Macromolecular Rapid Communications
www.mrc-journal.de

End Group Functionality of 95–99%: Epoxide Functionalization of Polystyryl-Lithium Evaluated via Solvent Gradient Interaction Chromatography

*Philip Dreier, Junyoung Ahn, Taihyun Chang, and Holger Frey**

End group functionality is a key parameter of functional polymer chains. The end-capping efficiency of living polystyryl lithium with various epoxides, namely ethylene oxide (EO), ethoxy ethyl glycidyl ether (EEGE) and isopropylidene glyceryl glycidyl ether (IGG), is investigated with solvent gradient interaction chromatography (SGIC). Generally, end-capping efficiencies >95% are observed. Hydroxy functional polystyrene (PS–OH, PS–EEGE–OH, and PS–IGG–OH) with molar masses ranging from 13.8 to 15.0 kg mol^{-1} are obtained, with dispersities of 1.05–1.06. Deprotection of the acetal (PS–EEGE–OH) and ketal protective group (PS–IGG–OH) is investigated. Nearly quantitative deprotection (>99%) resulting in the corresponding multihydroxy functional PS (PS–(OH)$_2$ and PS–(OH)$_3$) are observed via SGIC. Esterification of PS–OH with succinic anhydride shows a conversion of 98% to the corresponding ester. A detailed picture of side reactions during the carbanionic polymer synthesis subsequent epoxide termination is obtained, demonstrating 95–99% terminal functionality. Depending on the polarity of the end group, an elution order of PS–OH < PS–(OH)$_2$ < PS–(OH)$_3$ < PS–COOH is obtained in SGIC. The study demonstrates both the analytical power of SGIC and the exceptionally high terminal functionalization efficiency of anionic polymerization methods.

1. Introduction

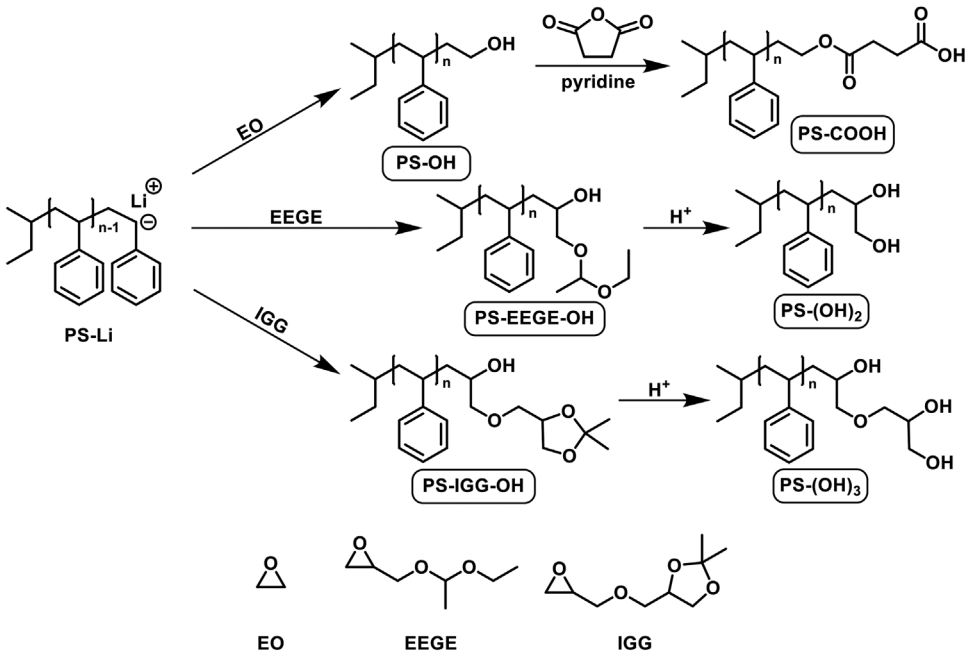
Living carbanionic polymerization (LAP) is the crucial polymerization technique for the precise synthesis of well-defined homo- and co-polymers as well as a vast variety of complex polymer architectures.[1] It is a characteristic feature of this method that transfer and termination reactions are absent, resulting in a Poisson distribution of the molar masses. In LAP, the α-functionality is commonly varied by the implementation of organolithium-based initiators bearing protected functionalities.[2] For the ω-terminus, functionalization is achieved by the end-capping reaction of the living chain end with a large variety of electrophiles, that is, epoxides,[3–8] thiiranes,[9] carbon dioxide,[10] alkyl halides,[11] aldehydes,[12] and sultones.[13] Especially ω-hydroxy-functionalized polymers are increasingly relevant, as they can be subsequently utilized as macroinitiators for the ring-opening polymerizations of epoxides,[14] cyclic esters (i.e., lactones),[15,16] or cyclic carbonates to generate block copolymers.[17] These materials are employed for different applications[18] ranging from polymer electrolytes[19] to nanoporous membranes.[16] ω-Hydroxy-functionalized polystyrene (PS–OH) is obtained via LAP of styrene and end-capping with ethylene oxide (EO),[3,4] as first described by Michael Szwarc.[20] For the end-capping step, high reactivity of the electrophile and the absence of side reactions are crucial to achieve high end group functionality and to reduce traces of non-initiating homopolymer. Consequently, the structure of the electrophile used for termination is of crucial importance. Quirk et al. investigated the addition of propylene oxide (PO)[5] and butylene oxide (BO)[6] to the living chain end of polystyryl lithium (PS–Li) in a detailed manner. They concluded that the end-capping efficiency drops from EO to BO and PO, which is explained by the proton abstraction at the methyl or methylene group in α-position to the oxirane ring of PO and BO, respectively.[21] The portfolio of epoxide reagents for the end-functionalization of PS–Li was further expanded to different glycidyl ethers.[7] Glycidyl ethers can be utilized for the introduction of a variety of additional (protected) functionalities to the chain end, resulting in multifunctional materials.[22]

How can one reliably determine end group functionality of polymer chains? The end-capping efficiency cannot be determined by the widely established size exclusion chromatography (SEC), as the method is commonly incapable of differentiating

P. Dreier, H. Frey
Department of Chemistry
Johannes Gutenberg University Mainz
55099 Mainz, Germany
E-mail: hfrey@uni-mainz.de
J. Ahn, T. Chang
Department of Chemistry and Division of Advanced Materials Science
Pohang University of Science and Technology (POSTECH)
Pohang 37673, Korea

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.202200560

DOI: 10.1002/marc.202200560



Scheme 1. Synthesis of PS–$(OH)_x$ (x = 1–3) and PS–COOH.

between chains with the same hydrodynamic radius but different chain end functionalities.[23] Hence, ^{1}H nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted light desorption/ionization time of flight mass spectrometry (MALDI-ToF MS)[24] have been applied to this end. However, their sensitivity and resolution capacity for end groups are dependent on the molar mass and molecular structure of the investigated polymer. Additionally, in MALDI-ToF MS, the ionization efficiency often differs between unfunctionalized and end-functionalized chains. The mass discrimination effect and fragmentation[25] during ionization of the samples can represent additional disadvantages of the MALDI-ToF MS technique, rendering precise quantification of end group functionality for some polymer classes challenging. In contrast, high-performance liquid chromatography (HPLC) has been established as a suitable method for the quantitative determination of end groups.[24,26,27] For example, Frey's group successfully quantified the products of the tosylation of poly(ethylene oxide).[28] On the other hand, Chang et al. separated and determined living and dead chains of polystyrene synthesized via reversible addition-fragmentation chain-transfer (RAFT)[29] and atom transfer radical polymerization (ATRP)[30] by the utilization of solvent gradient interaction chromatography (SGIC) and specially designed polar agents, demonstrating limited terminal functionalization by these highly popular synthesis methods in the range of 84–91% unless special reaction conditions are utilized.[31]

Although the latter method shows reliable results, to the best of our knowledge, the end-capping reaction of PS–Li with monosubstituted epoxides, especially glycidyl ethers, has not been evaluated by SGIC until today. We prepared different PS–$(OH)_x$ (x = 1–3) samples of molar mass exceeding 10 kg mol^{-1} via end-capping of PS–Li with EO and two hydroxyl-protected glycidyl ethers, namely, ethoxy ethyl glycidyl ether (EEGE) and isopropylidene glyceryl glycidyl ether (IGG). End-capping efficiency, deprotection to multi hydroxyl-functional PS and functionalization of the hydroxyl group were investigated via HPLC.

2. Results and Discussion

Monohydroxy functional polystyrenes PS–OH, PS–EEGE–OH, and PS–IGG–OH were synthesized via carbanionic polymerization of styrene in cyclohexane and subsequent addition of a slight excess of EO, EEGE or IGG[32] to living polystyryl lithium (PS–Li) (**Scheme 1**).[3,4,7] A theoretical molar mass of 15.0 kg mol^{-1} was targeted for all polymers to assure characterization via NMR, that is, precise integration of end group signals in ^{1}H NMR spectra. Prior to the addition to the living chain end, all epoxides were dried carefully with aliquots of *sec*-butyllithium to remove traces of protic impurities and water. We emphasize that this is an essential step to prevent undesired termination reactions.

PS–EEGE–OH and PS–IGG–OH were further deprotected under acidic conditions in THF to yield dihydroxy-functional (PS–$(OH)_2$) and trishydroxy-functional polystyrene (PS–$(OH)_3$), respectively. Molar masses (M_n) of PS–$(OH)_x$ were determined via ^{1}H NMR spectroscopy end group analysis. Comparison of the integrals of the *sec*-butyl initiator group (0.70 ppm) and the signals of the aromatic region (7.36–6.28 ppm) show values of M_n in the range of 13.7–15.0 kg mol^{-1} (**Table 1** and Figures S1–S5, Supporting Information). The SEC traces of all hydroxyl-functionalized PS show narrow monomodal molar mass distributions with low dispersity ranging from 1.05 to 1.06 (Table 1 and **Figure 1**).

For protected (PS–EEGE–OH and PS–IGG–OH) and deprotected samples (PS–$(OH)_2$ and PS–$(OH)_3$), hardly distinguishable SEC traces are obtained, due to the weak influence of the end group on the hydrodynamic radii of the corresponding polymers.[23] Consequently, determination of the end-capping and subsequent deprotection efficiency is not possible by SEC measurements. On the other hand, ^{1}H NMR spectra of

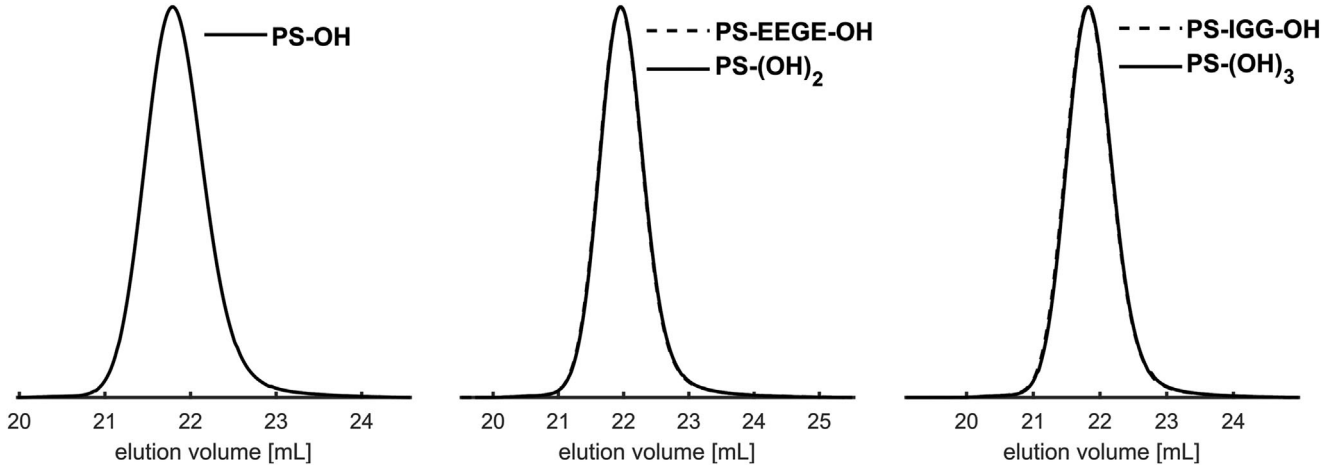


Figure 1. SEC traces (THF, PS calibration, RI detector) of the synthesized polymers; dispersities 1.05–1.06.

Table 1. Overview of the synthesized samples and their end group functionalities..

Sample	M_n [a] [kg mol^{-1}]	M_n [b] [kg mol^{-1}]	$Đ$ [a]	End group functionality [c]
PS–OH	15.0	15.0	1.05	0.99
PS–EEGE–OH	13.8	14.8	1.06	0.96
PS–$(OH)_2$	13.7	15.0	1.06	0.96
PS–IGG–OH	14.9	14.6	1.06	0.96
PS–$(OH)_3$	14.8	14.7	1.06	0.95
PS–COOH	15.0	15.0	1.05	0.98

[a] Determined by ^{1}H NMR spectroscopy ($CDCl_3$ or CD_2Cl_2, 400 MHz). [b] Determined by THF-SEC (PS calibration, RI detector). [c] Determined by SGIC.

PS–EEGE–OH (Figure S2, Supporting Information) and PS–IGG–OH (Figure S4, Supporting Information) and their deprotected analogs support the quantitative deprotection by the complete disappearance of the methine proton of the acetal group at 4.56 ppm (PS–$(OH)_2$) and the methyl protons of the ketal group at 1.44 ppm (PS–$(OH)_3$) (Figures S3 and S5, Supporting Information). The further functionalization of PS–OH to its carboxylic acid analog (PS–COOH) was adapted from Ferruti et al.[33] The esterification reaction was carried out with succinic anhydride in dry $CHCl_3$ in the presence of pyridine. New resonances are observed between 4.00–3.60 and 2.60–2.40 ppm in the ^{1}H NMR spectrum of PS–COOH (**Figure 2**), which are assigned to the methylene groups adjacent to the ester oxygen (a) and carbonyl groups of the succinic half-ester (b–c), respectively.

Additionally, the signal of the methylene group next to the hydroxyl group (a′) at 3.30 ppm of the PS–OH precursor is absent in the spectrum, which indicates quantitative esterification. Based on the results obtained via ^{1}H-NMR spectroscopy, end-capping, deprotection, and derivatization reactions of the end groups appeared to be quantitative processes (Figure 2 and Figures S2–S6, Supporting Information). However, as shown in the ensuing section, these common methods cannot detect low amounts of non-functionalized polymer chains.

To further quantify end-capping as well as deprotection efficiency and to separate potential different polymeric entities of the abovementioned synthesis, SGIC with a bare silica stationary phase and a THF/*n*-hexane mobile phase was employed. In contrast to SEC, in interaction chromatography, the separation of chains with different end-functionalization, despite the same molar masses and therefore hydrodynamic radii depends on the polarity of the polymers' functional end group.[23] Therefore, as-prepared samples were investigated with respect to their interaction behavior under SGIC conditions (**Figure 3**).

At the beginning of the measurement the solvent mixture was held constant at 25 $\%_{vol}$ THF and 75 $\%_{vol}$ *n*-hexane for 20 min. Subsequently, the THF content was increased to 75 $\%_{vol}$ over a 30 min time frame. A qualitative trend is obtained: With increasing polarity of the PS end group an increase in the elution time (t_E) of the samples is observed. Consequently, the primary hydroxyl group of PS–OH shows stronger interaction and a higher t_E of the sample compared to the secondary hydroxyl groups of PS–EEGE–OH and PS–IGG–OH. Furthermore, the additional ether oxygen of PS–IGG–OH appears to result in more pronounced adsorption compared to PS–EEGE–OH.

After removal of the acetal protecting groups for PS–$(OH)_2$ and PS–$(OH)_3$, t_E strongly increases compared to their protected analogs due to the stronger interaction of the multiple hydroxyl groups per chain-end with the stationary phase.[27,29] On the other hand, PS–COOH exhibits the highest elution time of all samples, which is explained by the high polarity of the carboxylic acid group in comparison to multiple hydroxyl groups. Therefore, the elution order of the different functional polymers is PS–OH < PS–$(OH)_2$ < PS–$(OH)_3$ < PS–COOH. In all samples, traces of non-functionalized (proton-terminated) PS are observed (**Figure 4**), which exhibit t_E comparable to the PS standard.

The undesired termination reactions might be explained by various reactions. On the one hand, traces of protic impurities or water could be present during the end-capping step and react with the living chain-end. On the other hand, the glycidyl ethers EEGE and IGG exhibit weakly acidic protons at the methylene group at the oxirane ring.[34] Consequently, the highly basic PS–Li may abstract a proton, resulting in an unfunctionalized chain. The latter reaction was observed by Quirk et al. for the end-capping of PS–Li with propylene oxide[5] and butylene oxide.[6] This pathway likely accounts for the considerable increase of

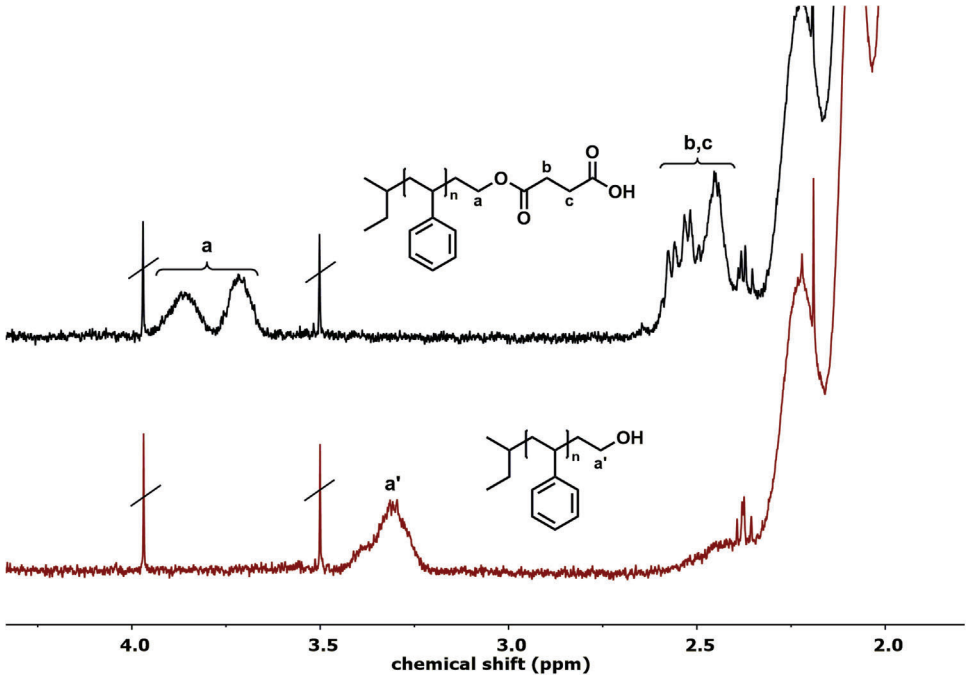


Figure 2. Section of ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of PS–OH (bottom) and PS–COOH (top).

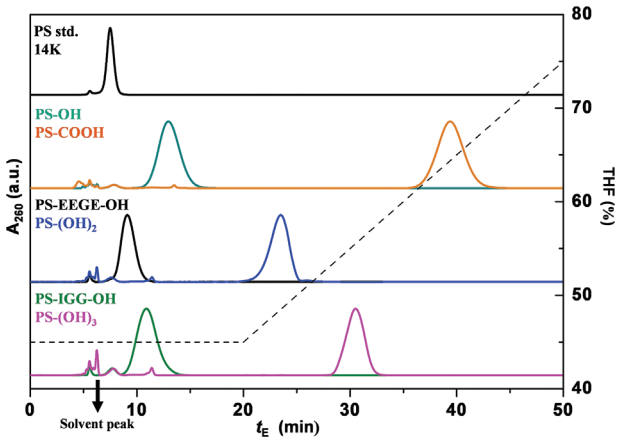


Figure 3. HPLC chromatograms of PS standard (top), PS–OH and PS–COOH (overlay, top middle), PS–EEGE–OH and PS–$(OH)_2$ (overlay, bottom middle), and PS–IGG–OH and PS–$(OH)_3$ (overlay, bottom).

Table 2. Overview and quantification of the different fractions in the HPLC chromatogram of PS–$(OH)_2$.

Fraction	Amount [%]
F1 (PS, dead chain)	2.5
F2 (PS–EEGE–OH)	0.7
F3 (PS–$(OH)_2$)	95.5
F4	1.3

proton-terminated, "dead" PS chains from 0.7% to 2.5% and 4.0% (Figure 4 and **Tables 2** and **3**), when comparing PS–EEGE–OH and PS–IGG–OH with PS–OH, since EO-termination cannot lead to this kind of proton abstraction.

Table 3. Overview and quantification of the different fractions in the HPLC chromatogram of PS–$(OH)_3$.

Fraction	Amount [%]
F1 (PS, dead chain)	4.0
F2 (PS–IGG–OH)	0.7
F3 (PS–$(OH)_3$)	95.3

The high end-capping efficiency (>99%) for PS–OH (Figure S7, Supporting Information) is in accordance with MALDI-ToF MS results reported by Quirk et al. for the end-capping efficiency of low molar mass PS–Li with EO.[3,4] The SGIC-based observations demonstrate the higher end group fidelity of carbanionic polymerization over controlled radical polymerization (CRP) techniques. In the latter case, terminal functionalities of merely 84%[30] and 91%[29] were observed for ATRP and RAFT polymerization via SGIC, respectively. These kinetic limitations can be suppressed to some extent with the utilization of specialized reaction conditions.[31]

A more detailed examination of the HPLC chromatograms of PS–$(OH)_3$ (Figure 4) also allows for quantification of the deprotection efficiency. Besides fraction 3 (F3) (PS–$(OH)_3$) (95.3%) and fraction 1 (F1) (4.0%) (dead PS), fraction 2 (F2) (0.7%) is assigned to PS–IGG–OH by the overlay of the HPLC chromatograms of PS–$(OH)_3$ (Table 3). This is a crucial observation, for instance regarding the subsequent synthesis of AB_3 star block copolymers. Insufficient deprotection will lead to the formation of ≈1% impurities in form of linear block copolymers, which are formed along with the targeted star block copolymers. The unprotected species (0.7%) was equally observed in the case of PS–$(OH)_2$ (Figure 4 and Table 2). However, in both cases a high deprotection

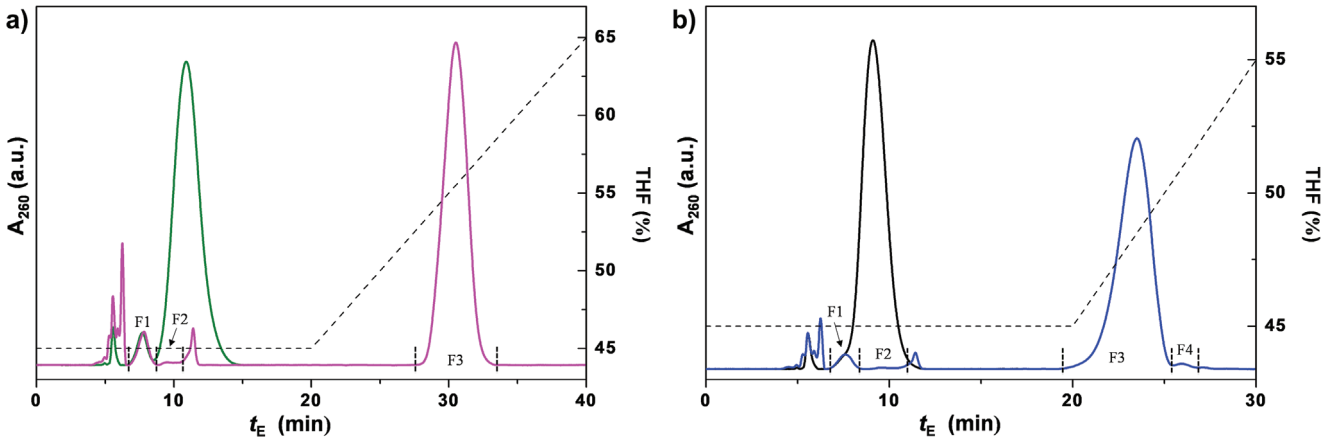


Figure 4. Overlay of HPLC chromatograms of a) PS–IGG–OH and PS–$(OH)_3$ and b) PS–EEGE–OH and PS–$(OH)_2$.

efficiency of >99% was obtained. Additionally, a sharp peak at t_E = 12 min was observed in the chromatograms of both PS–$(OH)_3$ and PS–$(OH)_2$, whose insignificant light scattering intensity points to a non-polymeric impurity (Figure S8, Supporting Information).

In case of the esterification reaction of PS–OH with succinic anhydride, small traces of non-functionalized chains (<0.2%) and PS–OH precursor (2.1%) are observed in the chromatogram of PS–COOH (Figure S7, Supporting Information). However, nearly all (97.7%) hydroxyl groups undergo the targeted esterification reaction, which is remarkable for a post-polymerization reaction and proves excellent addressability of the hydroxyl functionality.

3. Conclusion

The results of this study reveal the pitfalls of commonly used techniques (SEC and ^{1}H NMR) to assess the quality of a terminal functionalization method for polymers. From the results, it is obvious that these methods can only provide a first estimate of the actual functionalization. To the best of our knowledge, the SGIC-method has not been employed to date for the detailed evaluation of the end-capping efficiency of the well-known epoxide termination strategy for carbanionic polymerization. We employed PS–Li with molar masses of 13.8–15.0 kg mol^{-1} in combination with EO, as well as two typical glycidyl ethers, EEGE and IGG. The end-capping efficiency has been quantified with unprecedented precision via SGIC. Chain-end functionalization efficiencies of >99% with EO and >95% with EEGE and IGG were observed, and all occurring side-reactions could be quantified. The ensuing deprotection efficiencies of the acetal and ketal groups were determined to be >99% by HPLC. Traces of unfunctionalized PS chains were observed for all samples by SGIC. Further functionalization of PS–OH with succinic anhydride showed a conversion of 98% of the hydroxyl groups to the carboxylic acid moiety. The detailed results obtained via SGIC demonstrate that ^{1}H NMR measurements are insufficient to precisely assess the fraction of functionalized chains, since NMR indicated quantitative end-capping, deprotection, and derivatization reactions of the end groups.

In summary, this study clearly demonstrates the power of SGIC to determine end-capping and deprotection efficiency of polymer chains. Our observations further highlight the advantage of carbanionic polymerization over the widely used CRP techniques with 84–91% end group functionality according to previous studies. Functional groups at the chain end[35] are of crucial importance for the synthesis of pure block copolymers or complex polymer architectures in general.

Supporting Information

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

Acknowledgements

P.D. thanks Rebecca Matthes for fruitful discussions and Monika Schmelzer for support with SEC measurements.

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

carbanionic polymerization, chain end functionalizations, epoxides, polymer characterizations, solvent gradient interaction chromatography

Received: June 22, 2022
Revised: July 26, 2022
Published online: August 17, 2022

[1] N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou, *Chem. Rev.* **2001**, *101*, 3747.
[2] a) C. L. Elkins, K. Viswanathan, T. E. Long, *Macromolecules* **2006**, *39*, 3132; b) A. Hirao, Y. Matsuo, T. Oie, R. Goseki, T. Ishizone, K. Sugiyama, A. H. Gröschel, A. H. E. Müller, *Macromolecules* **2011**, *44*, 6345; c) I. Lee, F. S. Bates, *Macromolecules* **2013**, *46*, 4529; d) A. Touris, S. Lee, M. A. Hillmyer, F. S. Bates, *ACS Macro Lett.* **2012**, *1*, 768.
[3] R. P. Quirk, J.-J. Ma, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031.
[4] R. P. Quirk, R. T. Mathers, C. Wesdemiotis, M. A. Arnould, *Macromolecules* **2002**, *35*, 2912.
[5] R. P. Quirk, G. M. Lizárraga, *Macromolecules* **1998**, *31*, 3424.
[6] R. P. Quirk, Q. Ge, M. A. Arnould, C. Wesdemiotis, *Macromol. Chem. Phys.* **2001**, *202*, 1761.
[7] C. Tonhauser, D. Wilms, F. Wurm, E. B. Nicoletti, M. Maskos, H. Löwe, H. Frey, *Macromolecules* **2010**, *43*, 5582.
[8] a) R. P. Quirk, A. Contractor, M. J. Polce, C. Wesdemiotis, *Macromol. Chem. Phys.* **2006**, *207*, 2280; b) R. P. Quirk, H. Hasegawa, D. L. Gomochak, C. Wesdemiotis, K. Wollyung, *Macromolecules* **2004**, *37*, 7146.
[9] R. P. Quirk, M. Ocampo, M. J. Polce, C. Wesdemiotis, *Macromolecules* **2007**, *40*, 2352.
[10] a) S. Park, D. Cho, J. Ryu, K. Kwon, T. Chang, J. Park, *J. Chromatogr. A* **2002**, *958*, 183; b) R. P. Quirk, J. Yin, L. J. Fetters, *Macromolecules* **1989**, *22*, 85.
[11] K. Ueda, A. Hirao, S. Nakahama, *Macromolecules* **1990**, *23*, 939.
[12] R. P. Quirk, J. Kuang, *Polym. Int.* **1994**, *33*, 181.
[13] R. P. Quirk, J. Kim, *Macromolecules* **1991**, *24*, 4515.
[14] a) M. A. Hillmyer, F. S. Bates, *Macromolecules* **1996**, *29*, 6994; b) R. P. Quirk, J. Kim, K. Rodrigues, W. L. Mattice, *Makromolekulare Chemie. Macromol. Symp.* **1991**, *42–43*, 463; c) T. S. Bailey, H. D. Pham, F. S. Bates, *Macromolecules* **2001**, *34*, 6994.
[15] S. C. Schmidt, M. A. Hillmyer, *Macromolecules* **1999**, *32*, 4794.
[16] A. S. Zalusky, R. Olayo-Valles, J. H. Wolf, M. A. Hillmyer, *J. Am. Chem. Soc.* **2002**, *124*, 12761.
[17] A. Vora, R. J. Wojtecki, K. Schmidt, A. Chunder, J. Y. Cheng, A. Nelson, D. P. Sanders, *Polym. Chem.* **2016**, *7*, 940.
[18] a) T. H. Epps, III, R. K. O'reilly, *Chem. Sci.* **2016**, *7*, 1674; b) C. M. Bates, F. S. Bates, *Macromolecules* **2016**, *50*, 3.
[19] P. M. Ketkar, K.-H. Shen, L. M. Hall, T. H. Epps, *Mol. Syst. Des. Eng.* **2019**, *4*, 223.
[20] D. H. Richards, M. Szwarc, *Trans. Faraday Soc.* **1959**, *55*, 1644.
[21] R. P. Quirk, T.-H. Cheong, K. Jiang, D. L. Gomochak, T. Yoo, K. T. Andes, R. T. Mathers, *Macromol. Symp.* **2003**, *195*, 69.
[22] C. Tonhauser, H. Frey, *Macromol. Rapid Commun.* **2010**, *31*, 1938.
[23] T. Chang, *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1591.
[24] X. Jiang, P. J. Schoenmakers, J. L. J. Van Dongen, X. Lou, V. Lima, J. Brokken-Zijp, *Anal. Chem.* **2003**, *75*, 5517.
[25] R. S. Lehrle, D. S. Sarson, *Polym. Degrad. Stab.* **1996**, *51*, 197.
[26] a) R. Guo, Z. Shi, X. Wang, A. Dong, J. Zhang, *Polym. Chem.* **2012**, *3*, 1314; b) W. Lee, D. Cho, B. O. Chun, T. Chang, M. Ree, *J. Chromatogr. A* **2001**, *910*, 51.
[27] H. Gao, G. Louche, B. S. Sumerlin, N. Jahed, P. Golas, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 8979.
[28] H. Pohlit, M. Worm, J. Langhanki, E. Berger-Nicoletti, T. Opatz, H. Frey, *Macromolecules* **2017**, *50*, 9196.
[29] K. Kim, J. Ahn, M. Park, H. Lee, Y. J. Kim, T. Chang, H. B. Jeon, H.-J. Paik, *Macromolecules* **2019**, *52*, 7448.
[30] J. Oh, J. Kuk, T. Lee, J. Ye, H. Paik, H. W. Lee, T. Chang, *ACS Macro Lett.* **2017**, *6*, 758.
[31] G. Gody, T. Maschmeyer, P. B. Zetterlund, S. Perrier, *Macromolecules* **2014**, *47*, 639.
[32] F. Wurm, J. Nieberle, H. Frey, *Macromolecules* **2008**, *41*, 1909.
[33] P. Ferruti, M. C. Tanzi, L. Rusconi, R. Cecchi, *Makromol. Chem.* **1981**, *182*, 2183.
[34] M. Hans, H. Keul, M. Moeller, *Polymer* **2009**, *50*, 1103.
[35] D. Zhou, L.-W. Zhu, B.-H. Wu, Z.-K. Xu, L.-S. Wan, *Polym. Chem.* **2022**, *13*, 300.

