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Cite this: *Polym. Chem.*, 2025, **16**, 2494

# Biobased oleyl glycidyl ether: copolymerization with ethylene oxide, postmodification, thermal properties, and micellization behavior†

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Oleyl glycidyl ether (OIGE) is a highly hydrophobic monomer synthesized from a biobased fatty alcohol and epichlorohydrin. When combined with hydrophilic monomethoxy poly(ethylene glycol) (mPEG) macroinitiators, well-defined, highly amphiphilic AB block copolymers are obtained *via* anionic ring-opening polymerization ( $\bar{D} \leq 1.08$ ). Surprisingly, an investigation of the copolymerization kinetics of OIGE and ethylene oxide revealed an almost ideally random copolymerization ( $r_{EO} = 1.27$ ,  $r_{OIGE} = 0.78$ ) despite the significant structural differences. Both statistical and block copolymers were investigated regarding their behavior in aqueous solution. The block copolymers of the type mPEG-*b*-POIGE featured two distinct melting temperatures ( $T_m$ s). Besides a melting transition of mPEG, a second  $T_m$  is attributed to the crystallization of the *cis*-alkenyl side chains of the OIGE units. Varying degrees of side chain hydrogenation of the POIGE homopolymer using potassium azodicarboxylate (PADA) allowed for tailoring of the  $T_m$ . The thiol-ene click reaction permitted subsequent functionalization. This work does not merely highlight the prospect of novel polyether surfactants, it also suggests the potential of biobased long-chain polyethers for the development of drug delivery systems featuring temperature-controlled release.

Received 17th February 2025,  
Accepted 19th April 2025

DOI: 10.1039/d5py00159e

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## Introduction

Surfactants play a key role in numerous everyday applications, in which the combination of components with different polarity is required. They typically alter the surface properties of water. These applications include surfactants for cosmetics, coatings, paints, biotechnology, water purification, and many others.<sup>1,2</sup> Polymer surfactants provide a means to tune and finely control these behaviors in manifold ways, due to their vast structural options. Mostly, when discussing polymer surfactants, reference is made to block copolymers. However, the term ‘surfactant’ also includes polysoaps, which are random copolymers of hydrophilic and hydrophobic monomers, among many other architectural configurations. The domain of polymer surfactants is extensive, and comprehensive reviews are available.<sup>1,3</sup> The hydrophilic component of surfac-

tants can either be charged, as seen in examples such as poly(acrylic acid),<sup>4</sup> quaternized arylamines,<sup>5</sup> and sulfonates,<sup>6</sup> or uncharged, as in saccharides,<sup>7</sup> polyoxazolines,<sup>8</sup> and poly(ethylene glycol) (PEG).<sup>9</sup> The industry provides numerous series of ethoxylated compounds as surfactants, such as *e.g.* Tween®, Myrj®, Span®, Triton X®, and Brij®.<sup>10</sup>

Fats and oils represent renewable feedstocks for the chemical industry. Their substantial production volume (208.1 Mt in 2019) enables the cost-efficient supply of a diverse range of linear alkyl and alkenyl alcohols from triglycerides.<sup>11–15</sup> The side product glycerol can be converted to epichlorohydrin and is equally commercially available as Epicerol® in a green process from Solvay. Glycerol is chlorinated twofold with HCl and after one elimination reaction, epichlorohydrin is formed.<sup>16–18</sup> Epichlorohydrin can be utilized to introduce epoxide moieties in molecules.<sup>19</sup> With a growing emphasis on the development of biobased chemicals that do not affect the food chain,<sup>20,21</sup> it is crucial to underscore the effective utilization of triglycerides derived from non-edible oil plants as an alternative to using food crops.<sup>22</sup> Moreover, converting waste into chemicals proves to be significantly more economical when compared to biofuel or electricity production.<sup>23</sup> Ethylene oxide, the monomer used to produce PEG can be generated from biobased sources using two primary methods:

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†Electronic supplementary information (ESI) available: Additional experimental procedures, <sup>1</sup>H NMR, <sup>13</sup>C NMR, DOSY, evaluation data for <sup>1</sup>H NMR copolymerization kinetic, additional characterization data (SEC, MALDI-ToF, DSC, TEM, DLS and fluorescence spectroscopy). See DOI: <https://doi.org/10.1039/d5py00159e>

dehydration of bioethanol to produce ethylene, followed by oxidation<sup>24,25</sup> or electrosynthesis from bioethanol.<sup>26</sup> Another viable approach involves production from CO<sub>2</sub> and water.<sup>27</sup>

The field of drug solubilization *via* implementation of multifunctional polymer micelles is highly active in research, focusing on the purposeful treatment of diseases. These systems effectively handle the limitations of free hydrophobic drugs such as low solubility, dose-limiting toxicity, and inadequate biodistribution.<sup>28,29</sup> The trigger to release drugs from external stimuli-responsive polymers can be changes in pH, temperature, magnetic fields, light, engineered sensitivities to enzymes, or radiofrequency.<sup>30–32</sup> The lower critical solution temperature of poly(*N*-isopropyl acrylamide) can be employed to trigger drug release during local hyperthermia.<sup>33</sup> Magnetically responsive nanoparticles (Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>) can be incorporated into micelles or liposomes loaded with drugs while the drug release can be induced by an alternating external field.<sup>34</sup> Brazel *et al.* employed poly(EG)-*b*-poly( $\epsilon$ -caprolactone) micelles in combination with iron oxide nanoparticles. The release of doxorubicin was demonstrated to occur by melting of the crystalline core when subjected to external magnetic field-induced heating.<sup>35</sup> Block copolymers of PEG and glycidyl ethers with a hydrophobic chain have been synthesized and investigated for their use as cosurfactants,<sup>36</sup> and show low cytotoxicity for splenic immune cells.<sup>37</sup> ABA-type tri-block copolymers of these structures can also be employed to prepare thermoresponsive hydrogels, capable of taking up Nile red as a model for a hydrophobic drug. By variation of the alkyl side chain length, the *T*<sub>m</sub> of the hydrophobic block was altered to 49 °C in pure water.<sup>38</sup>

Here we introduce the monomer oleyl glycidyl ether (OlGE), prepared from oleyl alcohol and epichlorohydrin. This monomer was utilized in anionic ring-opening polymerization (AROP), affording homo- and block copolymers as well as statistical copolymers with ethylene oxide. Long-chain glycidyl ethers permit to modify the properties of highly water-soluble PEG, thereby allowing the fine-tuning of the physical characteristics of aqueous solutions.<sup>9,39</sup> Furthermore, mPEG-*b*-poly

(alkyl glycidyl ether) surfactants were synthesized and the ‘efficiency-boosting effect’ was investigated. The polymers increased the efficiency of medium- and longer-chain surfactants to stabilize water/oil interfaces.<sup>36</sup> Analogously, terpenoid-derived systems that cannot crystallize due to their branched structure were explored and showed comparable results.<sup>40,41</sup> We demonstrate that OlGE is a potentially biorenewable and versatile platform for a variety of surfactants.

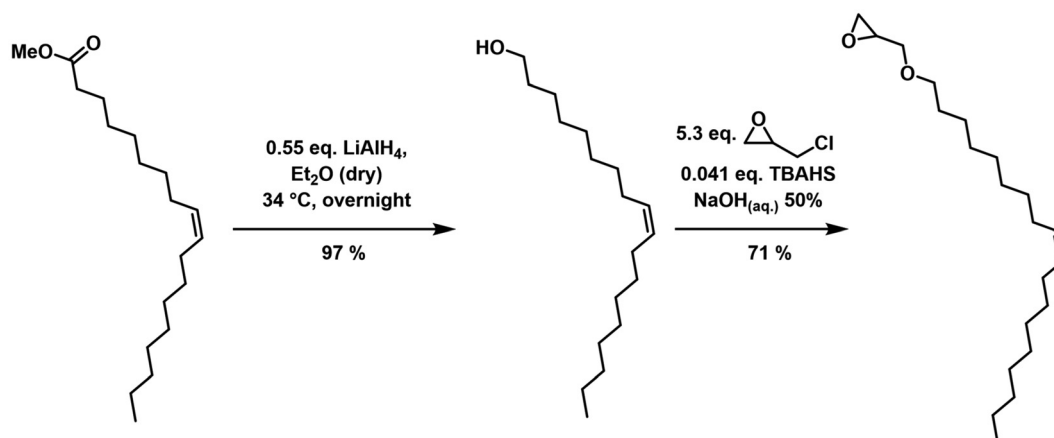
## Experimental section

Information regarding the reagents used, detailed monomer and polymer synthesis, as well as the analysis techniques employed, is available in the ESI.†

## Results and discussion

### Monomer synthesis

The precursor oleyl alcohol is typically obtained through the hydrogenation of methyl oleate in industrial settings. Conventional industrial methods employ hydrogen gas and catalysts for the hydrogenation of methyl oleate. However, we opted for a more classical reduction method that employs lithium aluminum hydride (LiAlH<sub>4</sub>, Scheme 1).<sup>42</sup> This choice was made to avoid the need for a high-pressure hydrogen gas apparatus. However, when considering large-scale synthesis, hydrogen gas would be the reducing agent of choice. Methyl oleate is a byproduct of transesterification, a process that involves triglycerides commonly sourced from large quantities of bio-derived oils and fats.<sup>12</sup> Additionally, epichlorohydrin can be obtained from both petroleum-based resources and glycerol, which is a byproduct of biodiesel production and is available in abundance from fats and oils.<sup>16,17</sup> The combination of oleyl alcohol and green epichlorohydrin obtained by this pathway results in a completely bio-based monomer.



**Scheme 1** Two-step reaction for the synthesis of the oleyl glycidyl ether monomer.



Oleyl glycidyl ether (OLGE) features a long hydrophobic side chain with a *cis* double bond at the C9 carbon atom. This prevents the side chain from crystallizing at room temperature and can serve as an anchoring point for post-polymerization modification if incorporated along the polymer backbone. The two-step reaction involves the reduction of methyl oleate followed by an etherification of the oleyl alcohol with epichlorohydrin (ECH) *via* phase transfer catalysis, as illustrated in Scheme 1. Hence, oleyl alcohol and epichlorohydrin underwent a two-phase reaction in the presence of a phase transfer catalyst under highly alkaline conditions, resulting in the formation of OLGE with yields of up to 71%. However, a known side reaction occurred during this process: the deprotonation of ECH with subsequent ring-opening led to 3-chloroallyl alcohol. This alcohol is capable of reacting with ECH, leading to the formation of 3-chloroallyl glycidyl ether.<sup>19</sup> The byproduct was effectively removed using Kugelrohr distillation, facilitated by the significant difference in boiling points between the byproduct and OLGE.

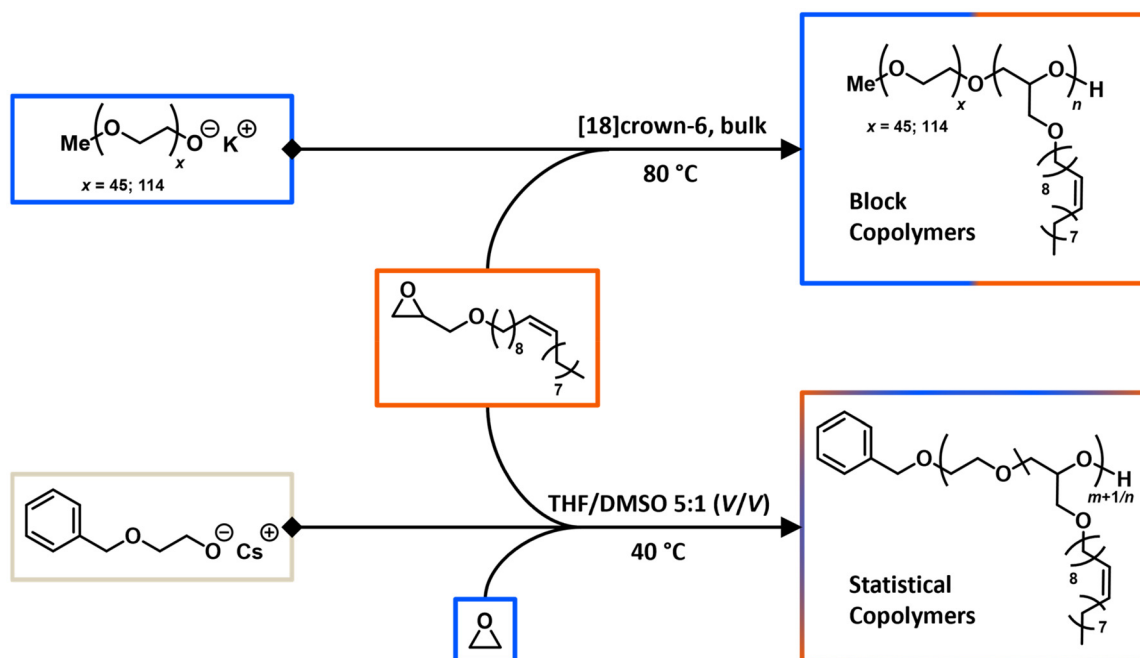
All experimental details as well as the characterization are given in the ESI.†

### Synthesis of oleyl glycidyl ether-based polymers

All polymers were synthesized using standard AROP techniques. Experimental details along with characterization are provided in the ESI.† For block copolymers, the monofunctional initiator monomethoxy poly(ethylene glycol) (mPEG) with molar masses of 2000 g mol<sup>-1</sup> (45 ethylene glycol units) and 5000 g mol<sup>-1</sup> (114 ethylene glycol units) was utilized. Prior to polymerization, mPEG was deprotonated to an extent of 90% using KO<sup>t</sup>Bu with the aid of [18]crown-6 and sub-

sequently, the dried monomer OLGE was added. After the polymerization, the active chain ends were terminated using acidified methanol, and the resulting polymer was purified by precipitation. POLGE homopolymers were synthesized in the same way, but potassium(2-benzyloxy)ethanolate was used as the initiator. Since POLGE homopolymers are not the primary focus of this study, they have been excluded in Scheme 2. In the case of statistical copolymers, CsOH·H<sub>2</sub>O was employed as the deprotonating agent. This choice was made to maintain consistency in the experimental procedures between the copolymerization kinetics measurements (as described below) and the actual polymer synthesis. The procedure involved dissolving the cesium(2-benzyloxy)ethanolate initiator salt in dry DMSO and THF, after which dried OLGE was introduced into the reaction vessel. Subsequently, ethylene oxide was condensed to the custom-made anionic flask. Statistical copolymers with an overall number of both repeating units of 120 were targeted. Slight deviations stem from difficult measuring of liquefied EO at -80 °C, as small temperature increases led to a volume expansion of EO in the graduated ampule.

Table 1 presents a summary of the synthesized polymers, including their characterization data and the intended composition compared to the calculated composition. Notably, all polymers based on oleyl glycidyl ether exhibited narrow dispersities ranging from 1.06 to 1.11. The shift in the SEC traces towards higher molar masses supports the block copolymer formation (Fig. S5 and S6†). Statistical copolymers showed slightly larger dispersities in the range of 1.11 to 1.15, although they still maintained a monomodal distribution, as illustrated in Fig. S9.† SEC analysis revealed an increase in molar mass for all polymers with the incorporation of higher



**Scheme 2** Synthesis of block and statistical copolymers containing oleyl glycidyl ether by employing AROP techniques.



**Table 1** Polymer characterization of the OIGE block copolymers, statistical copolymers, and homopolymers

| Polymer composition <sup>a</sup>                      | <i>n</i> (OIGE) <sup>th</sup> | <i>n</i> (EO) <sup>th</sup> | <i>M<sub>n</sub></i> (SEC) <sup>b</sup> (g mol <sup>-1</sup> ) | <i>M<sub>n</sub></i> (NMR) <sup>a</sup> (g mol <sup>-1</sup> ) | <i>D<sup>b</sup></i> |
|-------------------------------------------------------|-------------------------------|-----------------------------|----------------------------------------------------------------|----------------------------------------------------------------|----------------------|
| mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>2.4</sub>   | 3                             | —                           | 3000                                                           | 2800                                                           | 1.06                 |
| mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>5.0</sub>   | 6                             | —                           | 4300                                                           | 3600                                                           | 1.06                 |
| mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>7.5</sub>   | 9                             | —                           | 4500                                                           | 4400                                                           | 1.06                 |
| mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>11.3</sub>  | 12                            | —                           | 4800                                                           | 5700                                                           | 1.08                 |
| mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>2.9</sub>  | 3                             | —                           | 6400                                                           | 5900                                                           | 1.08                 |
| mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>5.8</sub>  | 6                             | —                           | 7700                                                           | 6900                                                           | 1.07                 |
| mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>7.3</sub>  | 9                             | —                           | 8200                                                           | 7400                                                           | 1.06                 |
| mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>9.9</sub>  | 12                            | —                           | 9100                                                           | 8200                                                           | 1.07                 |
| P(EG <sub>123</sub> - <i>co</i> -OIGE <sub>7</sub> )  | 6                             | 114                         | 7500                                                           | 7800                                                           | 1.14                 |
| P(EG <sub>94</sub> - <i>co</i> -OIGE <sub>13</sub> )  | 12                            | 108                         | 7800                                                           | 8500                                                           | 1.15                 |
| P(EG <sub>103</sub> - <i>co</i> -OIGE <sub>35</sub> ) | 30                            | 90                          | 16 300                                                         | 16 000                                                         | 1.12                 |
| POIGE <sub>13</sub>                                   | 10                            | —                           | 3400                                                           | 4400                                                           | 1.07                 |
| POIGE <sub>25</sub>                                   | 25                            | —                           | 5800                                                           | 8300                                                           | 1.11                 |

<sup>a</sup> Determined *via* <sup>1</sup>H NMR analysis. <sup>b</sup> Eluent THF, PEG calibration, RI detector, <sup>th</sup>theoretical.

amounts of OIGE. Variations are anticipated due to differences in the hydrodynamic volume behavior compared to the PEG calibration, which is particularly notable for POIGE homopolymers with their long side chains, leading to a bottlebrush-like structure (Fig. S12†). We would like to emphasize that achieving higher molar masses of the POIGE homopolymer was not tested, as this was beyond the scope of our study. It is essential to recognize that the molar mass calculated from SEC should be considered a rough estimate given the relative nature of the method employed. The NMR spectra can be found in the ESI (Fig. S3, S4, S7 and S8†). Differences observed between the theoretical and achieved degree of polymerization can be attributed to contamination by small amounts of OIGE homopolymer, initiated by residual traces of water. These polymers were subsequently removed during the work-up process.

### Reactivity ratios of OIGE/EO by *in situ* <sup>1</sup>H NMR copolymerization kinetics

Knowledge of microstructure is crucial to understand polymer characteristics. Depending on the type of monomers and polymerization techniques employed, various microstructures can typically be achieved, ranging from random copolymers to nearly blocklike, tapered structures. These microstructures have a significant impact on various polymer properties such as thermal and mechanical properties, micellization, and solubility among others.<sup>43,44</sup> In our study, we investigated the copolymerization behavior *via in situ* <sup>1</sup>H NMR analysis. To this end, EO and OIGE were copolymerized at 40 °C in an NMR tube equipped with a Teflon stopcock, using a mixture of DMSO-*d*<sub>6</sub> and THF-*d*<sub>8</sub> at a 1 : 5 (V/V) ratio. Cesium 2-(benzyloxy)ethanolate was used as the initiator for the polymerization. Cesium was chosen as a counterion for all statistical copolymers, as it enhances the propagation rate compared to potassium and reduces the time required for the kinetic investigation experiment.<sup>45</sup> Experimental details are given in the ESI.† Monomer consumption was tracked by observing the monomer reso-

nances at 2.68 ppm for OIGE and 2.58 ppm for EO during the copolymerization. Fig. 1 displays a selection of stacked spectra.

Both monomers exhibited nearly complete conversion after 55 hours. The gradual decrease of the signals is illustrated in Fig. 2, which shows the amount of unreacted monomer *versus* total conversion. Clearly, EO is incorporated more rapidly, while OIGE is consumed at a slightly lower rate. This already suggests that copolymerization is not ideally random.

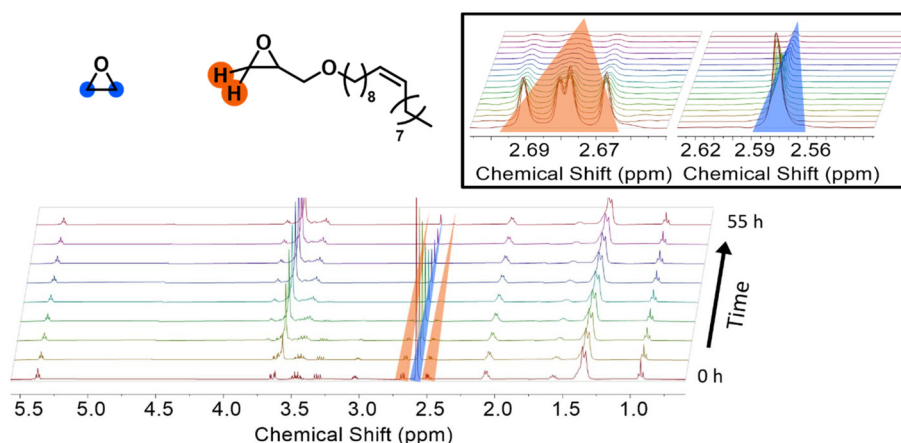
To determine reactivity ratios *r*<sub>1,2</sub> the data extracted from the kinetic experiment were fitted according to the Jaacks plot.<sup>46–48</sup> For this, the following eqn (1) was used.

$$\log\left(\frac{[M_1]_t}{[M_1]_0}\right) = r_1 \cdot \log\left(\frac{[M_2]_t}{[M_2]_0}\right) \quad (1)$$

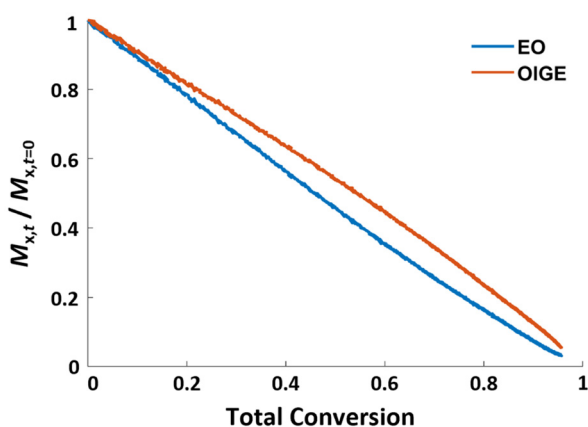
In an ideal copolymerization, the following correlation is defined: *r*<sub>1</sub>·*r*<sub>2</sub> = 1. Both reactivity ratios were determined with the results *r*<sub>EO</sub> = 1.27 and *r*<sub>OIGE</sub> = 0.78 (Fig. S39†). As the coefficient of determination *R*<sup>2</sup> was 0.99, an ideal or chain-end independent copolymerization can be concluded. The use of more complex terminal models such as the Meyer–Lowry method<sup>49</sup> should be avoided as long as the more simple, non-terminal model explains the data well. This principle was coined by Sir William Hamilton as “Ockham’s Razor”,<sup>50</sup> and its application to copolymerization kinetics was already described.<sup>51</sup> The fit is displayed in Fig. S40,† and the results are summarized in Table 2.

The obtained reactivity ratios enable the simulation of the comonomer composition in the course of the copolymerization (Fig. 3), which directly translates to the monomer gradient in the copolymer chains formed. As previously indicated in Fig. 2, EO is initially incorporated with a slight preference during copolymerization. With increasing conversion, approaching full monomer conversion, more OIGE units are incorporated at the chain end. This subtle variation in reactivity ratios results in the enrichment of monomer units towards either the beginning or the terminus of the polymer chains, respectively. We would like to emphasize that this gradient is

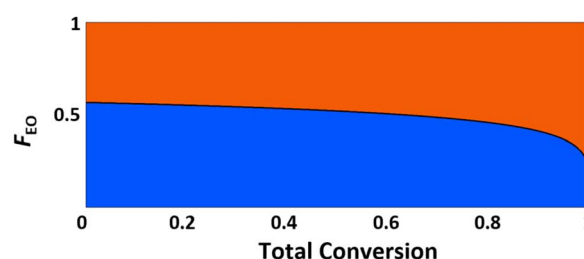




**Fig. 1** Stacked selection of  $^1\text{H}$  NMR spectra of the copolymerization of OIGE and EO. Zoom-in shows the decrease of the OIGE (orange) and EO monomer signals (blue). Polymerization temperature  $40^\circ\text{C}$ , solvent:  $\text{DMSO}-d_6$  and  $\text{THF}-d_8$  1 : 5 (V/V), 400 MHz. As spectra were collected every 2 min for 55 h, only every 200th spectrum is displayed.



**Fig. 2** Unreacted monomer versus total conversion of the *in situ*  $^1\text{H}$  NMR copolymerization kinetic study of EO with OIGE. Solvent:  $\text{DMSO}-d_6/\text{THF}-d_8$  1 : 5 (V/V),  $40^\circ\text{C}$ .



**Fig. 3** Simulated composition versus total conversion of the EO (blue)/OIGE (orange) comonomer pair for a hypothetical equimolar ratio.

not pronounced, compared to other systems like the carbanionic copolymerization of isoprene and styrene.<sup>48</sup> This result is remarkable in view of the large steric bulk of the OIGE monomer in comparison to EO.

Even though glycidyl ethers (GEs) exhibit a substituted epoxide functionality, usually the correlation  $r_{\text{EO}} \approx r_{\text{GE}} \approx 1$  is valid.<sup>37,52,53</sup> This observation is counterintuitive, especially since propylene oxide copolymerizes with a much stronger gradient with EO, which is assigned to the methyl group substitution.<sup>54</sup> Due to their ability to chelate the counterion and thereby activate the epoxide, glycidyl ethers show a transient

“crown ether-effect”.<sup>55</sup> Since the side chain contains additional oxygen atoms, glycidyl ethers react faster than the unsubstituted EO.<sup>56–58</sup> Bulky and/or inflexible side chains, in contrast, prevent sufficient chelation and also lead to hindered nucleophilic attack of an active chain end at the epoxide functionality, resulting in less favored incorporation.<sup>40,58–60</sup> This finding is confirmed by our study, as the bulky, apolar monomer is less prone to nucleophilic attack, translating to slower incorporation in the growing polymer chain.

### Amphiphilic nature and CMC determination of OIGE copolymers

The determination of the CMC is commonly achieved by employing pyrene as a fluorescent probe.<sup>2,61</sup> When pyrene transitions from a polar to an apolar environment, the emission spectrum experiences a pronounced shift towards higher values in the ratio of the  $I_3$  and  $I_1$  bands, correlated to the

**Table 2** Summary of different fitting models of the EO/OIGE copolymerization kinetic

| Method      | Model               | $r_{\text{EO}}$ | $r_{\text{OIGE}}$ |                |
|-------------|---------------------|-----------------|-------------------|----------------|
| Jaacks      | Non-terminal, ideal | $1.27 \pm 0.01$ | $0.78 \pm 0.01$   | $R^2 = 0.99$   |
| Meyer-Lowry | Terminal, non-ideal | $1.32 \pm 0.12$ | $0.80 \pm 0.14$   | NormRes = 0.38 |





alteration in the polarity of the surrounding molecules. The experimental procedure used in this work is based on the method described by Zhu *et al.*<sup>62</sup> In short, pyrene was mixed with the respective polymer solution in a serial dilution. Then the fluorescence spectra of pyrene were measured at 23 °C, and  $I_3/I_1$  was plotted against the logarithmic polymer concentration. A Boltzmann sigmoidal fit (eqn (S1)†) was performed and the CMC was determined from the inflection point of the fit.<sup>40,61</sup> The graphs are shown in the ESI (Fig. S18–S24).†

The hydrophilic–lipophilic balance (HLB) is an empirical scale ranging from 1 to 20, employed to assess the utility of surfactants in various applications. Higher HLB values are indicative of surfactants with a greater affinity for polar environments, making them suitable for tasks such as solubilization and oil-in-water emulsification. Conversely, lower HLB values denote surfactants with a stronger preference for non-polar environments, rendering them more appropriate for purposes such as water-in-oil emulsification and foam reduction. The HLB scale serves as a valuable tool for understanding the contrasting characteristics of surfactants.<sup>63</sup>

Table 3 gives an overview of the synthesized OIGE-containing polymers with their HLB values and the CMC determined by fluorometry. The sole water-soluble compound within the series of statistical copolymers was P(EG<sub>123</sub>-co-OIGE<sub>7</sub>), which exhibited a CMC of 24.5 mg L<sup>−1</sup>. Of the four block copolymers obtained from mPEG<sub>45</sub>, only two displayed water solubility and had a CMC threshold of 23.8 mg L<sup>−1</sup>. This observation is attributed to a significant increase in the weight percentage of the hydrophobic block due to the incorporation of additional 2.6 OIGE units, each with a high molar mass of 324 g mol<sup>−1</sup>, in contrast to ethylene glycol units with a mass of only 44 g mol<sup>−1</sup> each. A comparable outcome was noted in the case of block copolymers based on mPEG<sub>114</sub>. The CMCs exhibited a notable reduction from 73.4 to 25.4 mg L<sup>−1</sup>, with just a slight 2.1 mg L<sup>−1</sup> difference between mPEG<sub>114</sub>-b-POIGE<sub>7,3</sub> and mPEG<sub>114</sub>-b-POIGE<sub>9,9</sub>. As reported by Lodge *et al.*, the CMC decreases exponentially, but is weakly dependent on the hydro-

phobic block length for longer blocks and is notably less dependent on the hydrophilic block length.<sup>1,64</sup> Thereby, the difference in CMC between polymers with a small hydrophobic block (mPEG<sub>114</sub>-b-POIGE<sub>2,9</sub> and mPEG<sub>114</sub>-b-POIGE<sub>5,8</sub>) is more pronounced compared to block polymers with larger hydrophobic blocks (mPEG<sub>114</sub>-b-POIGE<sub>7,3</sub> and mPEG<sub>114</sub>-b-POIGE<sub>9,9</sub>). Noteworthy, all three varieties of copolymers exhibited a CMC threshold of approximately 25 mg L<sup>−1</sup>. When contrasting our system with existing literature, the CMC of Brij® 98, a twenty-fold ethoxylated oleyl alcohol, is reported to fall within the range of 7–29 mg L<sup>−1</sup>.<sup>65–68</sup> Variations in CMC values for the same compound may arise from differences in measurement methods, among other factors.<sup>69</sup> Block copolymers of mPEG<sub>114</sub>-b-poly(farnesyl glycidyl ether)<sub>m</sub> (*m* = 5 and 9) showed slightly lower CMCs of 53 and 15 mg L<sup>−1</sup>, respectively.<sup>40</sup>

### Dynamic light scattering of OIGE copolymers

Polymer solutions of the water-soluble copolymers were investigated by dynamic light scattering (DLS) to determine the hydrodynamic radius of the respective micelles and larger aggregates. Additionally, the results were compared to TEM observation of the aggregates. The polymer concentration was significantly above the CMC determined *via* fluorometry. The amplitude autocorrelation function was subjected to a biexponential fit (represented by eqn (S4)†), given that TEM images hinted at the presence of multiple types of aggregates for all copolymers. The diffusion coefficient of each measured angle was received from the relation  $D = (\tau_R \cdot q^2)^{-1}$ . This diffusion coefficient was subsequently plotted *versus*  $q^2$  to calculate the z-average diffusion coefficient for each specific aggregate. Additional details on the calculation of diffusion coefficients and hydrodynamic radii are described in the ESI.† A summary of the results obtained from DLS analysis is provided in Table 4. Among the statistical copolymers examined, P(EG<sub>123</sub>-co-OIGE<sub>7</sub>) was the only sample that could be analyzed, as the others were insoluble. The block copolymer mPEG<sub>114</sub>-b-POIGE<sub>9,9</sub> was not analyzed by DLS, as a turbid solution was obtained. P(EG<sub>123</sub>-co-OIGE<sub>7</sub>) exhibited aggregates with an  $R_{H,1}$  of 5.31 nm, corresponding to a single chain (micelle), as the comparable mPEG<sub>114</sub> unimer exhibited a hydrodynamic radius of 2 nm.<sup>40</sup> In contrast, the larger aggregates displayed a significantly greater  $R_{H,2}$  of 107 nm. This discrepancy is attributed to

**Table 3** Hydrophilic–lipophilic balances (HLBs) and critical micelle concentrations (CMCs) of the OIGE-containing copolymers

| Polymer                                      | mol% (OIGE) | w% (OIGE) | HLB  | CMC (mg L <sup>−1</sup> ) |
|----------------------------------------------|-------------|-----------|------|---------------------------|
| P(EG <sub>123</sub> -co-OIGE <sub>7</sub> )  | 5.4         | 30        | 14.1 | 24.5                      |
| P(EG <sub>94</sub> -co-OIGE <sub>13</sub> )  | 12.1        | 50        | 9.9  | n.d. <sup>a</sup>         |
| P(EG <sub>103</sub> -co-OIGE <sub>35</sub> ) | 25.4        | 71        | 5.7  | n.d. <sup>a</sup>         |
| mPEG <sub>45</sub> -b-POIGE <sub>2,4</sub>   | 5.1         | 28        | 14.4 | 41.9                      |
| mPEG <sub>45</sub> -b-POIGE <sub>5,0</sub>   | 10.0        | 45        | 11.0 | 23.8                      |
| mPEG <sub>45</sub> -b-POIGE <sub>7,5</sub>   | 14.3        | 55        | 9.0  | n.d. <sup>a</sup>         |
| mPEG <sub>45</sub> -b-POIGE <sub>11,3</sub>  | 20.1        | 65        | 7.1  | n.d. <sup>a</sup>         |
| mPEG <sub>114</sub> -b-POIGE <sub>2,9</sub>  | 2.5         | 16        | 16.8 | 73.4                      |
| mPEG <sub>114</sub> -b-POIGE <sub>5,8</sub>  | 4.8         | 27        | 14.5 | 44.2                      |
| mPEG <sub>114</sub> -b-POIGE <sub>7,3</sub>  | 6.0         | 32        | 13.6 | 27.5                      |
| mPEG <sub>114</sub> -b-POIGE <sub>9,9</sub>  | 8.0         | 39        | 12.2 | 25.4                      |

<sup>a</sup> Values could not be determined due to insufficient solubility in water.

**Table 4** DLS results of the investigated water-soluble OIGE copolymers. Index 1 denotes the smaller observed aggregates, whereas 2 denotes the larger observed aggregates

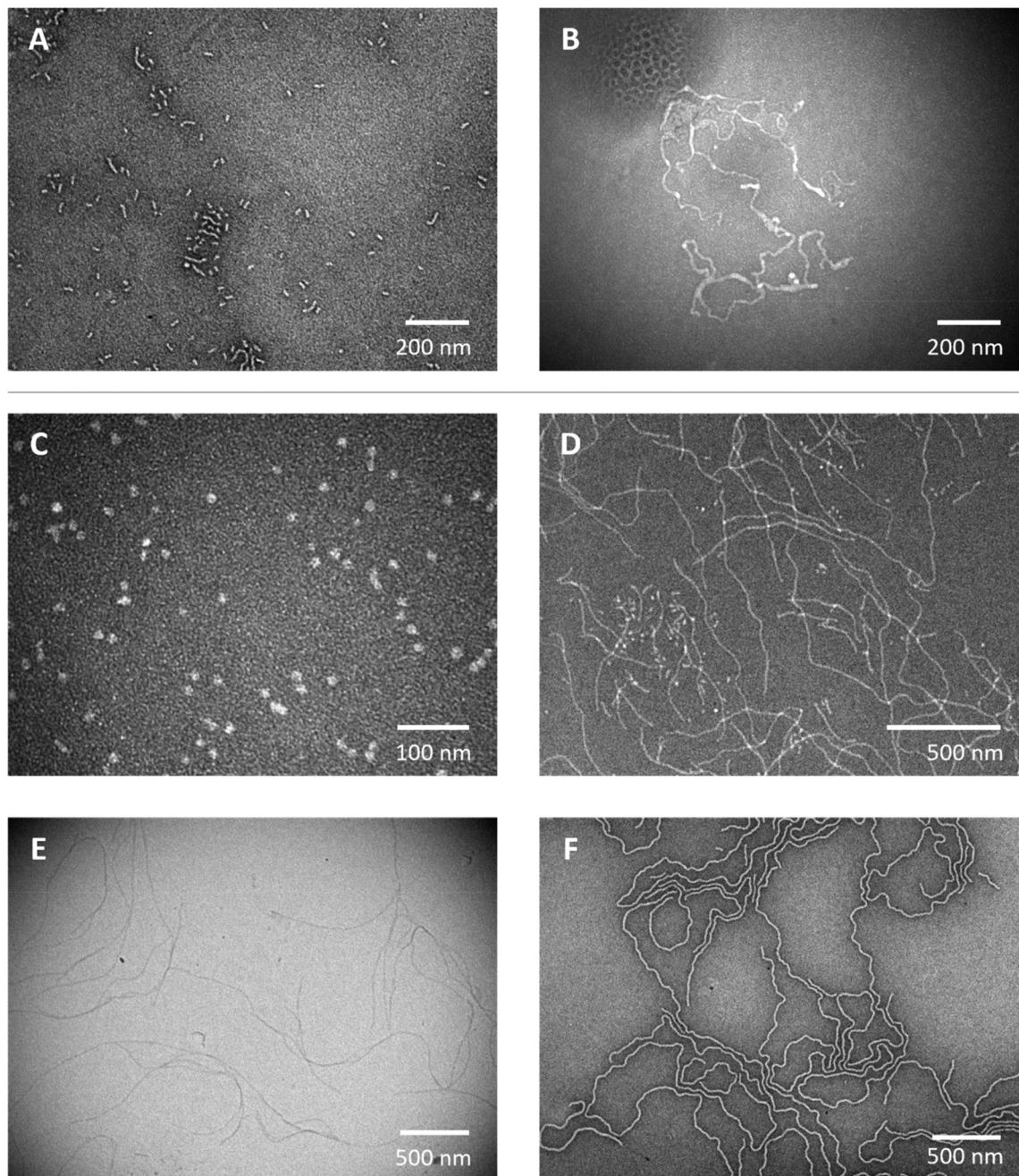
| Polymer                                     | $D_1$ (10 <sup>−7</sup> cm <sup>2</sup> s <sup>−1</sup> ) | $D_2$ (10 <sup>−7</sup> cm <sup>2</sup> s <sup>−1</sup> ) | $R_{H,1}$ (nm) | $R_{H,2}$ (nm) |
|---------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|----------------|----------------|
| P(EG <sub>123</sub> -co-OIGE <sub>7</sub> ) | 4.64 ± 0.03                                               | 0.23 ± 0.01                                               | 5.3 ± 0.1      | 107 ± 5        |
| mPEG <sub>45</sub> -b-POIGE <sub>2,4</sub>  | 2.54 ± 0.02                                               | 0.51 ± 0.05                                               | 9.7 ± 0.1      | 48 ± 4         |
| mPEG <sub>45</sub> -b-POIGE <sub>5,0</sub>  | 0.51 ± 0.02                                               | 0.12 ± 0.01                                               | 48 ± 2         | 206 ± 5        |
| mPEG <sub>114</sub> -b-POIGE <sub>2,9</sub> | 1.41 ± 0.02                                               | 0.35 ± 0.01                                               | 17.5 ± 0.2     | 70 ± 1         |
| mPEG <sub>114</sub> -b-POIGE <sub>5,8</sub> | 0.55 ± 0.03                                               | 0.10 ± 0.01                                               | 45 ± 2         | 240 ± 20       |
| mPEG <sub>114</sub> -b-POIGE <sub>7,3</sub> | 1.12 ± 0.01                                               | 0.21 ± 0.01                                               | 21.9 ± 0.2     | 117 ± 7        |



chain folding, resulting in the formation of multicompartiment micelles. This phenomenon has been discussed in previous studies.<sup>70–72</sup> The corresponding TEM micrograph equally indicates small circular structures as well as larger aggregates but with a smaller radius (Fig. S25†). While they are separated in the dry TEM micrographs, they probably stick to each other in solution, due to hydrophobic interactions between OIGE units in the corona-forming segments of different micelles. This

leads to the formation and observation of aggregates with a greater  $R_{H,2}$ . Potemkin *et al.* described this “stickiness” in a recent study.<sup>73</sup>

Block copolymers composed of mPEG<sub>45</sub> generally displayed larger  $R_{H,1}$  values, despite having a significantly greater number of repeating units in comparison to the statistical copolymer. This observation implies the aggregation of multiple chains into micelles. When the size of the POIGE block is



**Fig. 4** TEM micrograph of mPEG-*b*-POIGE<sub>*n*</sub> block copolymers in aqueous solution (0.1 g L<sup>-1</sup>). A: mPEG<sub>45</sub>-*b*-POIGE<sub>2.4</sub>, B: mPEG<sub>45</sub>-*b*-POIGE<sub>5.0</sub>, the circular structure in the upper left corner is caused by irradiation damage. C: mPEG<sub>114</sub>-*b*-POIGE<sub>2.9</sub>, D: mPEG<sub>114</sub>-*b*-POIGE<sub>5.8</sub>, E: mPEG<sub>114</sub>-*b*-POIGE<sub>7.3</sub>, F: mPEG<sub>114</sub>-*b*-POIGE<sub>9.9</sub>. Samples were treated with 2% uranyl acetate solution as a negative stain. Original micrographs obtained by the software can be found in the ESI (Fig. S26 and 27†).





doubled, there is a notable four- to fivefold increase in the hydrodynamic radius of both aggregates. This finding aligns with the structures observed in the TEM micrographs (Fig. 4A and B).

The behavior of block copolymers containing mPEG<sub>114</sub> demonstrates subtle variations. While the hydrodynamic radius ( $R_{H,1,2}$ ) for the POIGE<sub>*n*</sub> block (with  $n = 2.9$  and  $7.3$ , C and E) only experiences a slight increase as  $n$  increases, the block copolymer with  $n = 5.8$  (D) exhibits a larger  $R_{H,1,2}$  compared to the one with  $7.3$  OIGE monomer units. This outcome may seem unexpected, but it can be attributed to the fact that due to the larger hydrophobic block ( $n = 7.3$ ), there are fewer chains present within the respective micelles compared to mPEG<sub>114</sub>-*b*-POIGE<sub>5.8</sub>, resulting in a reduced aggregation number. Consequently, the hydrodynamic radius does not increase as one might anticipate. The polymer mPEG<sub>114</sub>-*b*-POIGE<sub>2.9</sub> reveals only small structures in the TEM micrograph, a finding that contrasts with the DLS analysis results indicating clustering in solution. The TEM micrograph of the block copolymer with the largest POIGE part, mPEG<sub>114</sub>-*b*-POIGE<sub>9.9</sub> (F), displays well-resolved, fibrillar structures. Nevertheless, further analysis has been deferred to a later study. Original TEM micrographs can be found in the ESI (Fig. S25–S27†).

### Thermal properties of polymers containing OIGE

PEG plays an important role as ointment base and tailoring the melting point slightly above human body temperature enables softening into a semi-solid during application and even spreading while lasting at the applied area.<sup>9,74,75</sup> The synthesized OIGE (co)polymers were investigated by differential scanning calorimetry (DSC) (Table 5). The thermograms are displayed in the ESI (Fig. S13–S17†). Detection of glass tran-

sition temperatures ( $T_g$ s) was performed with the second heating curve with a heating rate of  $10\text{ K min}^{-1}$ . As OIGE has a long, flexible side chain, the  $T_g$  is shifted towards lower temperatures compared to PEG ( $<-60\text{ }^\circ\text{C}$ ).<sup>9</sup> Melting temperatures ( $T_m$ s) and melting enthalpies were determined with a  $1\text{ K min}^{-1}$  heating rate. Reducing the heating/cooling rate to  $1\text{ K min}^{-1}$  allowed for ordering of the side chains and prevention of recrystallization. Otherwise, a pronounced recrystallization was detected during the melting event in the measurements with a heating/cooling rate of  $10\text{ K min}^{-1}$  (Fig. S13†). Substituted polyethers are typically amorphous materials. However, due to the elongated and linear structure of the side chain, POIGE displays a distinct  $T_m$ , despite the racemic monomer. This indicates a propensity for side chain crystallization. The microphase separation driven by crystallization was previously described in literature with comparable side chains, albeit for polyacrylates or polyesters.<sup>70,76,77</sup>

### Statistical P(EG-co-OIGE) copolymers

The random incorporation of 5 mol% OIGE in P(EG-co-OIGE) copolymers (Table 5, entry 3) results in a notable reduction in crystallinity, as evidenced by the decrease of the melting enthalpy ( $\Delta H_m$ ) of PEG. For comparison, mPEG<sub>114</sub> (Table 5, entry 11), which closely resembles the polymer under investigation, was utilized. 12 mol% OIGE (Table 5, entry 4) further inhibited crystallization of the polyether backbone, and the material showed the PEG  $T_m$  already below room temperature. When 25 mol% OIGE was incorporated (Table 5, entry 5), the  $T_m$  ( $-41.7\text{ }^\circ\text{C}$ ) was solely dominated by the OIGE side chain.

### mPEG-*b*-POIGE block copolymers

Block copolymers initiated by mPEG<sub>45</sub> showed decreasing  $\Delta H_m$  with increasing POIGE block (Table 5, entries 6–10), again indicating partial miscibility of the two different blocks. Comparing entries 8 and 9, an unusual behavior appears: with an increasing amount of POIGE (entry 9), the  $T_m$  of both copolymer blocks decreased. This indicated a transition zone where both blocks were too small to crystallize. By further increase of the POIGE content, the  $T_m$  of the POIGE block increased again (entry 10), whereas the thermal properties of the PEG block remained unchanged. Very similar thermal behavior was observed for mPEG<sub>114</sub>-*b*-POIGE block copolymers as well: both  $T_m$ s decreased with increasing POIGE content (entries 13 and 14), but with higher POIGE content the  $T_m$ s elevated again. This indicated that a more effective phase separation between the two polymers contributed to the rise in the  $T_m$ s (entry 15).

### Post-polymerization modification

**Hydrogenation via diimide reduction.** Oleyl alcohol exhibits a  $T_m$  of  $0\text{--}5\text{ }^\circ\text{C}$ ,<sup>78</sup> in contrast to its fully saturated alcohol counterpart, known as stearyl alcohol, showing a considerably higher  $T_m$  of  $57\text{ }^\circ\text{C}$ .<sup>79</sup> Accordingly, a similar correlation was expected for the respective GE monomers and the resulting polymers. The POIGE homopolymer exhibited a  $T_m$  of approximately  $-23\text{ }^\circ\text{C}$ . To cover a broad range of side chain  $T_m$ s, particularly in the physiological range, we aimed at partial to com-

**Table 5** Overview of the thermal properties of the OIGE (co)polymers

| Entry | Polymer                                              | OIGE, mol% | $T_g^a$ , $^\circ\text{C}$ | $T_m^b$ , $^\circ\text{C}$ | $\Delta H_m^b$ , $\text{J g}^{-1}$ |
|-------|------------------------------------------------------|------------|----------------------------|----------------------------|------------------------------------|
| 1     | POIGE <sub>13</sub>                                  | 100        | n.d.                       | $-27.8$                    | 32.2                               |
| 2     | POIGE <sub>25</sub>                                  | 100        | n.d.                       | $-23.2$                    | 63.4                               |
| 3     | P(EG <sub>123</sub> -co-OIGE <sub>7</sub> )          | 5          | n.d.                       | 35.7                       | 64.9                               |
| 4     | P(EG <sub>94</sub> -co-OIGE <sub>13</sub> )          | 12         | $-81$                      | 12                         | 46.5                               |
| 5     | P(EG <sub>103</sub> -co-OIGE <sub>35</sub> )         | 25         | $-80$                      | $-41.7$                    | 30.3                               |
| 6     | mPEG <sub>45</sub>                                   | 0          | $-60$                      | $-52.3$                    | $-164.7$                           |
| 7     | mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>2.4</sub>  | 3          | $-75$                      | n.d./48.1                  | n.d./104.0                         |
| 8     | mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>5.0</sub>  | 10         | n.d.                       | $-39.5/42.7$               | $9.0/67.1$                         |
| 9     | mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>7.5</sub>  | 14         | $-78$                      | $-46.8/37.2$               | $6.6/48.2$                         |
| 10    | mPEG <sub>45</sub> - <i>b</i> -POIGE <sub>11.3</sub> | 20         | $-79$                      | $-32.1/35.0$               | $21.8/45.4$                        |
| 11    | mPEG <sub>114</sub>                                  | 0          | $-60$                      | $-61.9$                    | $-190.1$                           |
| 12    | mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>2.9</sub> | 2          | $-79$                      | n.d./57.4                  | n.d./133.8                         |
| 13    | mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>5.8</sub> | 5          | $-80$                      | $-50.5/53.7$               | $4.2/108.5$                        |
| 14    | mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>7.3</sub> | 6          | $-76$                      | $-58.0/51.9$               | $0.8/89.8$                         |
| 15    | mPEG <sub>114</sub> - <i>b</i> -POIGE <sub>9.9</sub> | 8          | n.d.                       | $-41.3/53.3$               | $10.2/88.9$                        |

<sup>a</sup> Heating rate  $10\text{ }^\circ\text{C min}^{-1}$ , second heating curve. <sup>b</sup> Heating rate  $1\text{ }^\circ\text{C min}^{-1}$ , second heating curve. In the case of block copolymers, the first  $T_m$  and  $\Delta H_m$  denote the POIGE block crystallization, whereas the second denote the PEG block crystallization.





plete hydrogenation as a post-polymerization modification. While copolymerization of saturated and unsaturated monomers is possible, the transfer of a solid monomer *via* a syringe entails additional effort and may represent a challenge. Moreover, elucidating the reactivity ratios of the GE monomers would be essential. Traditional hydrogenation in organic synthesis involves reacting the unsaturated substrate with hydrogen gas and a palladium catalyst. Although this method is widely used in industrial settings, it requires high pressures and involves handling highly explosive hydrogen, making it impractical in a laboratory environment. Therefore, we turned to the reduction of the double bond using diimide reduction.<sup>80–83</sup> Potassium azodicarboxylate (PADA) was treated with acetic acid in pyridine to generate diimide. This compound transfers hydrogen to the *cis*-double bond of the OIGE side chain. The degree of hydrogenation was controlled by the amount of PADA equivalents used. In cases of high degrees of hydrogenation, PADA was employed in significant excess. Experimental details can be found in the ESI.† The decrease of the double bond resonance is visible in the <sup>1</sup>H NMR spectra of the hydrogenated polymer (Fig. 5). We achieved a maximum degree of hydrogenation of 95% (H95%), which we refer to as fully hydrogenated. As the copolymers comprise a polyether structure lacking bonds susceptible to cleavage under hydrogenation conditions, SEC still showed monomodal distributions with only minor changes in *M<sub>n</sub>* and *D* (Fig. S46†). Statistical as well as block copolymers were hydrogenated for testing purposes. However, since the melting points of the hydrogenated OIGE monomer overlapped with the PEG part, the changes in thermal properties were uncertain: whether they are attributed to the higher *T<sub>m</sub>* resulting from the hydrogenation of OIGE or a change in PEG crystallization. Therefore, only POIGE homopolymers were included in this study.

To confirm the anticipated effect of hydrogenation concerning side chain crystallization, the thermal properties after hydrogenation were investigated by DSC (Fig. S48†). With an increasing degree of hydrogenation, the *T<sub>m</sub>* of POIGE<sub>25</sub> rises above room temperature and reaches its peak at 51.9 °C when

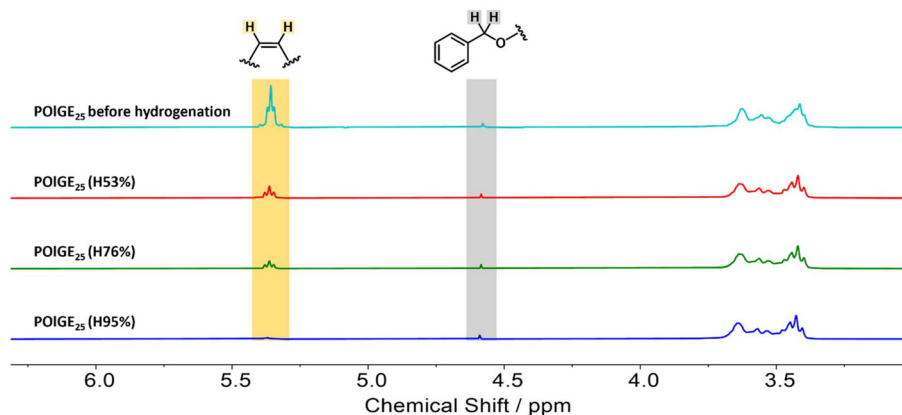
fully hydrogenated. Up to 53% of hydrogenation results in a significant increase of *T<sub>m</sub>*, whereas the difference in *T<sub>m</sub>* decreases with higher degrees of hydrogenation (entries 3 and 4). The melting enthalpy increases only slightly, going from 63.4 to 75.2 J g<sup>−1</sup>. This relatively small change occurs even though the hydrogenated side chains were expected to be hindered from crystallization due to the assumed miscibility of the saturated and unsaturated side chains. Here, the melting enthalpy is almost independent of the degree of hydrogenation, albeit the melting point increases by 75.1 °C in total. In summary, the hydrogenation experiments show that POIGE can be fully hydrogenated in a post-polymerization modification. With a *T<sub>m</sub>* in the physiological range, copolymers containing OIGE repeating units possess potential for applications in drug delivery systems. Tailoring can be conveniently performed, as no copolymerization of high and low *T<sub>m</sub>* monomers is necessary. Instead, one starting material is sufficient (Table 6).

Not only does the double bond content provide the opportunity to customize thermal properties, but it also allows for the modification of the structure to meet specific requirements. It enables the incorporation of hydroxyl groups or other functional groups, which enables the tuning of hydrophobicity and facilitates further coupling with various other groups.<sup>84–86</sup>

**Table 6** Thermal properties of POIGE<sub>25</sub> homopolymer before (H0%) and after hydrogenation at various degrees investigated by DSC

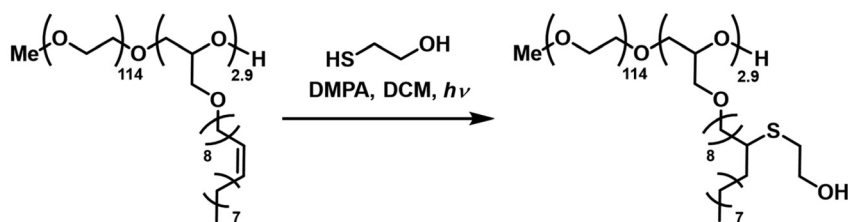
| Entry | Polymer <sup>a</sup>       | <i>T<sub>m</sub></i> <sup>b</sup> /°C | Δ <i>H<sub>m</sub></i> <sup>b</sup> /J g <sup>−1</sup> |
|-------|----------------------------|---------------------------------------|--------------------------------------------------------|
| 1     | POIGE <sub>25</sub> (H0%)  | −23.2                                 | 63.4                                                   |
| 2     | POIGE <sub>25</sub> (H53%) | 33.6                                  | 69.2                                                   |
| 3     | POIGE <sub>25</sub> (H76%) | 43.7                                  | 73.0                                                   |
| 4     | POIGE <sub>25</sub> (H95%) | 51.9                                  | 75.2                                                   |

<sup>a</sup> The value of *H* denotes the degree of hydrogenation. <sup>b</sup> Heating rate 1 °C min<sup>−1</sup>, second heating curve.



**Fig. 5** <sup>1</sup>H NMR spectra of POIGE<sub>25</sub> and the respective hydrogenated polymers (400 MHz, CDCl<sub>3</sub>). The value of *H* denotes the degree of hydrogenation. The intensity was locally normalized to the initiator benzyl group (gray).





**Scheme 3** Thiol-ene click reaction of mPEG<sub>114</sub>-b-POIGE<sub>2.9</sub> with thioglycol. Note that two possible addition products can be present.

**Thiol-ene click.** The addressability of the internal double bond of the side chains of the OIGE units as a proof of concept reaction was demonstrated by a thiol-ene click reaction with thioglycol in a typical post-polymerization modification. As a model polymer, mPEG<sub>114</sub>-b-POIGE<sub>2.9</sub> reacted with the thiyl radicals generated by irradiation of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) in DCM (Scheme 3).<sup>87</sup> Detailed experimental information is available in the ESI.†

Complete conversion was confirmed by <sup>1</sup>H NMR by the disappearance of the double bond and allylic proton signals. The appearance of the methine and methylene group of the respective thioether further confirmed the successful modification (Fig. S42†). SEC revealed a shift towards higher molar masses, again keeping the dispersity constant (Fig. S43†). DOSY NMR confirmed no residual thioglycol precursor after work-up by dialysis (Fig. S44†). MALDI-ToF MS analysis showed the new repeating unit with a molar mass of 402 g mol<sup>-1</sup> (Fig. S45†).

## Conclusion

Oleyl glycidyl ether (OIGE) has been introduced as a biorenewable, highly apolar epoxide building block for the AROP copolymerization with EO. Investigation of the reactivity ratios revealed a small deviation from ideal statistical copolymerization of OIGE ( $r_{\text{OIGE}} = 0.78$ ) with EO ( $r_{\text{EO}} = 1.27$ ), leading to an almost ideally random copolymer structure. This is a remarkable observation, considering the large steric bulk of the OIGE monomer in comparison to EO. In addition to statistical copolymers, using different mPEG macroinitiators yielded block copolymers. Capitalizing on block copolymerization of POIGE with mPEG, amphiphilic polymers were successfully produced. The CMCs of mPEG-based block copolymers show a limit in the same range as the established surfactant Brij® 98. The water-soluble statistical copolymer also showed micelle formation, owing to the long hydrophobic side chains. TEM and DLS revealed spherical and elongated micellar aggregates, which can be explained by the arrangement of the sterically demanding, linear side chains. The utilization of OIGE allows the synthesis of biobased surfactants from readily accessible starting materials. The bulk properties of the polymers showed two distinguishable  $T_{\text{ms}}$ . The *cis*-alkenyl side chain was successfully modified by a thiol-ene click reaction, demonstrating

the accessibility and emphasizing the versatility of the hidden functionality. This enables coupling of a wide range of thiol-containing compounds to the polymers. Partial hydrogenation of the double bond with potassium azodicarboxylate (PADA) enables adjusting the melting point of the materials, eradicating the mixing of monomers with high and low side chain  $T_{\text{m}}$ , respectively. The achieved range of melting points is suitable for developing potential thermoresponsive drug delivery systems, as it matches the human body temperature. In future drug delivery applications, active pharmaceutical ingredients could be released from micellar solutions, if the  $T_{\text{m}}$  of the precisely adjusted side chain is reached.

In brief, our study shows that the biobased novel monomer OIGE and its copolymerization can be employed to generate a wide range of structurally varied polymeric surfactants. This approach can pave the way for replacing traditional petroleum-based surfactants and also unlocks the potential for generating diverse and tailored polymer architectures. “Green” and conveniently modifiable polymers with respect to the requirements of a user, particularly with respect to melting temperatures or hydrophobicity, can offer a future platform for customized drug-delivery systems.

## Data availability

The data supporting this article have been included as part of the extended ESI.†

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

The authors thank Monika Schmelzer for SEC measurements, Elena Berger-Nicoletti for MALDI-ToF MS measurements. Frank Depoix and Elisabeth Sehn are acknowledged for introduction to TEM measurements and Lisanne Lörke for experimental support. Rebecca Matthes is thanked for thorough correction of the manuscript.



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