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Cycling Stability of Poly(ethylene glycol) of Six Molecular Weights: Influence of Thermal Conditions for Energy Applications

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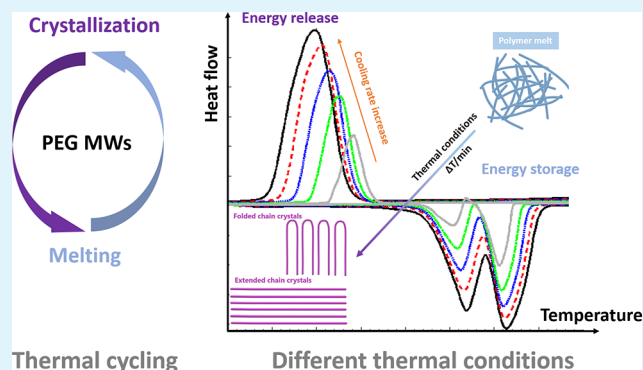
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ABSTRACT: Utilizing energy storage technologies is beneficial for bridging the gap between supply and demand of energy and for increasing the share of renewable energy in the energy system. Phase change materials (PCMs) offer higher energy density and compact storage design compared to conventional sensible heat storage materials. Over the past years, poly(ethylene glycol) (PEG) has gained attention in the PCM field, and several new composites of PEGs have been developed for thermal energy storage purposes. PCMs are investigated at a given heating/cooling rate to evaluate their phase change temperature and enthalpy. In the case of PEG, some molecular weights show a melting behavior that depends on the thermal history, such as the crystallization conditions. This study investigates the relationship between the molecular weights of PEGs (400–6000 g/mol), cooling/heating rates, and the behavior during phase transitions, to evaluate the performance of PEGs as a PCM under various thermal conditions. Experiments were performed using differential scanning calorimeter and the transient plane source method. All PEG molecular weights were subjected to the same cooling and heating conditions, cooling and heating rate, and number of cycles, to decouple the thermal effects from molecular weight effects. The behavior of phase transition for different thermal conditions was thoroughly analyzed and discussed. It was found that the melting temperature range of PEGs with different molecular weight was between 5.8 and 62 °C (at 5 °C/min). Each PEG showed unique responses to the cooling and heating rates. Generally, the behavior of the crystallization changed most between the thermal cycles, while the melting peak was stable regardless of the molecular weight. Finally, it is recommended that the characterization of PEGs and their composites should be conducted at a heating and cooling rate close to the thermal conditions of the intended thermal energy storage application.

KEYWORDS: poly(ethylene glycol) (PEG), molecular weight, phase change material (PCM), crystallization, melting, thermal energy storage (TES), thermal analysis, cycling stability



1. INTRODUCTION

New technologies and better utilization of intermittent renewable energy resources such as wind and solar power, as well as excess heat from industrial processes, require materials for energy storage. By shifting the energy supply in time to thermal energy storage (TES), the mismatch between energy production and consumption can be reduced. Latent heat thermal energy storage (LHTES) can save space compared to conventional sensible heat storage, due to its higher energy density. Phase change materials (PCMs) store heat and cold during the phase transition from solid to liquid and reversed.

Over the past years, poly(ethylene glycol) (PEG) gained attention in the PCM field, and several new composites were developed for thermal energy storage purposes.^{1–4} The wide range of melting temperatures makes it a suitable PCM for building applications. The phase change characteristics and physical properties of polymers vary with the molecular weight.

In general, the notation “PEG M_w ” is used where M_w is the molecular weight. PEG is widely used in the pharmaceutical industry as a drug carrier,⁵ as a plasticizer for some biopolymers,⁶ and to prevent phase separation in inorganic PCM.⁷ It is a water-soluble polymer that is nonflammable, nontoxic, and biodegradable and thereby also harmless to the environment [5].

There is a need of PCMs with high energy storage capacity and stable performance over multiple cycles. The study of their behavior at the laboratory scale should provide robust insights

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Table 1. Polyethylene Glycol as a Phase Change Material in the Literature

| PEG M_w | devices | scanning temp range (°C) | heating/cooling rate (°C/min) | cycling stability | thermal conductivity (W/(m·K)) |
|--|--|--------------------------|-------------------------------|--|--|
| PEG 6000 ³ | DSC Q100, TA Instruments, USA | -10 to 100 | 10 | 100 cycles (composite PEG and SiO ₂ stability) | |
| PEG 6000 ¹⁸ | DSC 204 F1, NETZSCH, Germany | 0 to 120 | 10 | 50 cycles (PEG composite stability between 20 and 100 °C) | 0.31 |
| PEG 1000, 4000 and 10000 ¹⁹ | (TCi) Hot Disk Thermal Constant Analyzer (Hot Disk 2500-O1, Sweden) | | | | |
| PEG 6000 ²⁰ | DSC Q8000, NETZSCH, Germany | 0 to 100 | 10 | 100 thermal cycles (PEG composite stability) | |
| PEG 2000 ²¹ | DSC, Mettler Toledo in-house thermal cycle test rig | 30 to 100 40 to 90 | 10 | 1500 cycles | |
| PEG 1000: 3400, 10000, 20000 35000 ²² | DSC, DSC131 SETARAM instrument | 0 to 100 | 10 | 10 cycles and isothermal stability at 80 °C for 861 h in the presence of air, nitrogen, and vacuum | |
| PEG-1500 ²³ | DSC, NETZSCH DSC 200 | 20 to 85 °C | 1, 2.5, 10, and 20 | | 0.233 (at 15 °C for PEG-epoxy nanocomposite) |
| PEG 1000 ²⁴ | DSC, SETARAM Micro DSC VII Evo (TCi) UNITHERM 6000 setup | 20 to 60 | 1 | | |
| PEG 6000 ²⁵ | PERKIN ELMER DSC-2C (TCi) hot disk thermal conductivity instrument transient plane source (TPS) | -10 to 110 | 10 | | 0.2985 (at room temperature) |
| PEG 2000 ²⁶ | DSC 2010, TA Instruments (TCi) DRL-III tester, Xiangyi Instrument, China | 10 to 90 | 5 | | 0.297 |
| PEG 3000, 4250, 7100, 10500, and 23000 ¹⁴ | DSC, NETZSCH STA449F3, Germany (TCi) Hot Disk TPS2500, Hot Disk AB Co., Sweden | 10 to 80 | 5 | 100 cycles (PEG composite stability) | 0.237 (at 25 °C) |
| | DSC TA thermal analysis system 9000 | isothermal | 0.5 | | |
| | synchrotron small-angle X-ray scattering beamline, X-14, at the National Synchrotron Light Source (NSLS) | | | | |

about the performance of the PCM, including energy storage capacity and phase change temperature, during several charging and discharging cycles, to meet the design requirements of thermal energy storage applications and to prevent potential failures. Real applications of PCMs are diverse in type and thermal requirements: LHTES systems, building envelope, and stabilization of temperature-sensitive devices. Each application uses a PCM which is subjected to different thermal conditions, and the volume of the PCM in these applications may vary. It may range from PCM nanoparticles and microparticles (capsules or dispersions) to massive components (macro-encapsulated PCM of a few kilograms). In general, the method for the characterization depends on the nature of the PCM. For instance, the supercooling of bulk PCM is lower than the supercooling of PCM emulsions⁹ and microcapsules. Furthermore, the increase of the size of the sample (e.g., DSC, *T*-history, and pilot plant scales) of salt hydrate decreases the degree of supercooling.¹⁰ Accordingly, the DSC is excluded from the measurement procedure for salt hydrate in the quality and testing specifications.¹¹ However, for organic PCMs, all known methods are used. The DSC provides reliable information about real scale behavior of paraffin (e.g., supercooling¹⁰) when compared to different PCM size (*T*-history and pilot plant scale). Besides, the size of the sample should be chosen to ensure the homogeneity of the sample. For PCM qualification, slow cooling and heating are usually recommended to measure phase transition properties.¹¹ Assuming that the solidification and melting properties of PCMs are independent of the cooling/heating steps, the results may deviate between different studies. This assumption is valid for some PCMs, such as *n*-alkane, while, for several other materials, the crystallization and melting properties are affected by the heating and cooling rates. These materials may exhibit complex crystallization and melting behavior, such as broad melting/crystallization peaks and multiple peaks, depending on the specific heating/cooling rates. Besides, some PCM show performance degradation depending on the cooling rate; for instance, for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, it was shown that the development of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ crystals depends on the cooling/heating rate.^{12,13} The development of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ induces phase separation and the decrease in energy storage capacity. The latter is visible only at a low cooling rate, e.g., 4 °C/h.¹³

It is known that PEGs show a melting behavior that depends on the preceding isothermal crystallization temperature and annealing time.¹⁴ Thus, the cooling conditions (i.e., slow or fast cooling) may influence the melting of PEGs. In the thermal energy storage system, the PCM is subjected to different cooling and heating conditions. For instance, in the case of LHTES, the cooling and heating rate is faster near the heat exchanger and slower close to the storage wall. Hence, the material is expected to crystallize and melt differently in the different parts of the storage. This is seldom captured in the testing procedures that are used today and described in the literature; see Table 1. Thus, there is a need to fully understand the behavior of the developed PEG with regard to thermal conditions. This is critical to reducing the discrepancy found, for some PCMs, between the material's performance on a small scale and at real scale applications.^{15–17}

As shown in Table 1, the previous studies have investigated different PEG-based composites,^{1–4,19,27} as well as pure PEGs with various chain lengths (molecular weights)^{20,22,28} under limited cooling and heating rates. These investigations aimed to evaluate their phase transition temperatures and enthalpies

under certain conditions. A review of organic phase change materials by Sarier and Onder⁸ discussed the properties of PEG 400 and PEG 20000. They report a supercooling of 27.2 and 31 °C for PEG 400 and PEG 20000, respectively. This result suggests that supercooling issues can be expected from PEGs, thus excluding them from being a useful PCM,²⁹ whereas Marcos et al.²⁸ showed that PEG 400 only had a supercooling of 7.2 °C at 1 °C/min heating/cooling rate. From previous studies, the cooling and heating rate, and the specimen size, are known to influence the crystallization and melting peaks' positions³⁰ because of the heat transfer effects within the specimen.³¹ However, in the case of PEG 400, the melting peak is basically not changed with the heating rate, while the crystallization peak was dramatically affected by the cooling rate. Indeed, the crystallization peak evolves substantially in terms of peak position and the appearance of multiple peaks, with the increase of the cooling rate.²⁸ The effects of the different heating/cooling rates on the measured phase transition properties, especially crystallization, are visible in the data collected for several PEGs in two review papers.^{8,27} The two reviews provide different values for the phase change properties for some of the same PEG molecular weights.

Pielichowski and Flejtuch²² investigated different molecular weights of PEG and their blends with organic materials for thermal energy storage applications.³² The studied molecular weights of PEG showed a melting temperature from 44.2 to 71.1 °C.²² The study²² also covers the effects of the cooling rate on the crystallization temperature for PEG 3400 and 10000. The results highlight the shifting of the crystallization peak to lower temperatures with increasing cooling rate. The melting of PEG 3400 shows two melting peaks, instead of one, during the heating step (at 10 °C/min). However, the change in the melting behavior of PEG 3400 crystals with the heating rate was not studied. Also, the study did not investigate the cycling stability of the phase transition and the thermophysical properties of PEG. The thermal conductivity of PEG can be found in the literature for some molecular weights, measured at a specific temperature. However, the thermal conductivity depends both on the temperature and physical state (liquid or solid) of the material.³³

Sharma et al.²⁰ investigated PEG 6000 as a potential energy storage material. To simulate five consecutive years, the authors conducted 1500 thermal cycles of cooling and heating between 40 and 90 °C. The calorimetric analysis of cycled PEG 6000 showed a change in the melting temperature and enthalpy after cycling. A total decrease of the melting enthalpy of 25% was found after the 1500th cycle, while only a 6.3% decrease was found in the melting temperature. However, the effects of thermal cycling on the crystallization of PEG 6000 were not studied.²⁰ The authors attributed this change, of melting characteristics, to the presence of impurities in the material since no change was detected in the FT-IR spectrum of transmittance of uncycled and cycled PEG 6000. Moreover, the stability of PEG 2000 was found to depend on the atmosphere (air, nitrogen, and vacuum).²¹

According to our literature study, the thermal cycling stability of the phase transition characteristics is not systematically studied for several PEG molecular weights (cf. Table 1). Moreover, usually a high and specific cooling and heating rate is adopted for the characterization and the thermal cycling stability test. Since PEGs show a melting behavior that depends on the thermal history, such as the crystallization conditions, the evaluation of PEG under varied thermal

conditions is of great importance to prevent undesirable effects in real applications. Therefore, the existing data and testing procedures that are used today for PEG and described in the literature should be expanded with an investigation of the different PEG when subjected to various thermal conditions. Consequently, this study focuses on the relationship between the molecular weight of PEG (400–6000 g/mol), cooling/heating conditions, and the behavior during phase transitions. In addition, we study the influence of thermal cycling stability on the phase transition of each PEG. We have studied how the thermophysical and phase change properties of PEGs vary with molecular weight. The experiments were performed using differential scanning calorimeter (DSC) and the transient plane source method (TPS) for calorimetric and thermophysical measurements. The selected PEGs in this study are of interest for low- and medium-temperature applications (e.g., cold storage, comfort temperature, and solar thermal energy storage). The melting temperature range of the investigated PEGs is between 5.8 and 62 °C. All of the PEGs were subjected to the same cooling/heating conditions (5, 4, 3, 2, and 1 °C/min) to decouple thermal effects from molecular weight effects. The thermal stability was performed for all PEGs under the same heating/cooling rate (60 cycles at 5 °C/min). The changes in phase transition with successive cycles were analyzed and discussed.

2. MATERIAL AND METHODS

2.1. Materials. Poly(ethylene glycol), $H-(O-CH_2-CH_2)_n-OH$, was investigated using differential scanning calorimeter (DSC) and the transient plane source method (TPS). The average molecular weights (M_w) of the selected PEGs were 400, 600, 1000, 1500, 4000, and 6000 g/mol. All of them were laboratory graded and supplied from Fisher Scientific. They are hereafter named as PEG 400, PEG 600, and so on.

2.2. Methods and Data Analysis. Samples of weights in the range of 10–30 mg were thermally evaluated using a differential scanning calorimeter DSC 1 from Mettler Toledo. For each measurement, the sample was placed and hermetically sealed in an aluminum pan, and as a reference, an empty pan of the same type was used. Each sample material was measured several times to ensure repeatability and to obtain average values for different thermal events and their related properties. Each measurement was performed by first heating the sample to a temperature well above the melting temperature and then cooling it to a temperature below the crystallization temperature. This procedure will hereafter be referred to as a thermal DSC cycle (or just cycle). For each cycle, the phase transition characteristics, i.e., both melting and crystallization temperatures as well as enthalpies, were determined as schematically shown in Figure 1.

To determine the melting and crystallization temperatures and enthalpies, all samples were evaluated at a temperature change of 5 °C/min, and a mean value was calculated from two separate 60 cycles runs. Measurements were also conducted to evaluate how the rate of temperature change affects the phase transition. The latter was done by decreasing the rate of temperature change in the successive cycling, from 5 °C/min to 4, 3, 2, and 1 °C/min on the same sample. For the samples of PEG 1000, 1500, and 6000, the temperature interval (Table 2) was slightly modified to reduce the total experiment time. PEG that is stored at a temperature lower than its melting temperature can achieve a higher degree of crystallinity than what is possible during the short time of a calorimetric cycle. Effects such as these will be observable during the calorimetric measurements. Hence, the first cycle is omitted from the evaluation as it reflects the previous thermal history of the material. As seen in Figure 2, for PEG 1000, the heat flow curve from the first cycle deviates distinctly from the curves from the second, third, and fourth cycles as a result of this phenomena. This behavior was also observed in a previous study of

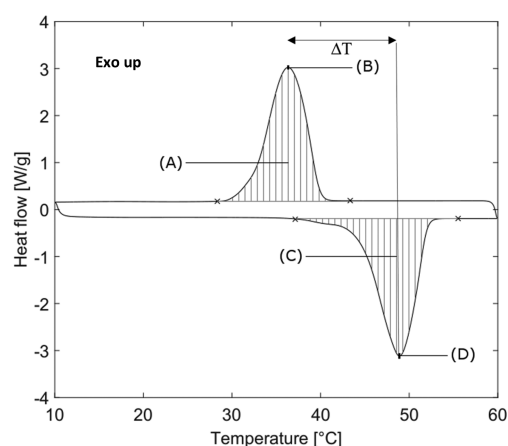


Figure 1. Five parameters of interest when evaluating DSC data for possible PCMs: (A) enthalpy of crystallization (shaded region), (B) peak maximum showing the crystallization temperature (maximum heat flow of crystallization), (C) enthalpy of melting (shaded region), (D) peak minimum showing the melting temperature and ΔT , which is the temperature difference between peaks B and D, i.e., the supercooling.

Table 2. Experimental Details for the DSC Measurements

| sample | temp interval (°C) | heating/cooling rate (°C/min) | no. of cycles |
|----------|--------------------|-------------------------------|-------------------------|
| PEG 400 | −30 to 15 | 5 | 60 |
| | −30 to 15 | 5, 4, 3, 2, 1 | one cycle for each rate |
| PEG 600 | −10 to 30 | 5 | 60 |
| | −10 to 30 | 5, 4, 3, 2, 1 | one cycle for each rate |
| PEG 1000 | 10–50 | 5 | 60 |
| | 15–50 | 5, 4, 3, 2, 1 | one cycle for each rate |
| PEG 1500 | 10–60 | 5 | 60 |
| | 20–60 | 5, 4, 3, 2, 1 | one cycle for each rate |
| PEG 4000 | 30–70 | 5 | 60 |
| | 30–70 | 5, 4, 3, 2, 1 | one cycle for each rate |
| PEG 6000 | 30–70 | 5 | 60 |
| | 30–75 | 5, 4, 3, 2, 1 | one cycle for each rate |

PEG 3400.² Due to this, the results obtained during the first cycle were not considered for the mean value calculations in order to get results of relevance for the long-term cycling behavior of the PCM. The complete experimental conditions for the DSC measurements are shown in Table 2.

The thermal conductivity was determined by the transient plane source method (TPS; Hot Disk TPS 2500 S) from Hot Disk AB (Sweden), which previously has been used for the identification of the activity of PCMs.^{34,35} TPS measures the increase in sample temperature as a combined heat source and temperature sensor supply a constant heating power over a specific time period. This approach enables the simultaneous evaluation of thermal conductivity, thermal diffusivity, and volumetric heat capacity. For each measurement, a kapton (insulation material) sensor 8563 with a radius of 9.868 mm was used. The setup for the TPS measurements was based on the one previously used by Sasic Kalagasis et al.³⁴ and Johansson et al.,³⁵ who used the technique for the study of crystallization and melting of PCMs. Before the measurements, the PEGs were melted in beakers on a hot plate and poured into a 160 mL plastic cup. To maximize the contact area between the sensor and the sample, and to

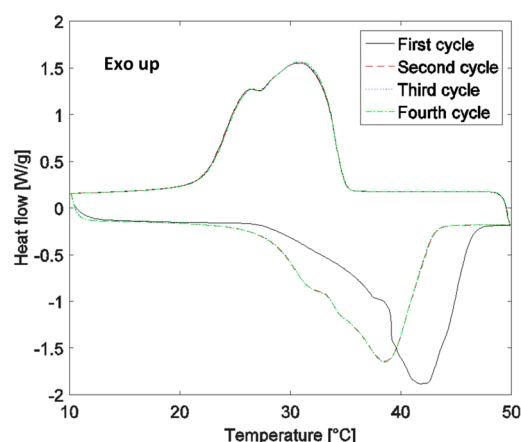


Figure 2. Typical DSC curves from four subsequent cycles of PEG 1000. Note the distinct deviation between the first (solid line) and the following cycles and that the following cycles are identical (rate of temperature change is 5 °C/min).

ensure repeatability, the sensor was then inserted vertically into the cup as the sample crystallized around the sensor at room temperature.

The TPS measurements were conducted in a temperature-controlled room at 22 °C. The same room was also used to equilibrate the samples for at least 24 h before the measurements. The heating power was set to 45 mW during a measurement time of 160 s. The distance between the sensor and the walls of the cup was at least 20 mm. The time between measurements was set to a minimum of 30 min in order to restore uniform temperature within the sample. Due to the low melting temperatures of the materials PEG 400 and PEG 600, and the problem of keeping a constant temperature below these, TPS measurements were not possible to perform on these samples. Conducting the TPS technique for these PEGs at 22 °C would imply measurements in the liquid phase (affected by heat convection) and, therefore, difficult to compare with the literature and the other samples measured in a solid phase.

3. RESULTS AND DISCUSSION

3.1. Phase Transition versus Molecular Weight.

Crystallization and melting of PEG were analyzed at the same rate of temperature change, 5 °C/min. Figure 3 shows the heat flow curves of all PEG molecular weights. Both

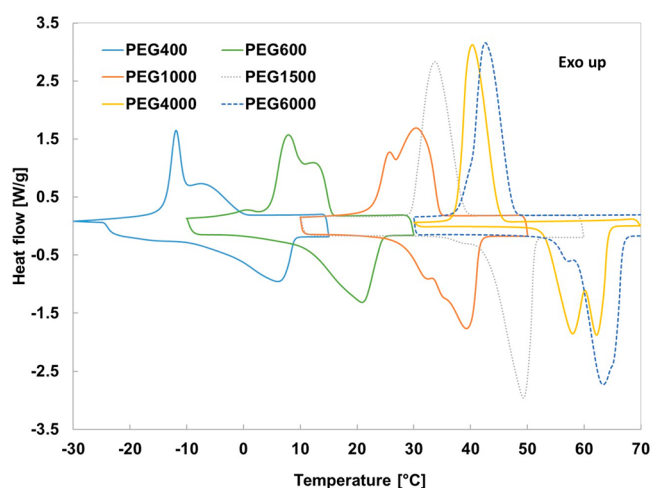


Figure 3. Normalized heat flow versus temperature for crystallization and melting of different PEG's molecular weights (rate of temperature change, 5 °C/min).

crystallization and melting of PEG may exhibit one or two peaks during cooling and heating steps, respectively. For PEG 1000 and for higher molecular weights, the crystallization peaks interfere with each other. The blending of different PEGs' molecular weights may provide customized phase change temperature and enthalpy.²² Moreover, the crystallization peaks become sharper with increasing molecular weight. This behavior can be attributed to the slow crystallization kinetics in the case of low molecular weights, which induces a broadening of the crystallization peak regarding cooling conditions. Besides, the differences in thermophysical properties of different PEG influence the material's response to temperature change. Regarding the melting behavior, several known parameters may influence the shape of the melting peak (i.e., broadening), the concentration of end groups, distribution of crystallite size, and molecular weight distribution (polydispersity).³⁶

For different PEGs the melting (T_m) and the crystallization temperatures (T_c) were determined from the mean peak values of the two 60 thermal DSC cycles. T_m and T_c as well as their temperature difference (ΔT (°C)) are shown in Table 3. The lowest and highest degrees of supercooling (ΔT (°C)) are obtained for PEG 1000 and PEG 4000, respectively, as shown in Table 3.

Table 3. Average Melting and Crystallization Temperatures with the Standard Deviation (sd) for PEG of Different Molecular Weights^a

| | T_m (°C) | | T_c (°C) | | ΔT (°C) | |
|----------|------------|-----|------------|-----|-----------------|-----|
| | av | sd | av | sd | av | sd |
| PEG 400 | 5.8 | 0.8 | -5.9 | 0.4 | 11.6 | 1.2 |
| PEG 600 | 20.7 | 1.1 | 9.5 | 0.7 | 11.2 | 0.9 |
| PEG 1000 | 39.0 | 0.9 | 29.8 | 1.6 | 9.3 | 2.4 |
| PEG 1500 | 48.7 | 0.2 | 34.0 | 1.8 | 14.6 | 1.6 |
| PEG 4000 | 61.3 | 0.3 | 40.6 | 0.7 | 20.8 | 0.9 |
| PEG 6000 | 62.1 | 0.6 | 42.5 | 1.0 | 19.5 | 1.6 |

^aAll measurements were conducted at a rate of temperature change of 5 °C/min.

In Figure 4, the melting and crystallization temperatures are plotted as a function of the molecular weight of PEGs. To extend the range of PEG molecular weights, the results are complemented by values obtained in previous studies on PEG of higher molecular weights.^{22,32,37}

From Figure 4, both melting and crystallization temperatures increase with increased molecular weight (M_w), and the minimum degree of supercooling is achieved for the PEG with a molecular weight of around 1000 g/mol (cf. Table 3). Both the melting and crystallization temperatures increase gradually from molecular weights of 400 g/mol (PEG 400) to approximately 10 000 g/mol. At higher molecular weights, both transition temperatures remain relatively constant; a similar behavior of the melting temperature versus molecular weight (i.e., chain length) was found for *n*-alkane.³⁶ As previously shown, with increased molecular weight, the chain-end effect on the crystalline structure decreases, and then the polymer crystallinity increases.²² An empirical equation for the evolution of phase change temperatures versus molecular weight is proposed and expressed by the following equation (eq 1):

$$T = AM_w^B + C \quad (1)$$

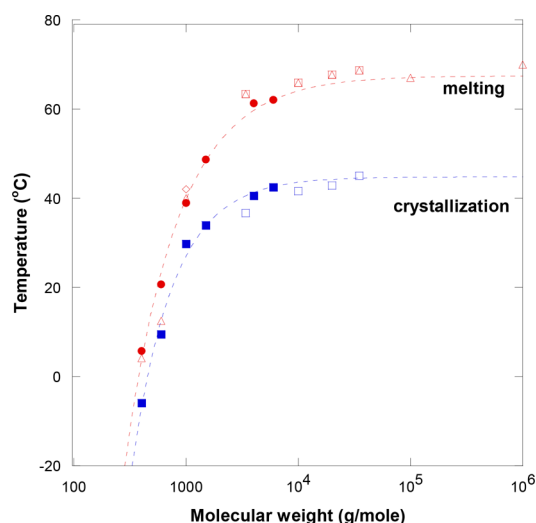


Figure 4. Melting and crystallization temperatures as a function of molecular weight. Filled symbols show the phase transition temperatures obtained in this study (circles and squares show melting and crystallization temperatures, respectively). The molecular weight range is extended by literature data, shown by open symbols (Δ ,³⁷ \square ,³² and \diamond ²²). It should be noted that the fitted functions are based on the results obtained from only our experimental study (rate of temperature change, 5 °C/min).

The coefficients for T_m (°C) and T_c (°C) are determined from the fitting of the present experimentally obtained data for PEG 400 to PEG 6000 and shown in Table 4.

Table 4. Coefficients Obtained from Curve Fitting by Equation 1 for the Melting and Crystallization Temperatures (°C)

| | A (°C mol/g) | B | C (°C) | R ² |
|-------|--------------|---------|--------|----------------|
| T_m | -6393 | -0.7618 | 71.83 | 0.996 |
| T_c | -95490 | -1.25 | 44.31 | 0.993 |

The melting and crystallization enthalpies of PEG are presented in Table 5 as mean values of the two 60 cycles DSC

Table 5. Mean Melting and Crystallization Enthalpies with the Standard Deviation (sd) for PEG of Different Molecular Weights^a

| | ΔH_{melt} (J/g) | | ΔH_{cryst} (J/g) | |
|----------|--------------------------------|------|---------------------------------|------|
| | av | sd | av | sd |
| PEG 400 | 84.1 | 7.7 | 82.2 | 1.3 |
| PEG 600 | 119.5 | 6.6 | 120.8 | 11.5 |
| PEG 1000 | 151.9 | 6.5 | 149.8 | 6.3 |
| PEG 1500 | 161.3 | 11.6 | 163.6 | 8.6 |
| PEG 4000 | 170.3 | 5.5 | 167.3 | 4.7 |
| PEG 6000 | 180.1 | 4.5 | 178.3 | 4.3 |

^aAll measurements were conducted at a rate of temperature change of 5 °C/min during two 60 cycles for each PEG.

cycle. In general, the melting and the crystallization enthalpies (ΔH_m and ΔH_c), increase with molecular weight, resulting in higher thermal energy storage capacity.

In Figure 5, the melting and crystallization enthalpies are plotted as a function of the PEGs' molecular weights. The results are complemented by, and compared with, previously

known values of PEG with other molecular weights obtained from the literature.^{22,32,37} It is shown that the values of ΔH_m (J/g) and ΔH_c (J/g) continuously increase with increasing molecular weight up to about 10000 g/mol. At about this molecular weight, the enthalpies, in a way similar to that of the phase transition temperatures, remain relatively constant with the molecular weight increase. It should be noted that the fitted functions, shown as dashed or dotted lines in Figure 5A,B, are extracted from the experimental data from our study only. Some of the values for polymers of higher molecular weights significantly deviate from the trend line. Probably the reason for this is that the exact thermal history (cooling and heating rates) of these high molecular weight polymer samples is not the same as in our study. Since the thermal history can influence the degree of crystallinity, these deviations are expected. Besides, the purity of the studied PEG can also affect phase change characteristics (temperatures and enthalpies).

3.2. Influence of the Rate of Temperature Change on Phase Change Kinetics.

Phase change materials are subjected to various thermal conditions in real thermal energy storage applications. Hence, understanding the behavior of these materials under varied thermal conditions is of great importance to prevent undesirable effects in real LHTES applications. In this section, the rate of the temperature change (heating and cooling) was varied to study its influence on phase change properties. Generally, the degree of supercooling provides an overview of the crystallization and melting. The degree of supercooling (ΔT) is shown in Table 6 for different molecular weights and temperature change rates. Some clear tendencies can be directly deduced, and it shows that the ΔT significantly decreases with the heating and cooling rate. Also, PEG 1000 shows the smallest temperature difference among all of the other PEG molecular weights regardless of the rates of temperature change.

The effect of the heating and cooling rate on the degree of supercooling is also illustrated in Figure 6A for PEG 1500, where the supercooling decreases from 14.8 °C at a rate of 5 °C/min to 7.9 °C at a rate of 1 °C/min. This is seen for all PEGs regardless of the molecular weight, as shown in Table 6.

In general, the area of the crystallization and melting peaks for a given PEG increases with the cooling/heating rate. In the representation of heat flow versus temperature, the latent heat of crystallization/melting is proportional to the area of the peak (Figure 1A), where the cooling/heating rate is the proportionality factor (cf. Appendix 2). Thus, the increase in the cooling/heating rate leads to an increase in the area of peaks, while the enthalpy is constant. Furthermore, a peak shift during cooling/heating is observed with the change of the heating/cooling rate and the sample size³⁰ because of the heat transfer effects within the specimen during experiment.³¹ However, it also depends on the kinetics of nucleation and crystal growth rate. Indeed, in Figure 6A, the melting temperature is seen to vary slightly with the heating rate, which is in contrast to the crystallization temperature that increases gradually as the cooling rate decreases. Consequently, the degree of supercooling ΔT (°C), which is more dependent on the cooling rate, is reduced with the decreasing rate of cooling. During the heating cycle of PEG 6000 (Figure 6B), a small peak/shoulder is observed before the main melting peak. Moreover, as the rate of temperature change decreases, another peak appears at high temperatures to become more visible at 1 °C/min. The observed changes in the melting peak are related to the

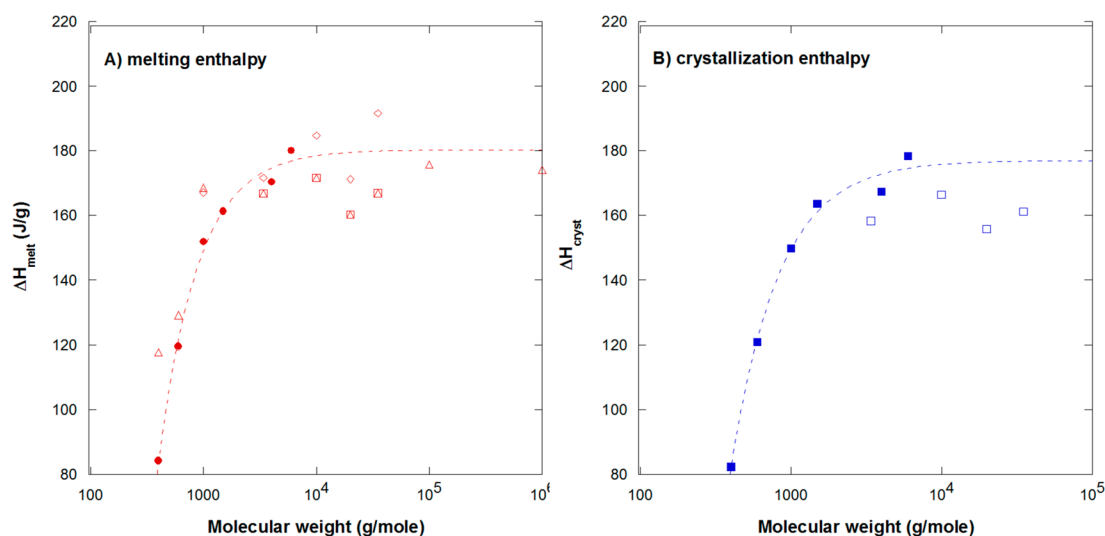


Figure 5. Melting (A) and crystallization (B) enthalpies as a function of molecular weight (at 5 °C/min). Data obtained from this study are shown by filled symbols (circles and squares show melting and crystallization enthalpies, respectively). The molecular weight range is extended by literature data as shown by open symbols (Δ ,³⁷ \square ,³² and \diamond ²²). Note here that the trend line is based on experimental data from only this study.

Table 6. Degree of Supercooling at Different Rates of Temperature Change

| | degree of supercooling (°C) | | | | |
|----------|-----------------------------|----------|----------|----------|----------|
| | 5 °C/min | 4 °C/min | 3 °C/min | 2 °C/min | 1 °C/min |
| PEG 400 | 18.2 | 17.3 | 10.1 | 8.0 | 5.9 |
| PEG 600 | 11.0 | 10.4 | 9.9 | 9.4 | 8.9 |
| PEG 1000 | 9.5 | 8.3 | 7.1 | 5.8 | 4.0 |
| PEG 1500 | 14.8 | 14.1 | 12.5 | 10.2 | 7.9 |
| PEG 4000 | 21.7 | 20.7 | 19.6 | 18.3 | 16.5 |
| PEG 6000 | 20.6 | 19.3 | 17.7 | 16.7 | 14.5 |

morphological changes within the crystal phase itself (cf. global discussion).

3.3. Cycling Stability of PEG. The long-term behavior of PEG, and specifically the impact of thermal cycling on the phase change properties, is a critical issue for the choice of a PCM for a given application.³³ Therefore, the changes in the melting and crystallization temperatures and the corresponding enthalpies, over multiple thermal cycles, were studied to

evaluate the cycling stability of each PEG. Mean values for melting/crystallization temperature and enthalpies obtained from cycles 2, 30, and 60 are presented in Table 7.

In general, during cycling stability, the melting temperatures and enthalpies are relatively constant for each PEG. However, the crystallization temperature varies differently with molecular weight. For instance, no significant change was observed for PEG 600 and PEG 1000; meanwhile, the impact is dramatic for PEG 400. The latter shows a noticeable increase in crystallization temperature with the number of cycles (cf. Figure 7). The increase of the crystallization temperature indicates that the density of nuclei is higher compared to the previous crystallization cycle, as the growth rate of crystals, from the polymeric melt, is a temperature-dependent process. This suggests that the activated nuclei in previous cycles did not melt/relax completely. Thus, during the subsequent cooling cycle, the growth of the crystal starts at higher temperatures (due to the presence of already stable nuclei); consequently, a higher crystallization temperature is obtained.

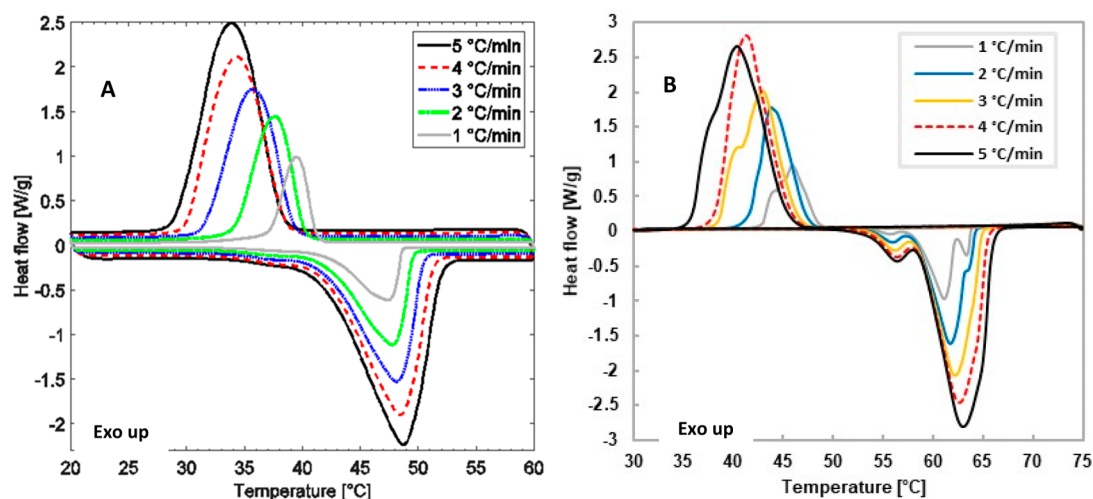


Figure 6. Measurements of (A) PEG 1500 and (B) PEG 6000 with DSC at the different heating and cooling rates.

Table 7. Melting and Crystallization Temperatures and Enthalpies from Cycles 2, 30, and 60 along with the Degree of Supercooling for Each Cycle for the Different PEGs^a

| | cycle | T_M (°C) | ΔH_M (J/G) | T_C (°C) | ΔH_C (J/G) | ΔT (°C) |
|----------|-------|---------------|-----------------------|---------------|-----------------------|--------------------|
| PEG 400 | 2 | 5.7 | 84.1 | -11.7 | 89.5 | 17.4 |
| | 30 | 5.8 | 85.6 | -5.1 | 81.4 | 10.9 |
| | 60 | 6.0 | 86.7 | -4.5 | 79.6 | 10.5 |
| PEG 600 | 2 | 20.7 | 110.5 | 8.5 | 107.0 | 12.1 |
| | 30 | 21.1 | 108.7 | 8.9 | 117.3 | 12.3 |
| | 60 | 21.1 | 109.2 | 8.9 | 117.2 | 12.1 |
| PEG 1000 | 2 | 38.5 | 147.1 | 30.9 | 144.1 | 7.7 |
| | 30 | 38.5 | 147.5 | 31.1 | 144.1 | 7.5 |
| | 60 | 38.6 | 147.6 | 31.1 | 144.2 | 7.5 |
| PEG 1500 | 2 | 48.4 | 171.6 | 34.7 | 172.0 | 13.7 |
| | 30 | 49.0 | 173.8 | 36.1 | 172.6 | 12.9 |
| | 60 | 49.0 | 173.9 | 37.1 | 172.9 | 11.9 |
| PEG 4000 | 2 | 61.4 | 168.0 | 41.5 | 164.6 | 19.9 |
| | 30 | 61.3 | 168.8 | 40.7 | 166.4 | 20.7 |
| | 60 | 61.3 | 168.5 | 40.3 | 166.7 | 21.1 |
| PEG 6000 | 2 | 61.9 | 183.6 | 44.1 | 181.6 | 17.8 |
| | 30 | 61.9 | 182.7 | 42.8 | 181.0 | 19.1 |
| | 60 | 61.8 | 182.3 | 41.9 | 180.6 | 20.0 |

^aAll measurements were conducted at a temperature change of 5 °C/min.

Another consequence is the change of the induced crystalline structure and/or the overall kinetics of crystallization (i.e., nucleation and crystal growth) of PEG 400 during cycling. As can be observed in Figure 7A), the initial crystallization (i.e., cycle 2) occurs in two steps: first, a shoulder (broad peak at high temperature) followed by a distinct peak (at low temperature). As the number of cycles increases, the intensity of the low-temperature peak decreases and the intensity of the high-temperature peak increases. This result implies that the fraction of the crystalline structure formed at the lower temperature decreases for each cycle, and a more favorable crystalline structure is built up at the higher crystallization temperature instead. However, for an exact determination of the induced crystalline structures, more detailed experiments are necessary. The impacts on cycling can also be interpreted in terms of the process of energy release of PEG 400. The transformation degree of PEG 400 at a given temperature T is defined as the ratio of the total heat released

until the temperature T to the total heat released during the crystallization process as expressed by the following equation:³⁸

$$\alpha(T) = \frac{\int_{T_i}^T \phi \, ds}{\int_{T_i}^{T_f} \phi \, ds} \quad (2)$$

ϕ is the heat flow (W/g), and T_i and T_f represent the onset and the end of the crystallization, respectively.

In Figure 7B), the degree of transformation of PEG 400 melt to the crystal phase depends on the cycle number. Heat extraction (during crystallization) is slower in the first cycle compared to the successive cycles.

Finally, the 60 times cycle had a relatively small impact on the crystallization temperature of PEG 4000. A crystallization temperature's decrease of only 1.2 °C between the second and the 60th cycle was measured (cf. Table 7). Meanwhile, the crystallization temperature decreased by 2.2 °C for PEG 6000. The reduction of the crystallization temperature, with successive thermal cycling, may indicate either a decrease in crystallization mechanism (nucleation and growth) or a change in the chemical structure of PEG (e.g., thermal degradation and chain scission). The latter mechanism results in lower molecular weight, leading to a decrease in the crystallization temperature (cf. Figure 4).

3.4. Thermophysical Properties Analysis. In the final part of the study, TPS measurements were conducted for PEGs of molecular weights 1000, 1500, 4000, and 6000 g/mol, which are all in a solid state at room temperature. The change in sample temperature was measured according to the method described above, and the results are presented in Table 8. All values are averaged values from 10 subsequent measurements for each PEG. As shown in Table 8, the thermal conductivity increases with the molecular weight up to 4000–6000 g/mol. Furthermore, it is seen that the thermal diffusivity is slightly higher for PEG 1000 than for other PEGs.

3.5. General Discussion. When discussing potential PCM applications, many studies stress the importance of the melting temperature and enthalpies (i.e., energy density). The effects of cooling and heating rates have not been previously systematically investigated for PCMs. In some cases, the PCM behavior depends on cooling/heating conditions, as shown in our study, where thermal conditions influence the crystallization and melting behavior. The large degree of supercooling is

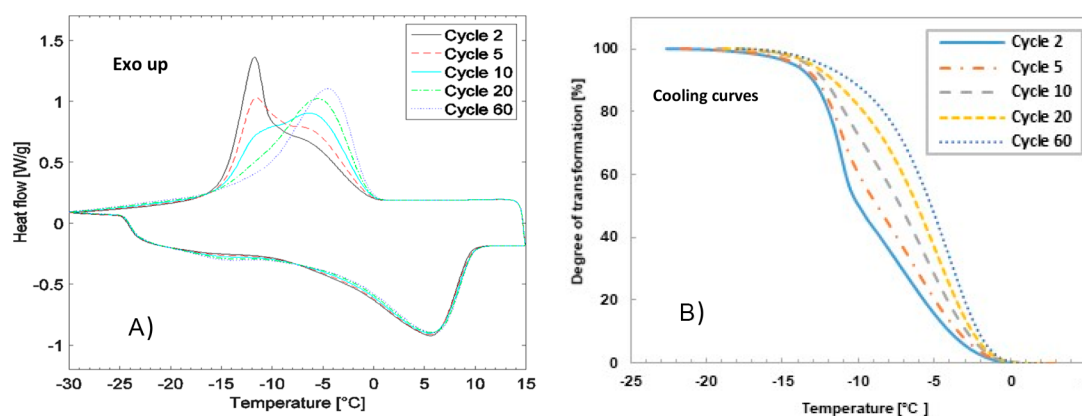


Figure 7. (A) Shift of the crystallization peak of PEG 400 to higher temperatures during repeated thermal cycles. (B) Degree of transformation versus temperature for different cycles. The shift is notable during the first 20 cycles, after which the crystallization peaks remain almost the same.

Table 8. Mean thermal conductivity, Thermal Diffusivity, and Volumetric Heat Capacity, With Standard Deviations (sd), for Solid PEG of Different Molecular Weights^a

| | thermal conductivity (W/(m·K)) | | thermal diffusivity (m ² /s) | | volumetric heat capacity (kJ/(m ³ ·K)) | |
|----------|--------------------------------|-------|---|-------|---|------|
| | av | sd | av | sd | av | sd |
| PEG 1000 | 0.158 | 0.001 | 0.458 | 0.015 | 345.5 | 9.2 |
| PEG 1500 | 0.166 | 0.001 | 0.322 | 0.009 | 514.7 | 11.0 |
| PEG 4000 | 0.192 | 0.001 | 0.365 | 0.003 | 524.6 | 3.0 |
| PEG 6000 | 0.187 | 0.002 | 0.360 | 0.011 | 520.0 | 11.3 |

^aThe values are averaged based on ten subsequent measurements with 30 min interval.

problematic for many potential PCMs for thermal energy storage applications, such as salt hydrates and sugar alcohols.^{34,37,39} Some studies reported a high degree of supercooling for some PEG M_w s. However, as shown in Figure 8, the supercooling of PEG is strongly affected by the

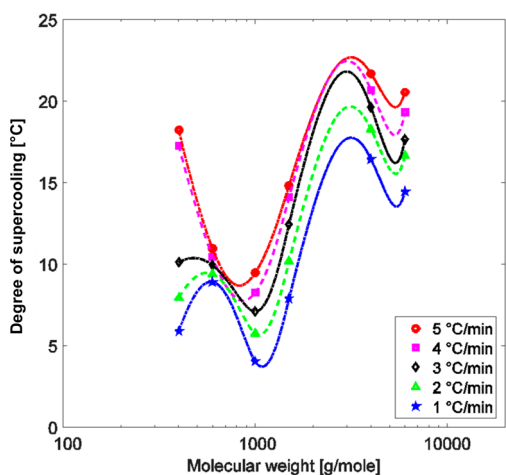


Figure 8. Degree of supercooling of PEG decreases with a lowering of the rate of temperature change. Depending on the molecular weight, some PEGs are affected more than others by a change of the heating and cooling rate. The rate of temperature change affects the growth rate of different crystalline structures of the polymer. This may result in a shift of the crystallization peak, thus further affecting the rate of supercooling. This effect is noticeable for PEG 400 between 4 and 3 °C/min. The dashed and dotted fitting lines are added for visualization purposes only.

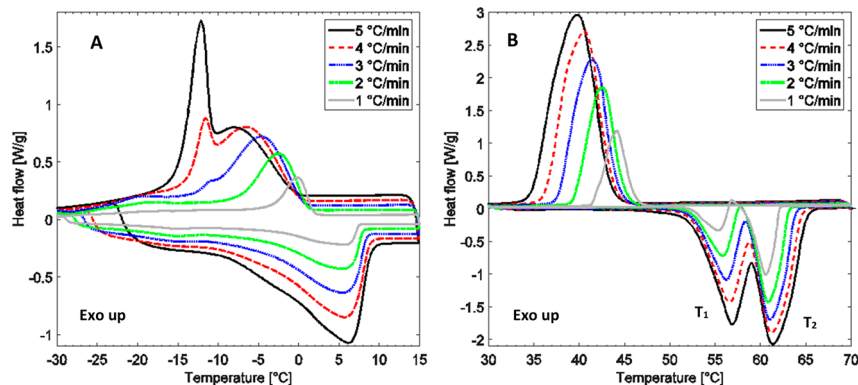


Figure 9. DSC curves for PEG 400 and PEG 4000 at five different heating and cooling rates: (A) crystallization peak transformation of PEG 400 due to decreased cooling rate and (B) melting of two “crystalline structures” of PEG 4000.

heating and cooling rate. For instance, most thermal comfort applications in building materials are expected to be exposed to rather slow temperature changes; no important supercooling is expected in this application.

Besides supercooling, the cooling/heating rates affect the crystallization and the melting peaks. PEG exhibits a complex crystallization and melting behavior during cooling (i.e., thermal energy release conditions) and heating (i.e., thermal energy storage conditions), depending on molecular weight (cf. Figure 3) and temperature change rate (cf. Figure 6B). For instance, PEG 400 exhibits double peaks during cooling at 5 °C/min (cf. Figure 3), which is different from the typical behavior of a PCM. The peaks evolve substantially during subsequent cycles at the cooling rate of 5 °C/min, as seen in Figure 7. Similar behavior is found during the study of the rate of temperature change effects, dramatic change in the crystallization peaks' position, and their shapes, as seen in Figure 9A.

In Figure 9A, the height of the crystallization's peak at the lower temperature decreases with lowering the rate of cooling, while the crystallization's peak at higher temperature increases. The presence of two heat flow maxima during cooling reflects the presence of two different crystallization mechanisms, one at higher temperatures and the other at lower temperatures. In general, this behavior can be induced by the presence of two crystals with different nucleation and growth kinetics or with different enthalpies of crystallization. Consequently, when the PEG samples are cooled rapidly, it favors crystalline structures that grow at low temperatures under a high rate of cooling. On the other hand, a reduced cooling rate results in crystalline structures that grow at high temperatures becoming more favored. A mild cooling rate can induce two peaks, as seen with 4 °C/min cooling. This effect can partly explain the peak transformation observed in Figure 9A for PEG 400.

The other reason for the shift of the crystallization temperature to a higher temperature is of generic kinetic character, which can be explained by the longer time the melt is in a supercooled regime at a slow cooling rate. Indeed, the slow cooling of the PEG 400 allows the crystal to grow and further nucleation at higher temperatures to take place, leading to a completed crystallization at higher temperatures and therefore lowering the supercooling degree.

During the crystallization of some PEG molecular weights and even after (i.e., storage at solid state), the PEG molecules can form different types of “crystals”; non-integral folding

chain crystal (NIF), integral folding crystal (IF), and extended chains crystal,^{14,40} which results in different crystalline lamellae thickness and different melting behaviors. The change of crystal lamellae thickness depends on the crystallization temperature, time, and molecular weight; the changes occur through thinning or thickening processes.¹⁴ These changes on NIF lamellae lead to either a reduction in the number of folds (thickening) until a full extension of the chain is obtained or to an increase in the number of folds (lamellae thickness reduced). During the melting (i.e., heating step), multiple melting peaks can be observed, which reflects a different population of crystalline lamellae. This “perfection” process explains the rise of crystallinity as well as the melting temperature of samples stored at a temperature lower than the melting temperature of PEG (cf. Figure 2 and Appendix 1).

Double melting peaks are seen in Figure 9B for PEG 4000. Both crystalline structures are formed simultaneously during the crystallization but melt at different temperatures. Thus, two melting peaks are observed when the sample is heated. Moreover, the melting behavior (peak height and position) depends on the heating rate as well. The lower melting peak height increases with the heating rate, and the ratio of the melting enthalpy of the lower melting peak (T_1) on the higher melting peak (T_2) increases with the cooling rate. The perfection can also occur during the heating step, especially at slow heating rates; in this case, the crystals (NIF) have time for more lamellae perfection, leading to an increase of the magnitude of the higher melting peak. Furthermore, at ambient temperature (i.e., during storage) and for enough time, only one melting peak can be found; see, for instance, the first DSC cycle of PEG 4000 (Appendix 1). The double melting peak was also reported for other polymers such as poly(lactic acid), where the double melting peaks were attributed to the perfection of crystalline lamellae during the heating cycle.³⁸

PEG 400 and PEG 4000 are two examples of the impacts of thermal conditions on the crystallization and melting kinetics. The rate of cooling/heating dictates the PCM's crystallization and melting behavior. Hence, a characterization of PEG based only on one cooling/heating rate does not provide reliable information about phase transition for TES design; it could be misleading. Furthermore, the residence time in the solid state of PEG leads to an increased crystallinity and melting temperature. Careful analysis of PEG under various thermal conditions is very crucial to prevent performance degradation during the real working conditions of the thermal energy storage system.

Thermophysical properties are also of importance during TES choice and design. These properties were also measured for PEG. Compared to other common PCM, PEG has a higher thermal conductivity than fatty acids and similar values as *n*-alkane (depending on the length of *n*-alkane).³³ Generally, organic materials for PCM applications are known for their low thermal conductivity. Although it has not been the purpose of this study to increase the thermal conductivity, it should be noted that several studies^{24,41,42} have shown that the thermal conductivity of PEG can be increased up to 0.8 W/(m·K).

4. CONCLUSIONS

In this work, we have performed a study of how the thermophysical and phase change properties of PEG vary with the molecular weight and thermal conditions. All PEGs' molecular weights (400–6000 g/mol) were analyzed under the same cooling and heating conditions to provide more insights

about the behavior with regard to thermal conditions and molecular weights. This study showed that the crystallization and melting behavior of PEGs are strongly dependent on the cooling and heating rate. Indeed, it governs the peaks' position (e.g., supercooling) and number of peaks. Besides, each PEG molecular weight showed a different response to the cooling and heating rates. Thus, it is recommended that the characterization of PEG should be conducted at a heating/cooling rate close to the thermal conditions of the intended TES application. The main findings of the study can be summarized in the following points:

- The slow cooling rate reduces the degree of supercooling of PEG, regardless of the molecular weight.
- The lowest supercooling degree was obtained with PEG 1000.
- The slow heating rate induces development of new melting peaks of PEG (e.g., PEG 6000).
- The lowest and highest energy densities were found for PEG 400 and PEG 6000, respectively.
- At solid state, the perfection process of the crystal phase of PEG 4000 continues and increases the melting enthalpy with time.
- The thermal stability over 60 cycles showed that considering only the melting peaks for phase change stability could be misleading since the crystallization process is most affected by the thermal cycling.

The physicochemical stability under real working conditions (e.g., presence of air), and the long-time exposure to high temperature should be further investigated, to quantify the thermochemical degradation of PEG with thermal cycling. Moreover, crystallization continues even at solid state due to the perfection process. Therefore, in future studies, it is necessary to further quantify the impact of this process on the cycling stability and thermal properties.

■ APPENDIX 1

The thermal history effects on PEG can be seen from DSC analysis. The sample was directly heated at 5 °C/min from 30 °C (temperature lower than the melting temperature) to 70 °C. The first cycle shows one melting peak (representative of the thermal history of PEG 4000), with a melting temperature of 61.7 °C and enthalpy of 188 J/g, while, during the second melting cycle, two melting peaks are observed for PEG 4000 (Figure 10), with an overall melting peak (located on the second melting peak) at 61.25 °C and enthalpy of 171 J/g.

■ APPENDIX 2

The peak areas increase with cooling/heating rate in Figures 6 and 9; this does not imply that the enthalpy of crystallization and melting increases with cooling/heating rate. Visually, one integrates the heat flow with respect to temperature. The DSC software (in our case STARE software) integrates the curve correctly with respect to time (see ref 43, p 51). The enthalpy is calculated as follow:

$$\Delta H = \int_{t_1}^{t_2} \phi(t) dt \quad (3)$$

Variable substitution leads to

$$\Delta H = \int_{T_1}^{T_2} \phi(T) \frac{dT}{\varphi} = \frac{1}{\varphi} \int_{T_1}^{T_2} \phi(T) dT \quad (4)$$

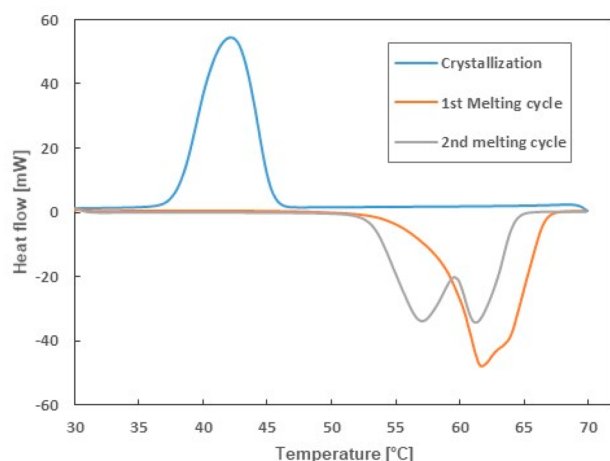


Figure 10. Heat flow versus temperature for PEG 4000.

$$\varphi = \frac{dT}{dt} \text{ cooling/heating rate}$$

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Notes

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