One-Pot Synthesis of Alternating (Ultra-High Molecular Weight) Multiblock Copolymers via a Combination of Anionic Polymerization and Polycondensation

Matthias Heck, Carlo Botha, Manfred Wilhelm, and Valerian Hirschberg*

This article presents a fast, straightforward synthesis approach to polymerize alternating multiblock copolymers, ultra-high molecular weight (UHMW) (homo)polymers as well as precursors for complex macromolecular topologies such as comb or barbwire architectures. The one-pot synthesis strategy proposed in this work is based on anionic polymerization via a bifunctional initiator and the subsequent linking of macro dianions with a bifunctional linker, additionally overcoming the limitations associated with the monomer reactivity. Thus, the synthetic route guarantees the repeating size of polymer blocks and an equal distribution of functional groups in precursors for complex topologies. Dianions of polystyrene (PS), polyisoprene-*b*-polystyrene-*b*-polyisoprene, and poly-2-vinylpyridine-*b*-polystyrene-*b*-poly-2-vinylpyridine are linked with α, α'-dibromo-para-xylene to UHMW and multiblock copolymers. Multiblock copolymers with on average up to 50 well-defined alternating A and B blocks are accessible within 15 min.

1. Introduction

Block copolymers are one of the most important class of polymers to design macroscopic material properties, but the main focus is on the simplest block order, that is, linear AB diblock copolymers and ABA triblock copolymers.[1–3] Polymers with more than three to five blocks are very rarely investigated,[4] although trends in the past years have shown that new high performance materials are not necessarily created with new monomers, but rather properties are engineered via topology as for a block copolymer, for example, the number of blocks or block order.[5–7]

M. Heck, C. Botha, M. Wilhelm, V. Hirschberg
Institute for Technical Chemistry and Polymer Chemistry
Karlsruhe Institute of Technology
Engesserstraße 18, 76131, Germany
E-mail: valerian.hirschberg@kit.edu

Alternating multiblock copolymers are an emerging type of materials.[8–10] For block copolymers, the microscopic[11] and macroscopic properties highly differ from di- to triblock copolymers and further change with increasing block number.[12–17] For thermoplastic elastomers, for example, for polystyrene/polyisoprene block copolymers, the mechanical properties typically improve with the number of blocks.[18,19]

Anionic polymerization[20,21] allows in general the stepwise, that is sequential, synthesis of multiblock copolymers, however this technique faces several inconveniences and limitations regarding the reactivity of the employed monomers and termination due to impurities of high block numbers.

Macroanions are only able to initiate the polymerization of monomers forming less reactive anions, that is, the multiblock copolymers consisting of polystyrene and polymethyl methacrylate are not producible by a simple sequential anionic polymerization. Furthermore, obtaining identical block sizes in multiblock copolymers via sequential anionic polymerization is challenging due to termination via impurities in each step.[15,18] Consequently, the degree of polymerization of the stepwise synthesized polymer blocks changes and the resulting broadening and shoulders in the molecular weight distribution highly impact the phase separation and the microstructure.[22] Additionally, the monitoring of the synthesis of a multiblock copolymer by a sequential approach is accompanied by a multitude of characterization steps after every newly synthesized polymer block. Techniques to reduce the number of monomer additions for the anionic polymerization of PS/PI multiblock copolymers use the direct addition of an isoprene/styrene mixture, which does not result in sharply separated PS and PI blocks.[18,19] Approaches based on other living polymerization techniques, such as reversible addition–fragmentation chain transfer (RAFT) are typically limited by the number of monomer units per block and reaction time.[23]

Several strategies to synthesize multiblock copolymers combine anionic polymerization and polycondensation.[13,24–28] For example, the synthesis of polystyrene-*b*-polybutadiene (PS-*b*-PB)$_n$ multiblock copolymers is reported by linking α, ω-dihydroxy PS and PB with the difunctional linker isophorone diisocyanate.[13] Another route via "classic" click chemistry[29,30] is often proposed to synthesize multiblock copolymers, for example, of polystyrene-*b*-polyisoprene (PS-*b*-PI)$_n$ by reacting α-azide, ω-alkine PS-*b*-PI

Table 1. Dispersity Đ, peak molecular weight M_p, fraction of styrene Φ_S, and average block number $< n >$ of the multiblock copolymers for the four investigated samples of PS, PS-*b*-P2VP, and PS-*b*-PI.

Sample	Polymer	Φ_S [vol%]	Đ	M_p	$< n >$ [kg mol^{-1}]
1	PS	1	1.08	61	1
Figure 2a	(PS)$_n$	1	3.2	1125	18
2	PS	1	1.09	29	1
	P2VP-*b*-PS-*b*-P2VP	0.32	1.17	75	3
	(PS-*b*-P2VP)$_n$	0.32	3.2	1184	32
3	PS	1	1.13	58	1
	P2VP-*b*-PS-*b*-P2VP	0.49	1.25	95	3
Figure 2b	(PS-*b*-P2VP)$_n$	0.49	5.3	2305	48
4	PS	1	1.12	59	1
	PI-*b*-PS-*b*-PI	0.53	1.21	84	3
Figure 2c	(PS-*b*-PI)$_n$	0.53	2.2	650	16

diblock copolymers.[25] However, those click or rather linking strategies have several disadvantages, as they are often designed for special initiators for anionic polymerization and special pairs of monomers, and need several time-consuming reaction and purification steps. Whereas the linking of the α, ω-dihydroxy polymers with the linker isophorone diisocyanate did not yield in multiblock copolymers with more than 10 to 15 A and B blocks,[13] the α-azide, ω-alkine click reaction yielded low average coupling numbers, very broad molecular weight distribution with several maxima, and a significant fraction of ring product.[25,27,28] Furthermore, for the click reaction, the reaction kinetics are very slow and even after 216 h reaction time changes in the SEC trace can be observed.[25]

One of the advantages of anionic polymerization compared to other living polymerization techniques is the fast access to high molecular weights. To provide sufficient mechanical performance, (amorphous) homopolymers need to have at least a number average molecular weight M_n of around seven to eight times the entanglement molecular weight.[31,32] Other advantages are the easy control over molecular weight (polymer block sizes) and the absence of branching due to side reactions. This makes the proposed technique ideal for the synthesis of model systems with complex topologies. In the presented approach different samples of homo- and copolymers have been synthesized. The focus of

this article is on the general synthetic approach, which may be transferred to other polymer sorts, not on the specific polymer samples themselves.
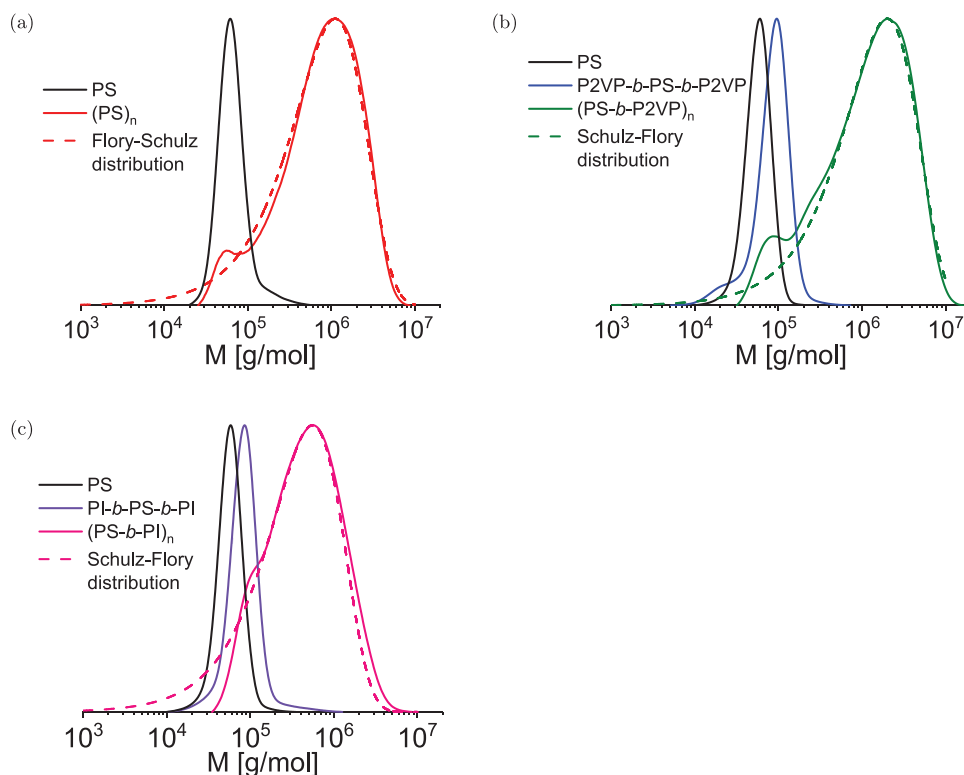
2. Results and Discussion

The presented one-pot approach allows the synthesis of ultra-high molecular weight (UHMW) polymers, including alternating multiblock copolymers in less than 15 min with in average up to 50 blocks (e.g., sample 3 in **Table 1**). A combination of anionic polymerization for the synthesis of the polymer building blocks and a polycondensation reaction for their linking is used, by reaction an A or ABA dianion with α, α'-dibromo-para-xylene as a linker, as shown schematically in **Figure 1**a,b, respectively. In tetrahydrofurane (THF) at −80 °C, the reaction was initiated by a bifunctional initiator of PS via an electron transfer from potassium naphthalenide (KNp) to styrene, forming radical anions, immediately dimerizing to bifunctional anions.[33] To obtain multiblock copolymers, 2-vinyl-pyridine (2VP) or isoprene were added, respectively, to synthesize ABA dianions of poly-2-vinylpyridine-*b*-polystyrene-*b*-poly-2-vinylpyridine (P2VP-*b*-PS-*b*-P2VP) (samples 2 and 3 in Table 1) or polyisoprene-*b*-polystyrene-*b*-polyisoprene (PI-*b*-PS-*b*-PI) (sample 4 in Table 1). The monomers and the solvent were purified as described elsewhere in the literature or in the Supporting Information.[2,12] For the synthesis of the multiblock samples, the dianions obtained after the polymerization of the respective monomers were linked with α, α'-dibromo-para xylene, dissolved in THF.

This bifunctional initiator system is also used in other synthetic approaches, where a bidirectional growth of a polymer chain is essential, as in the synthesis of polymer rings.[34–36] The formation of polymer rings is a one-sided reaction, which may occur, but can be suppressed by adjusted reaction conditions. Furthermore, this approach allows to overcome the limitations of the monomer order for sequential (anionic) polymerization of multiblock copolymers, as the linking S_N2 reaction is not only limited to styrenic carbanions, but also works for acrylate carbanions as well as alkoxides.[4,37] As for other polycondensation reactions a minute balance of the different reactants is essential and thus may limit the average number of connected building blocks $< n >$ of the final polymer chain on a lab scale. The proposed one-pot reaction highly benefits from its kinetics, that is, the fast and irreversible reaction of the carbanion and the alkyl halide group,
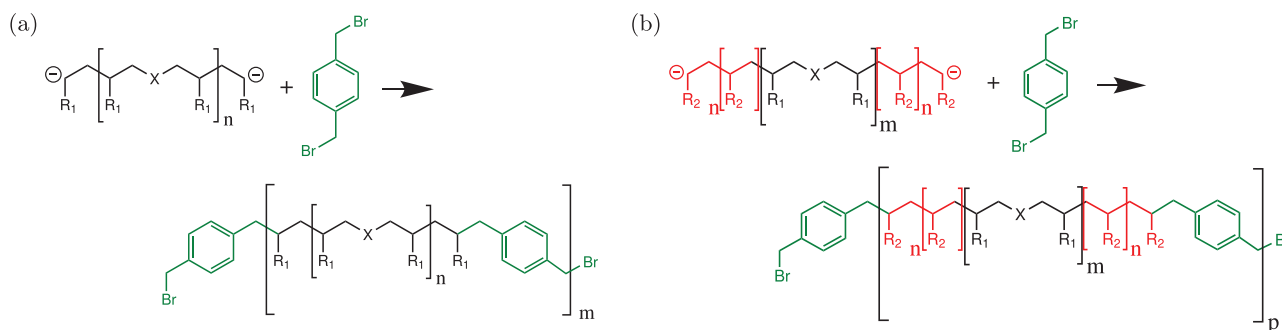
Figure 1. General reaction scheme of the polymerization of a) ultra-high molecular weight homopolymers and b) AB multiblock copolymers, with the bifunctional initiator X.
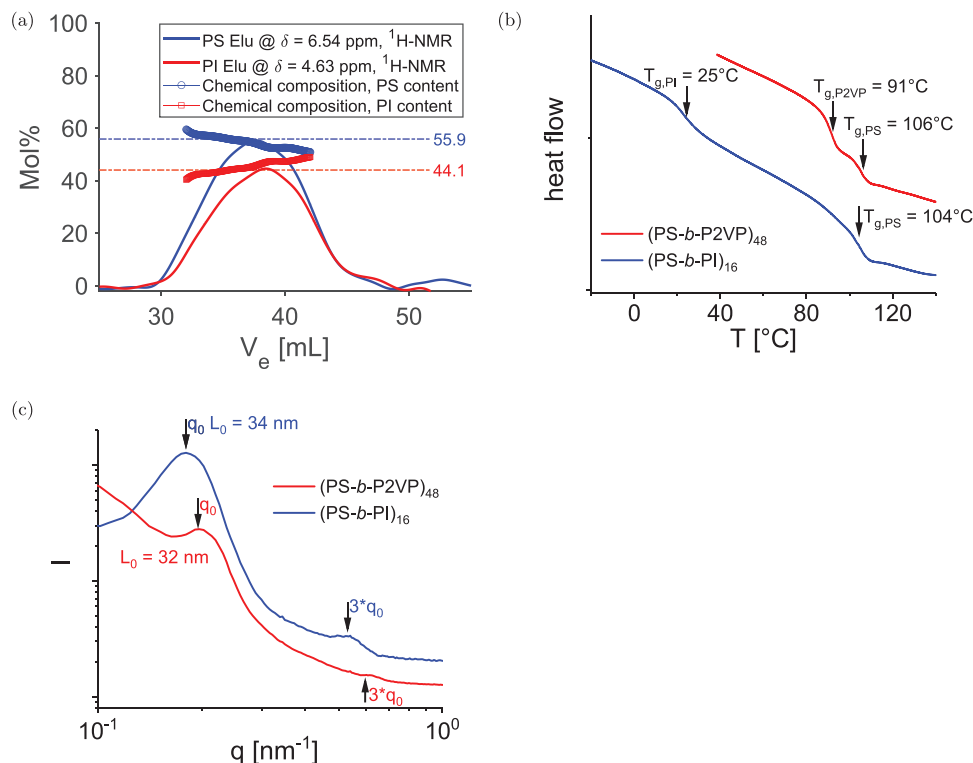
ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

[M]acro-
molecular
Rapid Communications
www.mrc-journal.de

Figure 2. SEC traces for a) linked UHMW PS, b) a (PS-P2VP)$_n$ multiblock, andc) a (PS-PI)$_n$ multiblock. The dashed lines correspond to a Schulz–Flory distribution, that is, the expected molecular mass distribution for a polycondensation reaction with a dispersity of 2.[39]

resulting in a rapid and complete conversion. Thus high block numbers and molecular weights are obtainable by this technique.

The SEC analysis shown in **Figure 2** revealed that both UHMW homopolymers (sample 1 in Table 1; peak molecular weight M_p = 1125 kg mol^{-1}) and multiblock copolymers were obtained with high average block numbers up to 50 A and B blocks, with 18 linked building blocks for the UHMW PS (sample 1; corresponding to "m" in Figure 1), 48 linked building blocks for the PS-*b*-P2VP multiblock copolymer (sample 3, M_p = 2305 kg mol^{-1}) and 16 linked building blocks for the PS-*b*-PI multiblock copolymer (sample 4; M_p = 650 kg mol^{-1}, corresponding to $p/2$ in Figure 1). The details of the samples are summarized in Table 1. The prelinked building blocks have narrow dispersities, whereas the linked multiblock (co)polymers have a broader dispersities, as expected for a polycondensation reaction. The dispersity of the multiblock copolymers represents the distribution of the number of the building blocks per polymer chain and does not correlate with the dispersity of the individual building blocks. However, the dispersity of the building blocks highly influences the phase separation and the resulting microstuctures due to self-assembly of the polymer chains, such as the sharpness of the phase separation as well as the complete shape of a phase diagram.[22,38]

Compared with the Schulz–Flory distribution,[39] presented in Figure 2 by the dashed red lines, the obtained multiblock copolymers miss especially the tail at low molecular weights. The shoulder in the SEC traces in Figure 2 can be associated with side reactions such as termination due to impurities, the monobromo xylene byproduct as well as ring formation. It is important to notice that this shoulder is only visible, because the proposed approach

yieldis the linking of such high block numbers, else this shoulder would just vanish within the main peak. The area of those byproduct shoulders also causes the broad dispersity reported in Table 1 for the final multiblock copolymer. The byproducts can be removed easily via fractionation and for the main peak the dispersity would be around 2, as expected for a polycondensation reaction. The area of these shoulders compared to the rest is small, typically well below 10% (for sample 1 5%, for sample 2 9%, for sample 3 8%, and for sample 4 8%, integrated from the elution volumes), when the one time coupling product is also included. Consequently, the side reaction of ring formation can be assumed as very limited and may be further decreased by optimizing the reaction conditions. The formation of polymer rings is favored for conditions, which favor an intramolecular reaction instead of intermolecular reactions, that is, mainly at low polymer concentrations and low molecular weights.[34] On a lab scale, the block number < n > is limited by a slightly inexact match of the reactants and local mismatches caused, for example, an aggravated mixing by a strong viscosity increase due to the linking of the individual building blocks. Termination reactions occurring on one side of the difunctional macroanion or monofunctional impurities in the linker may further limit the maximal obtainable number of linked building blocks. The amount of a monofunctional contamination of the linker was determined by ^{1}H-NMR, yielding a 2.5 mol% contamination with monofunctional linker. Therefore, the maximal obtainable building block number < n > can be estimated as around 40 linking reactions, that is, for the linking of an ABA dianion in average up to 80 blocks can be linked. A deliberate addition of monofunctional reagents

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

[M]acro-
molecular
Rapid Communications
www.mrc-journal.de

Figure 3. a) Molecular weight dependent chemical composition of the PS-*b*-PI multiblock copolymer (sample 4 in Table 1) determined by on-line SEC-NMR measurements. b) DSC traces and c) SAXS patterns with long period spacing L_0 for (PS-*b*-P2VP)$_n$ and (PS-*b*-PI)$_n$ multiblock copolymers, with 48 and 16 blocks (samples 3 and 4 in Table 1), respectively. Theoretical T_g values are for PS 106 °C, for P2VP 90 °C for 1,2 PI 9 °C, 3,4 PI 33 °C. Both, DSC and SAXS, show clear phase separation.[19]

to the reaction mixture might be a strategy to control the number of linked units.

As for any polycondensation reaction, the degree of polymerization is hard to control. The approach presented here is considered to be the most straight forward one. However, it is also possible to react an A dianion with an α,ω-bromide polymer as another way to synthesize alternating AB multiblock copolymers. The approach to synthesize multiblock copolymers by linking homopolymer building blocks does not guarantee the exact same polymer block sizes along the polymer chain, because an undesired linking of two identical polymer blocks may be possible and thus the reaction conditions have to be changed to reduce the probability of this side reaction.

The molecular composition of a PS-*b*-PI multiblock copolymer sample (sample 4 in Table 1) in relation to the molecular weight is displayed in **Figure 3**a. The composition was determined by on-line SEC-NMR measurements. In this setup a medium resolution (80 MHz), benchtop ^{1}H-NMR spectrometer is coupled to an SEC instrument, where the NMR spectrometer acts as an on-line chemical selective detector. This characterization technique is described in more detailed in the literature.[40] As displayed in Figure 3a, the molecular composition is approximately constant over the whole molecular weight range as it is expected if similar building blocks are connected to form a larger polymer. At high elution volumes some PS homopolymer and some nonlinked PS-*b*-PI building blocks can be seen. However, due to data evaluation artifacts in regions with a low polymer concentration in the elu-

ent, the molecular composition is only displayed for the center of the peak of the linked product.

To investigate phase separation of the multiblock copolymers, differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS) measurements were performed, the DSC traces and the SAXS pattern are shown in Figure 3b,c. For the (PS-*b*-P2VP)$_{48}$ and the (PS-*b*-PI)$_{16}$ multiblock copolymers, the DSC traces reveal two distinctly separated T_g for the two different components of each multiblock copolymer, clearly indicating phase separation. The SAXS pattern shows scattering with peaks at q_0 and $3*q_0$, indicating phase separation and symmetrical lamellae as expected by the synthesis of these samples.

As shown in **Figure 4**a, the presented approach can also be used to create via a CBAABC dianion an (CBAABC)$_n$ multiblock terpolymer, where in principle there is no limitation for the number of different monomers polymerized. Another approach to synthesize terpolymers is via the reaction of a BAB dianion with an α,ω bromide C, resulting in (BABC)$_n$ block copolymers. The reaction of the proposed approach is theoretically never terminated with a proton, but rather always kept "alive" with two highly reactive α,ω functional groups, in the case of α,α'-dibromo-para-xylene as a linker, a methyl bromide group.[34,41] So, the endgroup can be employed for further reactions to form tailor-made block (multiblock) copolymers and topologies, or to be converted into another functional group, for example, an azide group, allowing click chemistry. The remaining α,ω functional groups can be used to continue the reaction with new
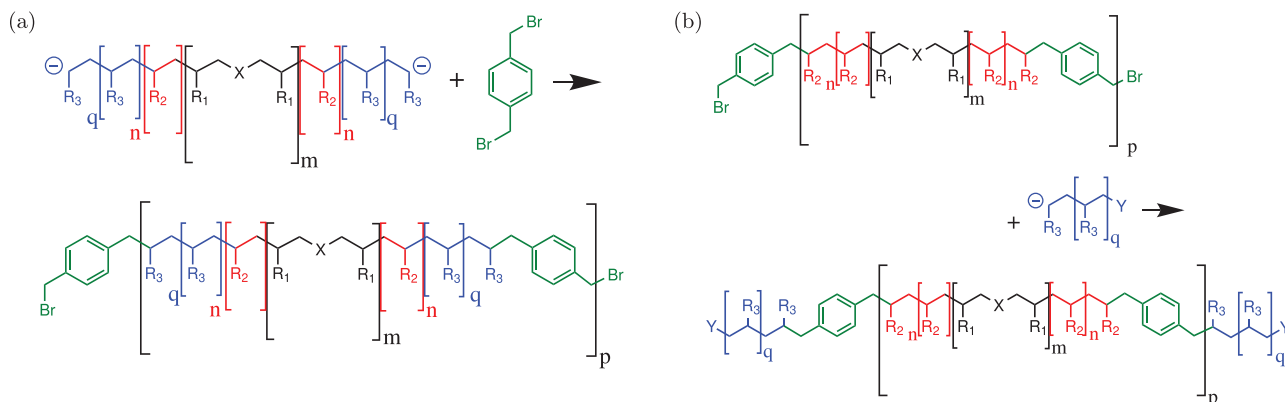
Figure 4. Reaction scheme for AB multiblock and different possible ABC terpolymers. a) A terpolymer macroanion (CBAABC) is linked to form a (CBAABC)$_n$ multiblock terpolymer. b) An end functionalized (BAAB)$_n$ multiblock terpolymer is endcapped with a polymer block C to further tune the multiblock copolymers' properties.

mono- or dianions. The introduction of further dianions allows to obtain even higher molecular weights, or to copolymerize another or several more monomers. If a monoanion C is added as shown as an example in Figure 4b, it reacts at both ends of the multiblock copolymer. So, properties can be engineered, for example, micelles with a hydrophobic multiblock as a core and hydrophile endblocks of both sides as micelle shelf. Reacting the end functionalized multiblock copolymer with further dianions, either of a polymer C or of the polymers A or B, higher block numbers and molecular weights can be obtained. At very low concentrations, high molecular weight ring topologies are accessible by linking the bromine end functionalized multiblock with a dianion. A terminal halide group also allows to add polymer blocks by different polymerization methods such as atom transfer radical polymerization (ATRP) and thus to overcome limitations concerning the range of monomers polymerizable by anionic polymerization.[42,43]

Whereas here only data are presented for the coupling of anionic polymerized vinylic components, the same concept should be possible with monomers polymerized via ring opening polymerization, if a difunctional initiator is used.[44] Tailor-made difunctional initiators also allow for the use of nonpolar solvents as a reaction media[45] and thus allows the synthesis of different microstructures (like PI(-block copolymers) with 1,4-cis-PI as the main topology).[46] Employing a multifunctional linker of different reactivities of the functional groups gives the opportunity to synthesize very fast complex topologies with very well defined molecular parameters. For example, a trifunctional linker with two similar reactive groups and one less reactive group[47–49] can be used to first synthesize a backbone with functional groups allowing a grafting onto reaction into a comb or barbwire topology with well-controlled, uniformly distributed distances between the branches. Another important point to mention is that the presented approach is also highly compatible with the synthesis process of commercial polymers that are produced by anionic polymerization as, for example, PS/PI block copolymers. Additionally, some of the problems connected to the synthesis in a small scale of some grams may be overcome when this technique is transferred to an industrial scale.

3. Conclusion

In conclusion, a very versatile and very fast one-pot approach is proposed to synthesize in UHMW, alternating multiblock copolymers, UHMW homopolymers, and precursors for complex topologies. The approach is based on a combination of polymer dianions obtained by living anionic polymerization and a subsequent polycondensation reaction with a bifunctional linker such as dibromo-para xylene. Block numbers of up to 50 blocks were obtained, with a very narrow distribution of the molecular weight of the blocks.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

[1] F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

[2] M. Heck, L. Schneider, M. Müller, M. Wilhelm, *Macromol. Chem. Phys.* **2018**, *219*, 1700559.

[3] I. W. Hamley, I. W. Hamley, *The Physics of Block Copolymers*, Vol. *19*, Oxford University Press, Oxford **1998**.

[4] N. Hadjichristidis, S. Pispas, G. Floudas, *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*, John Wiley & Sons, Hoboken, NJ **2003**.

[5] A. S. Abd-El-Aziz, M. Antonietti, C. Barner-Kowollik, W. H. Binder, A. Böker, C. Boyer, M. R. Buchmeiser, S. Z. Cheng, F. D'Agosto, G. Floudas, H. Frey, G. Galli, J. Genzer, L. Hartmann, R. Hoogenboom, T. Ishizone, D. L. Kaplan, M. Leclerc, A. Lendlein, B. Liu, T. E. Long, S. Ludwigs, J.-F. Lutz, K. Matyjaszewski, M. A. R. Meier, K. Müllen, M. Müllner, B. Rieger, T. P. Russell, D. A. Savin, et al., *Macromol. Chem. Phys.* **2020**, *221*, 2000216.

[6] T. P. Lodge, *Macromol. Chem. Phys.* **2003**, *204*, 265.

[7] A.-V. Ruzette, L. Leibler, *Nat. Mater.* **2005**, *4*, 19.

[8] V. P. Beyer, J. Kim, C. R. Becer, *Polym. Chem.* **2020**, *11*, 1271.

[9] F. S. Bates, M. A. Hillmyer, T. P. Lodge, C. M. Bates, K. T. Delaney, G. H. Fredrickson, *Science* **2012**, *336*, 434.

[10] J. L. Yarger, B. R. Cherry, A. Van Der Vaart, *Nat. Rev. Mater.* **2018**, *3*, 18008.

[11] A. B. Chang, F. S. Bates, *Macromolecules* **2020**, *53*, 2765.

[12] V. Hirschberg, L. Faust, D. Rodrigue, M. Wilhelm, *Macromolecules* **2020**, *53*, 5572.

[13] I. Lee, F. S. Bates, *Macromolecules* **2013**, *46*, 4529.

[14] I. Lee, T. R. Panthani, F. S. Bates, *Macromolecules* **2013**, *46*, 7387.

[15] L. Wu, E. W. Cochran, T. P. Lodge, F. S. Bates, *Macromolecules* **2004**, *37*, 3360.

[16] R. J. Spontak, S. D. Smith, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 947.

[17] E. Galanos, E. Grune, C. Wahlen, A. H. Muller, M. Appold, M. Gallei, H. Frey, G. Floudas, *Macromolecules* **2019**, *52*, 1577.

[18] E. Grune, M. Appold, A. H. Müller, M. Gallei, H. Frey, *ACS Macro Lett.* **2018**, *7*, 807.

[19] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.

[20] M. Szwarc, M. Levy, R. Milkovich, *J. Am. Chem. Soc.* **1956**, *78*, 2656.

[21] N. Hadjichristidis, H. Iatrou, S. Pispas, M. Pitsikalis, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.

[22] N. A. Lynd, A. J. Meuler, M. A. Hillmyer, *Prog. Polym. Sci.* **2008**, *33*, 875.

[23] G. Gody, R. Barbey, M. Danial, S. Perrier, *Polym. Chem.* **2015**, *6*, 1502.

[24] K. Sugiyama, T. Oie, A. A. El-Magd, A. Hirao, *Macromolecules* **2010**, *43*, 1403.

[25] A. Touris, N. Hadjichristidis, *Macromolecules* **2011**, *44*, 1969.

[26] L. Zhang, L. R. Kucera, S. Ummadisetty, J. R. Nykaza, Y. A. Elabd, R. F. Storey, K. A. Cavicchi, R. Weiss, *Macromolecules* **2014**, *47*, 4387.

[27] P. L. Golas, N. V. Tsarevsky, B. S. Sumerlin, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 6451.

[28] P. L. Golas, N. V. Tsarevsky, B. S. Sumerlin, L. M. Walker, K. Matyjaszewski, *Aust. J. Chem.* **2007**, *60*, 400.

[29] H. C. Kolb, M. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

[30] C. Barner-Kowollik, F. E. Du Prez, P. Espeel, C. J. Hawker, T. Junkers, H. Schlaad, W. Van Camp, *Angew. Chem. Int. Ed.* **2011**, *50*, 60.

[31] V. Hirschberg, L. Schwab, M. Cziep, M. Wilhelm, D. Rodrigue, *Polymer* **2018**, *138*, 1.

[32] L. H. Sperling, *Introduction to Physical Polymer Science*, John Wiley & Sons, Hoboken, NJ **2005**.

[33] M. Morton, *Anionic Polymerization: Principles and Practice*, Elsevier, Amsterdam **2012**.

[34] G. Hild, A. Kohler, P. Rempp, *Eur. Polym. J.* **1980**, *16*, 525.

[35] D. Cho, K. Masuoka, K. Koguchi, T. Asari, D. Kawaguchi, A. Takano, Y. Matsushita, *Polym. J.* **2005**, *37*, 506.

[36] B. Vollmert, J. X. Huang, *Die Makromol. Chem., Rapid Commun.* **1981**, *2*, 467.

[37] N. Hadjichristidis, A. Hirao, Y. Tezuka, F. Du Prez, *Complex Macromolecular Architectures: Synthesis, Characterization, and Self-Assembly*, John Wiley & Sons, Hoboken, NJ **2011**.

[38] Y. Li, H.-J. Qian, Z.-Y. Lu, *Polymer* **2013**, *54*, 3716.

[39] P. J. Flory, *J. Am. Chem. Soc.* **1936**, *58*, 1877.

[40] C. Botha, J. Höpfner, B. Mayerhöfer, M. Wilhelm, *Polym. Chem.* **2019**, *10*, 2230.

[41] G. Hild, C. Strazielle, P. Rempp, *Eur. Polym. J.* **1983**, *19*, 721.

[42] K. Matyjaszewski, *Adv. Mater.* **2018**, *30*, 1706441.

[43] X. Guo, B. Choi, A. Feng, S. H. Thang, *Macromol. Rapid Commun.* **2018**, *39*, 1800479.

[44] Y. Wang, C. Zhou, J. Cheng, *Macromolecules* **2020**, *53*, 3332.

[45] P.-C. Lee, C.-C. Wang, C.-Y. Chen, *Eur. Polym. J.* **2020**, *124*, 109476.

[46] S. Ayano, S. Yabe, *Polym. J.* **1970**, *1*, 706.

[47] A. Hirao, K. Inoue, T. Higashihara, *Macromolecular symposia*, Vol. *240*, Wiley Online Library **2006**, pp. 31–40.

[48] Y. Zhao, T. Higashihara, K. Sugiyama, A. Hirao, *J. Am. Chem. Soc.* **2005**, *127*, 14158.

[49] N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou, *Chem. Rev.* **2001**, *101*, 3747.