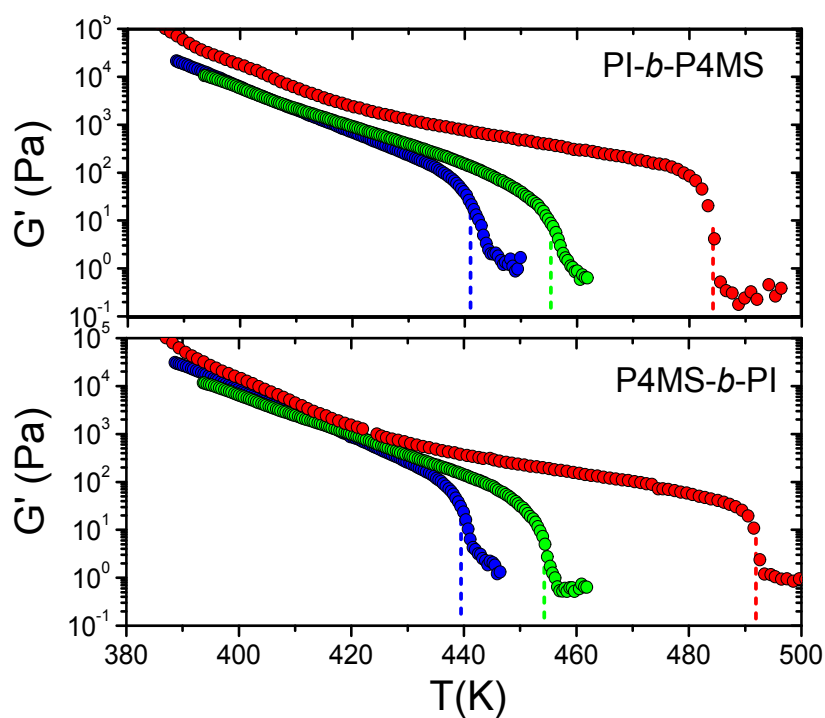


Figure S4: Temperature dependence of the storage modulus, G' , obtained at a frequency of $\omega=1$ rad/s with a low strain amplitude on heating the sequential diblock copolymers 30KP($PI-b-P4MS$) (Table S1 Entry 16) (blue), 35KP($PI-b-P4MS$) (Table S1 Entry 18) (green) and 40KP($PI-b-P4MS$) (Table S1 Entry 20) (red) (top) and the inverse diblock copolymers 30KP($P4MS-b-PI$) (Table S1 Entry 17) (blue), 35KP($P4MS-b-PI$) (Table S1 Entry 19) (green) and 40KP($P4MS-b-PI$) (Table S1 Entry 21) (red) (bottom). Vertical dashed lines indicate the respective T_{ODT} 's.

Tensile Testing

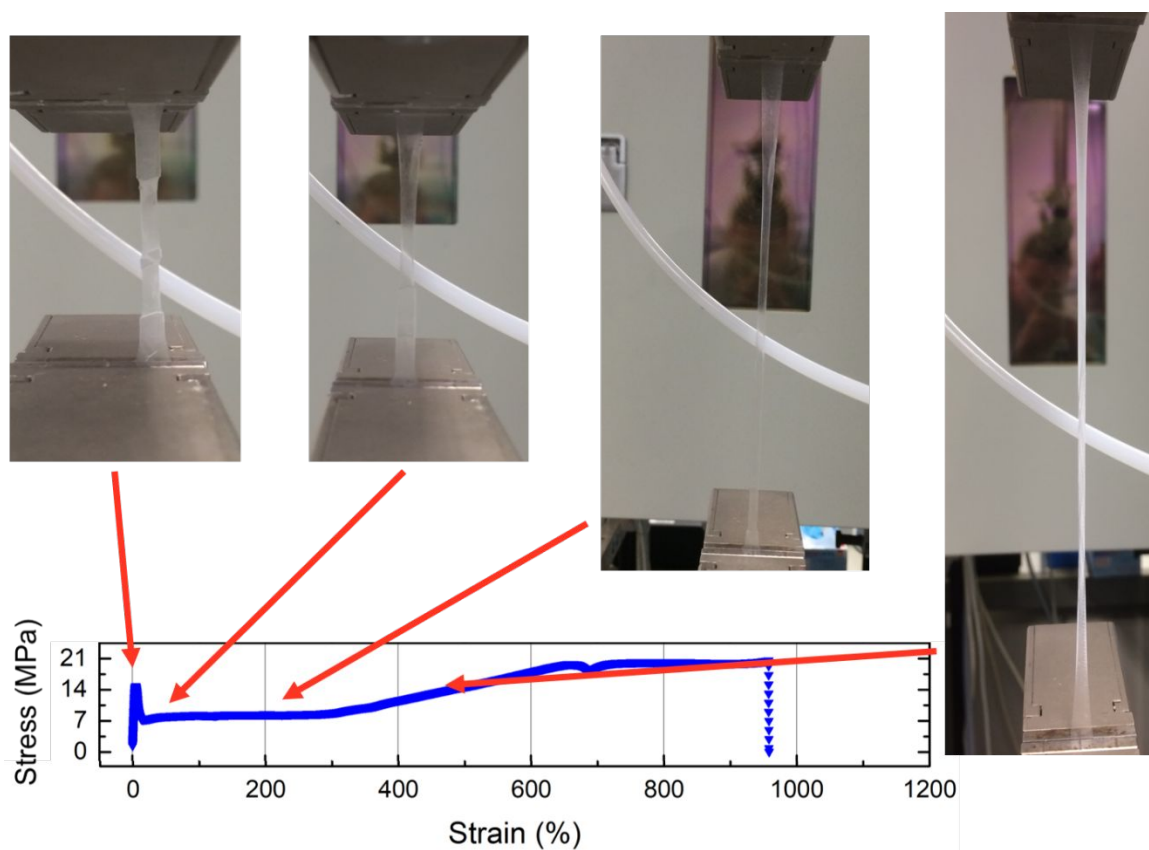


Figure S5. Tensile testing of a multiblock sample.

TEM

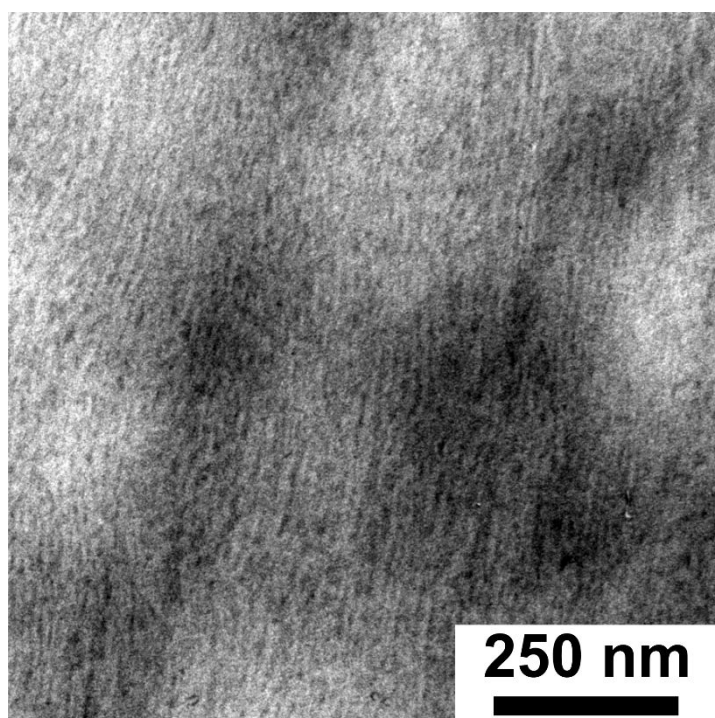


Figure S6: TEM image of a hexablock copolymer (240 kg/mol) (Table S1 Entry 8), showing very fine lamellar structures.

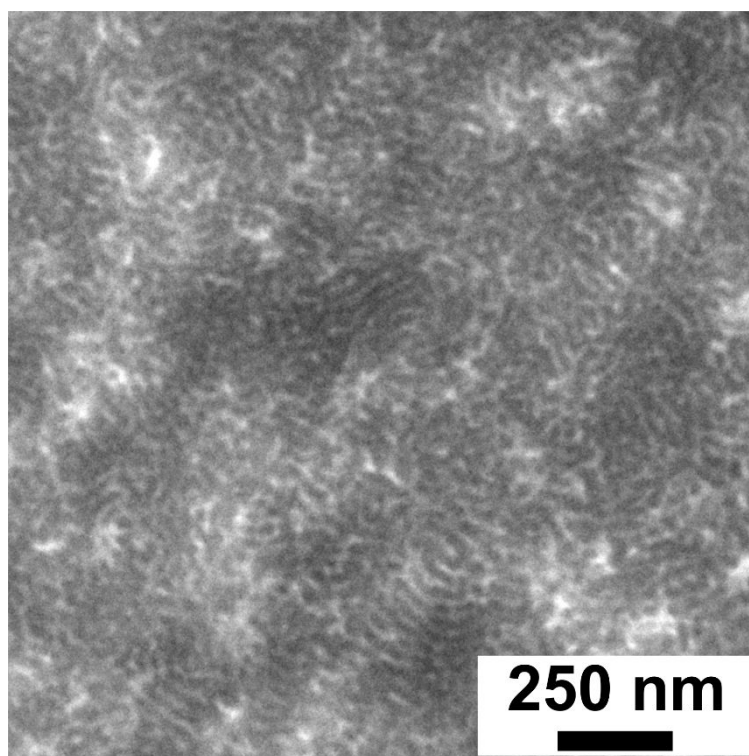


Figure S7: TEM image of a hexablock copolymer (400 kg/mol) (Table S1 Entry 13), showing a lamellar morphology.

Summarized Results

Table S1. Molecular characteristics of the tapered multiblock copolymers P(I-*co*-4MS) and of the sequential PI-*b*-P4MS (i.e. “normal”) and P4MS-*b*-PI (i.e. “inverse”) diblock copolymers.

Entry	Sample	number of blocks	M_n^{theo} (kg/mol)	M_n^a (kg/mol)	\bar{D}^a	Isoprene content ^{theo} (mol%)
1	80K2B	2	80	94.7	1.06	50
2	80K4B	4		82.4	1.12	50
3	80K6B	6		81.1	1.10	50
4	80K8B	8		78.7	1.15	50
5	80K10B	10		77.5	1.18	50
6	240K2B	2	240	237.8	1.11	50
7	240K4B	4		227.2	1.11	50
8	240K6B	6		308.1	1.26	50
9	240K8B	8		253.1	1.24	50
10	240K10B	10		232.2	1.17	50
11	400K2B	2	400	481.2	1.09	50
12	400K4B	4		313.4	1.05	50
13	400K6B	6		356.3	1.11	50
14	400K8B	8		431,7	1.22	50
15	400K10B	10		423,9	1.23	50
16	30KP(I- <i>b</i> -4MS)	2	30	38.3	1.15	50
17	30KP(4MS- <i>b</i> -I)	2		37.7	1.17	50
18	35KP(I- <i>b</i> -4MS)	2	35	41.8	1.15	50
19	35KP(4MS- <i>b</i> -I)	2		40.3	1.16	50
20	40KP(I- <i>b</i> -4MS)	2	40	45.6	1.17	50
21	40KP(4MS- <i>b</i> -I)	2		46.4	1.18	50

^a Determined by SEC at 25°C in THF

References

(1) Grune, E.; Appold, M.; Müller, A. H. E.; Gallei, M.; Frey, H. Anionic Copolymerization Enables the Scalable Synthesis of Alternating (AB)_n Multiblock Copolymers with High Molecular Weight in $n/2$ Steps. *ACS Macro Lett.* **2018**, 807–810.

(2) Grune, E.; Johann, T.; Appold, M.; Wahlen, C.; Blankenburg, J.; Leibig, D.; Müller, A. H. E.; Gallei, M.; Frey, H. One-Step Block Copolymer Synthesis versus Sequential Monomer Addition: A Fundamental Study Reveals That One Methyl Group Makes a Difference. *Macromolecules* **2018**, 51, 3527–3537.

(3) Steube, M.; Johann, T.; Galanos Eftysis; Appold, M.; Rüttinger, C.; Metzger, M.; Gallei, M.; Müller, A. H.E.; Floudas, G.; Frey, H. Isoprene/Styrene Tapered Multiblock Copolymers with up to 10 Blocks: Synthesis, Phase Behavior, Order and Mechanical Properties. *Macromolecules* **2018**.