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RESEARCH ARTICLE

AROMA: Anionic ring-opening monomer addition of allyl glycidyl ether to methoxy poly(ethylene glycol) for the synthesis of sequence-controlled polymers

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Abstract

Herein, a new method to synthesise epoxide-based sequence-controlled polymers via anionic ring-opening monomer addition, a form of anionic ring-opening polymerisation, is presented. This technique allows in combination with post-polymerisation modification (PPM) reactions for the successful preparation of modified mPEG-*b*-oligo(allyl glycidyl ether) featuring the incorporation of one repeating unit on average at a time. Due to the possible introduction of a vast variety of molecules to the polymeric system via PPM reactions, a multitude of advanced functional polymeric materials can be generated. This, in combination with the chain extension reactions, allows for the synthesis of well-controlled and programmable architectures with particular properties. The structure of the sequence-controlled polymer was confirmed via ^{1}H NMR spectroscopy, size exclusion chromatography, attenuated total reflection Fourier-transform infrared spectroscopy, and differential scanning calorimetry.

Introduction

The structural design of macromolecules has a significant influence on their characteristics and properties (Mark, 2007), and therefore their application. The total control of the macromolecular structure and the subsequent influence on the properties is therefore of high interest to the field of polymer chemistry and materials science. Hence, inspired by nature, the control of the sequence of repeating units along a macromolecular chain has recently received particular attention (Lutz, 2017). An example of such a well-defined macromolecule in nature is deoxyribonucleic acid (DNA). In contrast, the easiest example of a synthetic sequence-controlled polymer is a block copolymer, being prepared from only two different monomers that are polymerised in sequence. By increasing the number of monomers, complex macromolecules with a defined sequence can be generated, that is, multiblock copolymers, yet still missing the perfection of those found in nature. In the last decade, synthetic ways were investigated to synthesise sequence-defined molecules like DNA. Even though those processes were improved (e.g., the use of solid-phase chemistry) over time, they are still highly tedious (Lutz et al., 2013).

In recent years, single monomer addition techniques based on atom transfer radical polymerisation (Tong et al., 2011) and reversible addition−fragmentation chain-transfer polymerisation (Houshyar

et al., 2012) emerged and allowed for the synthesis of sequence-defined polymers (SDPs) with one repeating unit at a time. Such macromolecules with a precisely known and defined sequence allow for different applications, such as information storage via molecular coding (Trinh et al., 2014), antimicrobial peptides (Hamuro et al., 1999; Porter et al., 2000), or polymeric drug transporters (Wieczorek et al., 2013; Celasun et al., 2019). Regarding SDPs, their applications, and their synthesis, several studies and reviews have been published over time (Nanjan and Porel, 2019; Deng et al., 2021).

Besides using specific monomers to introduce certain properties into a polymeric material, a pre-synthesised polymer can be modified to achieve similar results. Important for such *post-polymerisation modification* (PPM) reactions, also known as *polymer analogous modification*, are functional monomers, which later enable a reaction with a variety of reactants to yield polymeric materials with different properties, yet all originating from the same precursor polymer (Gauthier et al., 2009; Chen and Michinobu, 2022). Two examples of PPM reactions are the modification of poly(allyl ethylene glycol vinyl ether)s with different thiols via *thiol-ene* reactions (Butzelaar et al., 2021) and the aminolysis of poly(pentafluorophenyl methacrylate) with allylamine (Singha et al., 2011).

In 2012, Ree's group presented the synthesis of homopolyethers and diblock copolyethers based on the functional epoxide allyl glycidyl ether (AGE) via a metal-free anionic ring-opening polymerisation (AROP) at room temperature, promoted by the *Schwesinger base* P_4-*t*-Bu (Kwon et al., 2012). Already in 1996, Möller's group reported the AROP of ethylene oxide using the strong phosphorazene base with alkyllithium compounds (Esswein and Möller, 1996), paving the way for further research. Due to the water solubility, low toxicity (Fruijtier-Pölloth, 2005), good electrochemical stability, and compatibility with lithium salts (Xue et al., 2015), poly(ethylene oxide) (PEO), also known as poly(ethylene glycol) (PEG), has a broad field of application, reaching from the medical department (e.g., drug delivery [Knop et al., 2010] and tissue engineering [Tessmar and Göpferich, 2007]) to commercial use (cosmetics and soaps) (Jang et al., 2015) and battery research (Xue et al., 2015). In comparison to PEO, poly(AGE) bears a pendant alkene group, allowing for possible PPM reactions, like *thiol-ene* reactions, and therefore the creation of polymeric material with different applications. Poly(AGE) has been investigated as a solid polymer electrolyte for lithium-sulphur batteries (Mallela et al., 2020) as well as part of a copolymer for micellar drug delivery systems (Hrubý et al., 2005). The advantages of a functional polymers like poly(AGE) in combination with a well-defined sequence could be of high interest for further developments in the medical field, data storage, and catalytic processes.

Therefore, a new method to synthesise sequence-controlled polymers based on mPEG-*b*-oligo(AGE), featuring an average of one repeating unit, is presented in this study. Those well-controlled polymers with narrow molar mass distributions of 1.05–1.08 were synthesised by a combination of chain extension (CE) reactions via an AROP technique and PPM reactions. Due to the addition of an average of one unit to the chain, we propose to call this method anionic ring-opening monomer addition (AROMA). This novel method allows for the preparation of functional, programmable polymeric materials with a controlled architecture and particular properties. The repetitive steps of successful CE and PPM reactions were confirmed via ^{1}H NMR spectroscopy, size exclusion chromatography (SEC), attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy, and differential scanning calorimetry (DSC).

Results and discussion

The overall synthetic scheme of AROMA is shown in Scheme 1. As a synthetic support, an mPEG initiator was chosen that allows for a successful synthesis and subsequent characterisation. A detailed description of the synthetic processes as well as the assignment of ^{1}H NMR and ATR FT-IR spectra can be found in the Supplementary Material.

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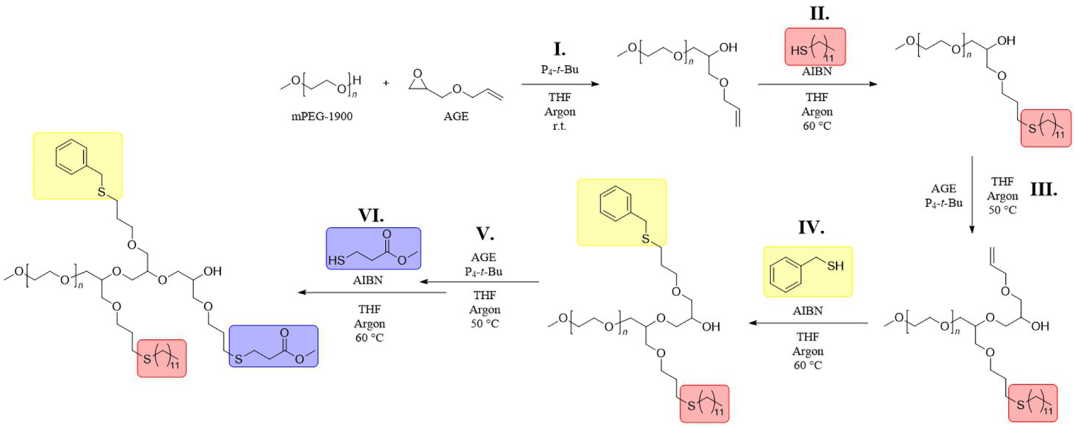

Scheme 1. *The overall synthetic scheme of the anionic ring-opening monomer addition of AGE to mPEG-1900 to synthesise sequence-controlled polymers. The individual steps of chain extension (I., III., and V.) and post-polymerisation modification (II., IV., and VI.) reactions are displayed.*

Table 1. *Overview of all conducted reactions, including equivalents, reaction time, temperature, molar mass, dispersity, and the theoretical average repeating unit.*

Entry	Equiv. monomer	Equiv. thiol	Time (h)	Temp.	$M_{n,\mathrm{exp}}$ (g mol^{-1})	$Đ$	Theoretical average repeating units
P1	20.0	–	2.5	r.t.	5,000	1.03	20
CE-1	1.25	–	5	r.t.	3,200	1.05	1.02 ± 0.07
CE-2	1.25	–	5.5	50°C	4,100	1.05	1.02 ± 0.06
CE-3	1.25	–	5.5	50°C	4,400	1.05	0.88
PPM-1	–	4.00	24	60°C	3,800	1.05	–
PPM-2	–	4.00	20	60°C	4,200	1.05	–
PPM-3	–	4.00	20	60°C	4,800	1.08	–

Anionic ring-opening polymerisation

Based on the results of Ree's group regarding the AROP of AGE promoted by P$_4$-*t*-Bu, this system was considered for the synthesis of sequence-controlled polymers. Thus, the polymerisation and kinetics of the AROP of AGE were investigated first. All reactions are summarised in Table 1. The AROP (P1) of 20 eq. of AGE relative to the initiator was conducted in dry tetrahydrofuran (THF) and under an inert atmosphere (argon) at room temperature for 2.5 hr. Methoxy PEG with an average molar mass of 1,900 g/mol (mPEG-1900) was chosen as the initiator and acted as a precipitation agent, to simplify the purification process. A conversion of AGE of ≥99% was determined via ^{1}H NMR spectroscopy. The successful synthesis of mPEG-*b*-poly(AGE) was confirmed via SEC (Figure 1a) and ^{1}H NMR spectroscopy (Figure 1b). The SEC elugram showed a symmetrical peak with a number-average molar mass (M_n) of approximately 5,000 g/mol and a dispersity ($Đ$) of 1.03 without any further peaks, being indicative for the absence of side reactions and hence a polymerisation with a living character. The ^{1}H NMR spectrum displays all characteristic proton signals expected for polymer P1 and is in accordance with those reported in the literature for poly(AGE) (Lee et al., 2011).

In addition to the direct polymerisation, a kinetic study of the polymerisation with 20 eq. of AGE was conducted. To determine the conversion of the polymerisation, samples were taken directly from

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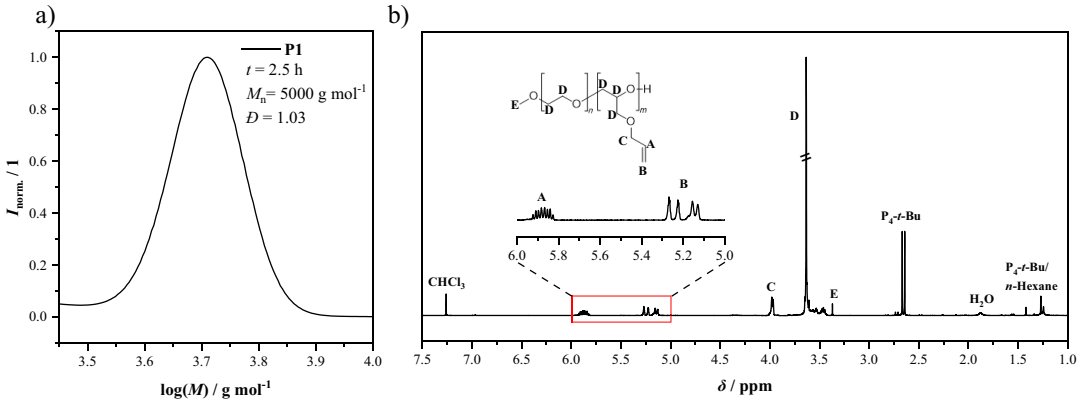

Figure 1. *(a) Size exclusion chromatogram and (b) ^{1}H NMR spectrum (solvent: $CDCl_3$) of P1.*

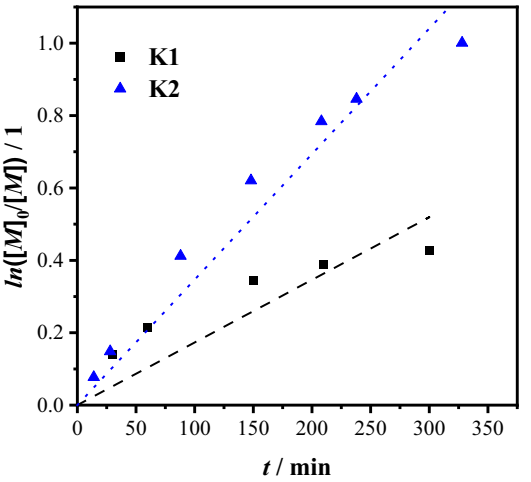

Figure 2. *Kinetic study of the polymerisation of AGE using non-treated (K1; blue) and dried (**K2**; black) mPEG-1900.*

the reaction mixture after specific times and analysed via ^{1}H NMR spectroscopy. In order to identify the influence of the initiator system, two polymerisations were studied: (i) one in which the initiator was used as received (K1; black squares) and (ii) another, where mPEG-1900 was pre-dried under reduced pressure at 40°C (**K2**; blue triangles). Both kinetic plots are displayed in Figure 2. Noticeable for the first polymerisation using the non-treated initiator, the curve at longer reaction times is levelling off, instead of the expected linear behaviour (Figure 2, black dashed line) for a living polymerisation. This implies a change of the propagating species over time, which may potentially result from side reactions. The side reactions could be minimised by pre-drying mPEG-1900, leading to a more linear trend (Figure 2, blue triangles and dotted line), but not eliminated. This suggested an occurring termination process initiated by water, which was present in mPEG-1900.

An initiator with a lower affinity towards water might further minimise or even eliminate the termination processes; however, mPEG-1900 was used nevertheless because of its similarity to the poly(AGE) backbone and possible biomedical applications. Overall, this observation clearly states the importance of dry and purified chemicals for this polymerisation technique to achieve a reaction in a living manner.

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Anionic ring-opening monomer addition

First chain extension

Based on the successful polymerisation of AGE using mPEG-1900 as the initiator and the *Schwesinger* base as the catalyst, attempts were made to synthesise sequence-controlled polymers with an average repeating unit of one per 'block'. Due to the anionic ring-opening character of the technique, as well as the addition of the monomer, we suggest to call this conducted method AROMA. Again, pre-dried mPEG-1900 was chosen as the initiator, to act as a precipitation agent and therefore make the purification process easier. The chain was extended and subsequently modified via a *thiol-ene* reaction. This procedure was conducted three times, to investigate the multiple applicability of the method. The first CE (**CE-1**) was conducted in THF with a slight feed excess of AGE (1.25 eq.) at room temperature for 5 hr. The obtained polymer was characterised via ^{1}H and ^{13}C NMR spectroscopy, SEC, IR, and DSC. Exemplary results are displayed in Figure 3. The SEC elugram (Figure 3a) showed a single symmetrical peak with an M_n of 3,200 g/mol and a $Đ$ of 1.05 after the extension, indicating a successful reaction without any side reactions. With the AROMA method, it was possible to obtain macromolecules with an average relating unit of AGE of 1.02 ± 0.07, which was confirmed via ^{1}H NMR (Figure 3b) by comparing the signal ratio of the initiator's methoxy group (3.36 ppm) with the AGE double bond (6.00–5.77 ppm). The difference in the experimental value (repeating units: 1.02 ± 0.07) to the theoretical value (repeating units: 1) for an addition reaction can be explained by the technique the AROMA method is based on. The anionic (ring-opening) polymerisation is capable to synthesise polymers with low dispersity ($Đ$ = 1.01–1.1) (Morsbach et al., 2016) but not monodisperse macromolecules, which would be necessary to exactly link a single monomer unit to every chain. Therefore, the AROMA method can only be used to prepare sequence-controlled and not necessary SDPs. The ^{13}C NMR spectrum (Supplementary Material) was in accordance with the literature (Barteau et al., 2013), confirming the addition of AGE to the chain. A DSC of the AROMA-polymer determined a melting temperature (T_m) of 54.2°C. The thermogram of the second heating cycle can be seen in Figure 3c. To further confirm the presents of an AGE unit on the chain end, ATR FT-IR spectroscopy was used to identify the double bond. In Figure 3d, the comparison between the ATR FT-IR spectra of mPEG-1900 (black) and the chain-extended polymer (blue) is displayed. Visible is the appearance of a weak signal at 1,645/cm, which can be assigned to the C=C double bond's stretching vibration of the newly added AGE (Gorin et al., 1971). The signal intensity is rather weak, due to the small fraction of the AGE relative to the total structure of the polymer. After the successful CE of mPEG-1900 with AGE, the AROMA-polymer was further used in a modification reaction, as discussed in detail in the 'Post-polymerisation modification of mPEG-b-oligo(AGE)' section.

Further chain extensions

After the successful first CE and modification of mPEG-1900, further CEs were conducted, to confirm that the AROMA method can be repeated multiple times at will. Furthermore, this could give insight about possible interactions of the modified pendant groups with the chain end. Especially bulky or longer molecules could be able to cover the OH-group due to steric hindrance, impeding the AROMA process. Therefore, the newly added 1-dodecanethiol was a suitable candidate to investigate this hypothesis. In the following section, the focus is on the results of the second CE. Graphs and further analytical data of the third extension can be found in the Supplementary Material. The procedure for further extensions was similar to the first CE with 1.25 eq. of monomer in relation to the macroinitiator mPEG-*b*-oligo(AGE), but at higher temperature (50°C) and for 5.5 hr. Previous experiments suggested that an increase in the temperature for a successful second CE is necessary to achieve a sufficient high conversion. A possible explanation for this observation is the change from a primary to a secondary alcohol at the chain end after the first extension, requiring a higher temperature.

The success of the second monomer addition was confirmed via ^{1}H NMR spectroscopy, SEC, ATR FT-IR spectroscopy, and DSC. In Figure 4a, the SEC elugram of the second addition is displayed, showing a shift of M_n to higher values (3,800–4,100 g/mol) while maintaining a $Đ$ of 1.05.

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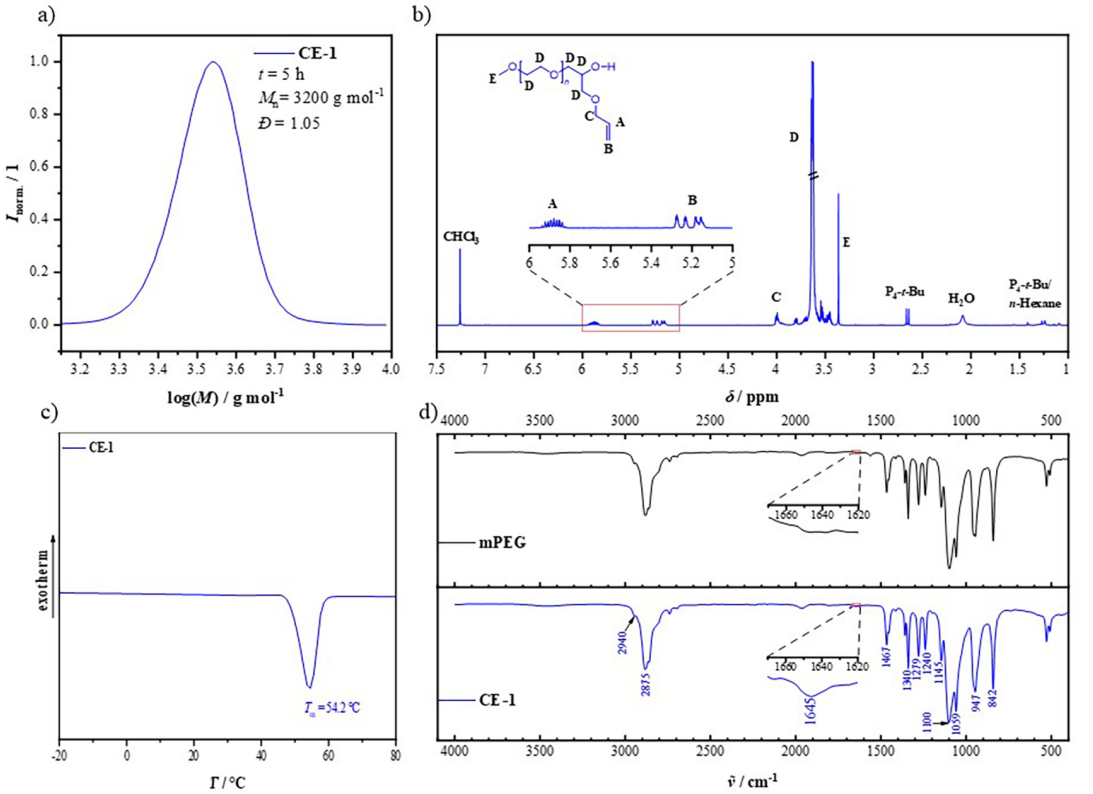

Figure 3. *(a) Size exclusion chromatogram after the first chain extension (**CE-1**) of mPEG-1900 with AGE. (b) ^{1}H NMR spectrum of the AGE chain-extended mPEG-1900. The new signals between 5.00 and 6.00 ppm confirm a successful CE. Solvent: $CDCl_3$. (c) Differential scanning calorimetry thermogram (heating curve; 2. cycle) of AGE chain-extended mPEG with a visible T_m at 54.2°C. (d) Attenuated total reflection Fourier-transform infrared spectrum of mPEG-1900 (black) and **CE-1** (blue). After the CE, a new signal at 1,645/cm appears, which could be assigned to the C=C double bond of the AGE.*

The symmetrical shape as well as no visible shoulder suggests the absence of side reactions like the cross-linking of the pendent double bonds. With a $Đ$ of 1.05 and an increase of approximately 100 g/mol to the precursor polymer, the results for the third CE were similar. The average number of repeating units was determined like before via ^{1}H NMR (Figure 4b) and resulted in a value of 1.02 ± 0.06 for the second and 0.88 for the third extension, confirming an addition of AGE to the chain. For the ratio calculation of the third addition, the CH_3-signal of the 1-dodecanethiol was used as reverence because the previously used initiator signal was overlapping with one of the benzylthiol signals. The T_m of the twice chain-extended polymer was determined to be 53°C via DSC (thermogram in Figure 4c), which is slightly lower than the precursor polymer (T_m = 55.2°C). However, the difference was expected to be minimal due to the small fraction of AGE in the polymer. The slight decrease in the temperature might be, therefore, the result of the error margin of the instrument. Also visible is an exothermic peak directly in front of T_m, which might be due to a cold crystallisation during the heating process. To further prove a successful CE, the polymer was investigated via ATR FT-IR spectroscopy. Again, the spectrum (Figure 4d) showed a weak signal at 1,645/cm which can be assigned to the C=C double bond's stretching vibration of AGE. The weak intensity of the signal can be explained again by the small fraction of the newly incorporated AGE relative to the overall molecular structure.

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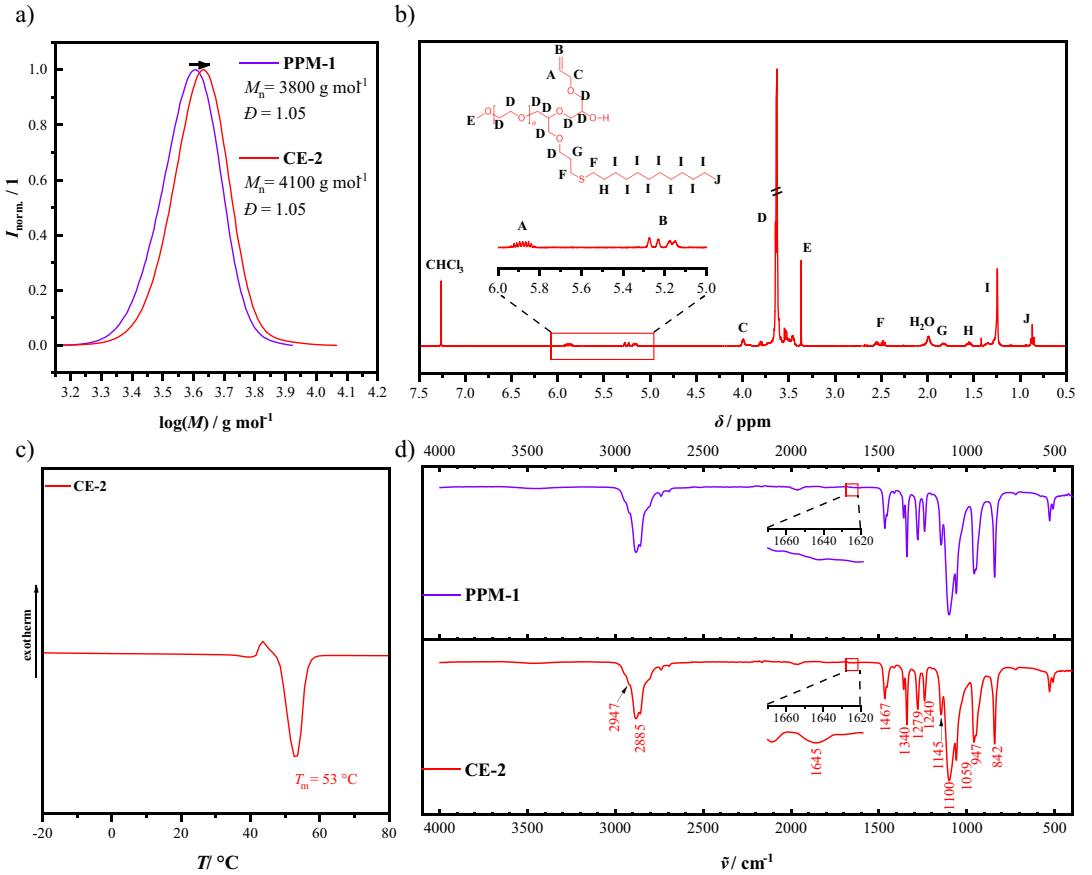

Figure 4. *(a) Size exclusion chromatogram after the second chain extension (**CE-2**). After the extension, a shift to higher molar masses is visible. (b) ^{1}H NMR spectrum of the twice chain-extended mPEG-1900. Again, the signals of the double bond between 5.00 and 6.00 ppm are visible, confirming a successful CE. (c) Differential scanning calorimetry thermogram (heating curve; 2. Cycle) of twice chain-extended mPEG-1900 with a visible T_m at 53°C. (d) Attenuated total reflection Fourier-transform infrared spectrum of once modified mPEG-1900 (**PPM-1**; violet) and twice chain-extended mPEG-1900 (**CE-2**; red). After the CE, a new signal at 1,645/cm appears, which could be assigned to the C=C double bond of the AGE.*

Overall, the second and third CEs were also successful, which was confirmed via multiple analytical methods. This suggests that it is possible to create sequence-controlled polymers with a desired number of sequences with the AROMA method, by combining CEs with PPM reactions. Furthermore, the results for both CEs showed no evidence for an influence of the thiol-modified pendant groups on the next addition process, which is important to ensure the feasibility of the AROMA approach.

Post-polymerisation modification of mPEG-b-oligo(AGE)

First post-polymerisation modification of mPEG-b-oligo(AGE) with 1-dodecanethiol via thiol-ene reaction

After the successful AROMA, the polymer was further used and modified via *a thiol-ene* reaction. For this, a benchmark reaction using 1-dodecanethiol as thiol was conducted at 50°C and under inert conditions. The obtained polymer was characterised via ^{1}H NMR spectroscopy, SEC, ATR FT-IR spectroscopy, and DSC. In the SEC elugram (Figure 5a), a shift in the molar mass to higher values (3,200–3,800 g/mol) can be observed after the modification reaction, signifying a change in structure

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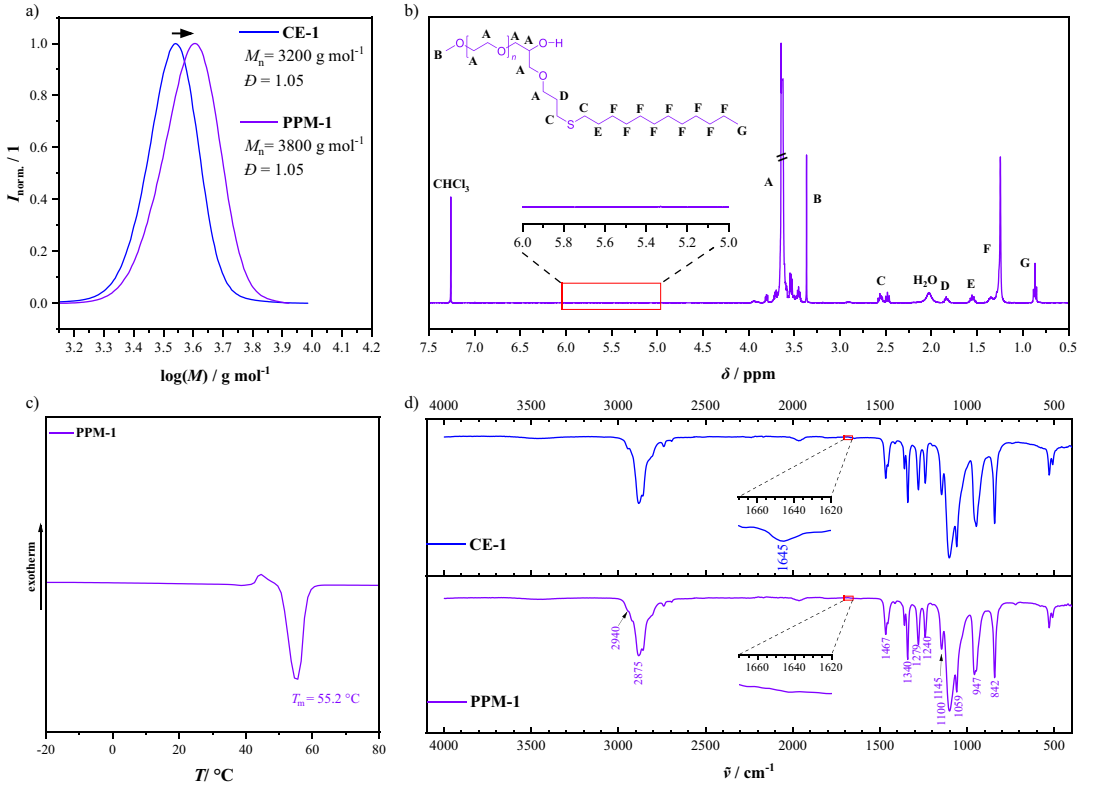

Figure 5. *(a) Size exclusion chromatogram after the first modification of chain-extended mPEG-1900 (**PPM-1**, violet). After the modification, a shift to higher molar masses is visible in comparison to the previous polymer (**CE-1**; blue). (b) ^{1}H NMR spectrum of chain-extended mPEG-1900 after the thiol-ene reaction with 1-dodecanethiol. After the reaction, the signals of the double bond between 5.00 and 6.00 ppm disappeared and the thiol signals (e.g., around 0.8 ppm) appeared, confirming a successful modification reaction. Solvent: $CDCl_3$. (c) Differential scanning calorimetry thermogram (heating curve; 2. cycle) of 1-dodecanethiol modified chain-extended mPEG-1900 with a visible T_m at 55.2°C. (d) Attenuated total reflection Fourier-transform infrared spectrum of once chain-extended mPEG-1900 (**CE-1**; blue) and the 1-dedcanthiol modified polymer (**PPM-1**; violet). After the modification, the signal at 1,645/cm disappeared, which confirms a successful modification.*

and therefore a successful modification. The difference between the determined value of 3,800 g/mol and the theoretical value of 3,400 g/mol can be explained by the difference in the structure of the polymer and the structure of the polystyrene standard used for calibration.

The ^{1}H NMR spectrum (Figure 5b) showed the total disappearance of the characteristic signals of the C=C double bond (6.00–5.77 ppm and 5.25–5.16 ppm) as well as the appearance of the thiol signals (0.92–0.80 ppm) after the reaction. By comparing the integrals of the methoxy group of the initiator with the methyl end group of the thiol, a ratio of 1:1 ± 0.01 was determined. This, as well as the total disappearance of the signal in the spectrum, confirmed the total conversion of the C=C double bond and a successful modification. The DSC thermogram (Figure 5c) of the thiol-modified polymer showed a small increase of 1°C of the T_m (54.2–55.2°C). The ATR FT-IR spectrum also suggests a change in the polymer's structure after the PPM reaction. The previously visible signal of the C=C double bond's stretching vibration at 1,645/cm disappeared after the reaction (Figure 5d), indicating also a successful modification. In summary, the overall picture of the results presented via ^{1}H NMR spectroscopy, SEC, ATR FT-IR spectroscopy, and DSC confirmed a successful modification of the AGE chain-extended mPEG-1900.

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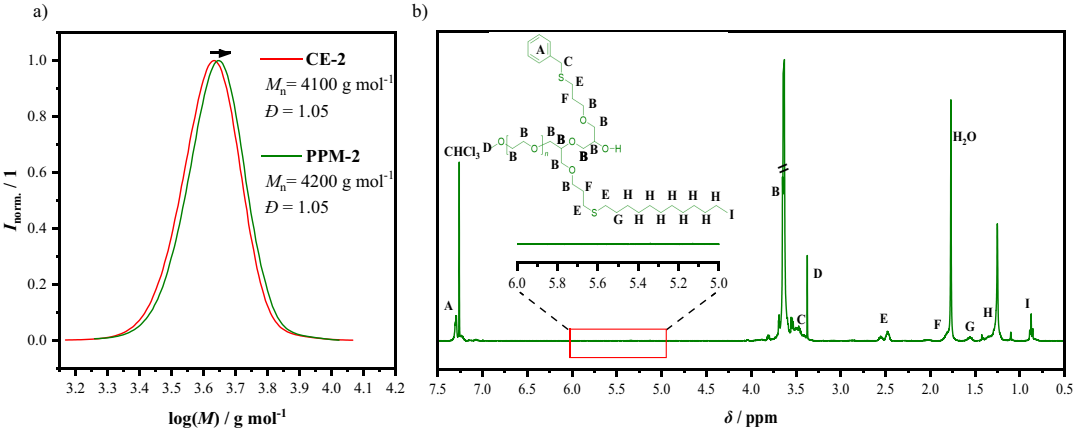

Figure 6. *(a) Size exclusion chromatogram after the second modification of chain-extended mPEG-1900 (**PPM-2**, green). After the modification, a shift to higher molar masses is visible in comparison to the previous polymer (**CE-2**; red). (b) ^{1}H NMR spectrum of twice chain-extended mPEG-1900 after the thiol-ene reaction with benzylthiol. After the reaction, the signals of the double bond between 5.00 and 6.00 ppm disappeared and the thiol signals (e.g., around 7.30 ppm) appeared, confirming a successful modification reaction. Solvent: $CDCl_3$.*

Further post-polymerisation modifications of mPEG-b-oligo(AGE) with benzylthiol and methyl-3-mercaptopropionat via thiol-ene reaction

Because the AROMA method relies on the repeated application of CE and PPM reactions, the second (route IV. in Scheme 1) and third (route VI. in Scheme 1) modification reactions of the twice/thrice chain-extended mPEG-1900 (route III. and V. in Scheme 1) were conducted to prove the applicability of this technique. The reaction conditions were similar to the first one; however, this time benzylthiol and methyl-3-mercaptopropionat were used as thiols to expand the number of possible thiol derivatives. The obtained polymer was characterised again via ^{1}H NMR spectroscopy and SEC. In the following section, the results of the second modification will be exemplarily discussed. Graphs and further information on the third extension can be found in the Supplementary Material. After the second modification, the SEC elugram (Figure 6a) showed a symmetrical peak with a $Đ$ of 1.05 and a small shift to higher molar masses after the modification (4,100–4,200 g/mol). With a $Đ$ of 1.08 and an increase of approximately 400 g/mol in comparison with the precursor, the results of the third modification were slightly different to the previous one. In addition, a small shoulder with twice the molar mass of the main peak emerged, indicating a slight dimerisation initiated by the radical source (AIBN). Besides the small change in the molar mass for the second modification, a real indicator of a successful modification was the appearance of a strong UV signal covering the peak after the reaction, which is a result of the newly attached benzylthiol units.

Similar to the modification reaction using 1-dodecanethiol, the ^{1}H NMR spectra of the second and third modifications (Figure 6b for the second modification) showed the disappearance of the double bond in the range of 6.00 to 5.77 ppm after the reaction, indicating a total conversion. Due to the benzylthiol, a new signal around 7.30 ppm emerged. The results of the ^{1}H NMR spectroscopy as well as the SEC confirmed a successful second and third modification of the polymer, therefore paving the successful route for the possibility of synthesising sequence-controlled polymers using the AROMA method.

Discussion on the influence of the sequence-controlled structure on the physical properties

The analytic methods used in this study mainly gave information about the structure of the synthesised AROMA-polymer. For example, the ^{1}H NMR and FT-IR spectroscopy directly confirmed the addition

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and modification of the AGE units, due to the characteristic double bond signals, while the SEC showed a change in the hydrodynamic radius and therefore a change in the structure. Direct information on the physical properties could be determined by DSC measurements in the form of T_m. By comparing the temperatures, only a small difference was noticeable, which can rather be traced back to the error margin of the device than to the change in the macromolecular structure. However, this observation was to be expected considering the overall macromolecular structure. With an average unit of one, the share of AGE in the polymer is too small to influence the T_m. To get a noticeable change in the physical properties, the number of AGE units per repeating unit needs to be increased significantly, leading to a more block-like structure. If the AROMA method should be maintained, a larger number of CEs must be carried out than presented in this study. Additionally, the molar mass and functional groups of the molecules added via PPM have to be considered because they also influence the properties of the polymer, which is why the PPM step is of high interest for further applications. The presented concept of combining CEs and modification reactions can be used as a tool to synthesise and program macromolecules with a specific sequence in functional groups. A possible field of application for such material could be as tracer molecules in the medical department (e.g., drug release).

Conclusion

Herein, a novel method for the preparation of an epoxide-based sequence-controlled polymer bearing an average repeating unit of one is presented. By combining CE with subsequent PPM reactions from a precursor, mPEG-*b*-oligo(AGE) functional sequence-controlled polymers with a desired structure could be synthesised. Due to the addition of an average monomer unit of one via an AROP technique, we suggested to call the used method 'AROMA'. The CE and modification reactions were conducted three times to confirm the feasibility of this method to create macromolecular structures with multiple and different repeating units. The successful steps were confirmed via ^{1}H NMR spectroscopy, SEC, ATR FT-IR spectroscopy, and DSC. After all three extensions, the number of newly added units was determined by comparing the ratio of the initiator (or another characteristic signal) with the monomer, which in all cases led to an average number of nearly one. By utilising *thiol-ene* reactions, three structurally different reactants, 1-dodecanethiol, benzylthiol, and methyl-3-mercaptopropionat, were attached as side groups, showing for the first time to our knowledge the possibility to synthesise functional sequence-controlled polymer utilising only one monomer for the actual polymerisation. The versatility of the PPM allows for the introduction of numerous functional units to the polymeric system by using different reactants, creating a variety of materials all based on the same monomer. This, in addition to the CE reaction, grants the AROMA method the possibility to prepare well-controlled and programmable macromolecular architectures. Due to its adaptability, the AROMA method could find utilisation in a broad field of disciplines, for example, the medical field, battery research, and material science.

Supplementary materials. The supplementary material for this article can be found at http://doi.org/10.1017/pma.2023.7.

Data availability statement. The data supporting the findings of this study are available in the Supplementary Material of this article.

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Competing interest. The authors declare none.

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