

UC Berkeley

UC Berkeley Previously Published Works

Title

Random copolymer of poly(polyethylene glycol methyl ether)methacrylate as tunable transition temperature solid-solid phase change material for thermal energy storage

Permalink

<https://escholarship.org/uc/item/5xx609q3>

Authors

Khomein, Piyachai
Nallapaneni, Asritha
Lau, Jonathan
et al.

Publication Date

2021-06-01

DOI

10.1016/j.solmat.2021.111030

Peer reviewed

Random copolymer of poly(polyethylene glycol methyl ether)methacrylate as tunable transition temperature solid-solid phase change material for thermal energy storage

*Piyachai Khomein,^a Asritha Nallapaneni,^{b, c} Jonathan Lau,^a Drew Lilley,^d Chenhui Zhu,^b
Sumanjeet Kaur,^a Ravi Prasher,^{a, d} Gao Liu^{a,*}*

^a Energy Storage and Distributed Resources Division, Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

^b Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, United States

^c Department of Polymer Engineering, University of Akron, Akron, OH 44325 United States

^d Department of Mechanical Engineering, University of California Berkeley, Berkeley, California 94720, United States

Abstract

Polymer based phase change materials (PCM) for thermal energy storage (TES) applications have gained some attention recently due to their high stability and potential solid to solid phase transition. Here, we are the first to utilize a simple copolymerization strategy for static tunability transition temperature (T_t) of polymeric PCM. The copolymerization between short and long side chain polyethylene glycol based methacrylate polymers was designed to tune T_t with minimum impact on their energy density. Polarized optical microscope and x-ray techniques were also used to understand the relationship between crystal structure and T_t of different copolymer composition which was discussed in the context. The solid to solid transition polymeric PCM were successfully developed with tunable T_t ranged from 18°C to 35°C which is suitable toward building envelop applications.

Keywords: Phase change material, polyethylene glycol, random copolymer, solid to solid transition, tunable transition temperature

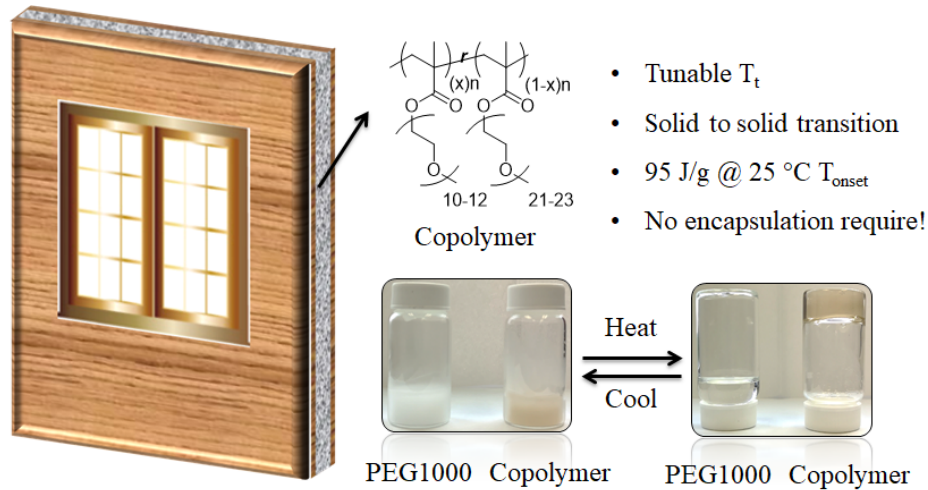


Figure 1. Random copolymerization based poly(ethylene glycol methacrylate) for tunable transition temperature polymeric PCM for thermal energy storage in building envelop applications.

1. Introduction

Thermal energy storage (TES) systems using phase change materials (PCMs) in which the thermal energy is stored or released during phase transition in the form of latent heat have been widely studied for decades [1–3]. The use of these TES systems have been investigated for many applications such as waste heat recovery [4], clothing and textiles [5,6], food packaging [7–9], and buildings [10–13]. The most commonly used PCMs for these applications, such as paraffin waxes and salt hydrates, involve a phase transition between solid and liquid. Although these PCMs have high energy storage densities (enthalpy change, ΔH , typically in the range of 150-250 J/g) [14], they require encapsulation techniques to prevent leakage of the liquid phase. Encapsulation reduces the overall energy density of the PCM systems and also has its own challenges. It requires the capsules to be compatible with PCM and be mechanically strong to withstand the increase in the internal pressure due to the volume expansion during phase change. Owing to these shortcomings there is an increased interest in exploring solid-to-solid phase transitions for TES, which could be encapsulation free.

Solid to solid phase transition also known as “solid state (SS) PCM” involves reversible phase transition between a solid crystalline (or semi-crystalline) phase and another solid crystalline (or semi-crystalline, or amorphous) phase. Many SS-PCM have been developed

including polyols [15,16], polymeric [17,18], organometallic [19,20], as well as inorganic [21] materials. The differences in thermal properties (phase transition temperature T_t and ΔH) of SS-PCMs depend of their material compositions, strength of the bonds and structures. For example, organic SS-PCMs have T_t between 25 and 190 °C with ΔH in range of 15 – 270 J/g. On the other hand, the T_t of inorganic (Fe based) SS-PCM is 680°C-1000°C with ΔH (30 – 60 J/g).

We are particularly interested in designing and developing SS-PCM for buildings as the buildings sector accounts for 41 percent (~40 quads) of United States energy consumption more than any other end-use sector. Space heating and cooling represent ~36 percent (14.5 quads) of the energy used in buildings. With more than 120 million buildings in the US, utilization of the large surface areas of the buildings to provide thermal energy storage (TES) is a large untapped potential. For example, a typical 186 m² (2000 ft²) residential building can store an estimated 44 Ton-hours (~150kWh_t) of thermal energy*. This is equivalent of 9 hours of storage assuming 5 ton of cooling. This can be achieved by inclusion of TES in the envelope (walls), which provides distributed energy storage as opposed to centralized bulk energy storage. Typically the thermal comfort for living in a house is in the range of 20 – 26 °C, hence it requires a PCM with T_t in that range. Yet, only a few of SS-PCM with the proper T_t have been reported and they mostly have low heat energy storage (< 60 J/g) [22].

Here in, we propose a new approach for designing SS-PCM with T_t in the range of 20-26°C and energy storage capacity of 100 J/g as shown in Figure 1. Inspired by the fact that addition of impurity will lower melting temperature of pure solid, we utilized copolymerization method to introduce the impurities in polymeric SS-PCM for tuning T_t . The advantage of copolymerization over regular blend method is that it prevents the phase separation during thermal cycling and enhances stability of the material. The copolymerization technique is simple and yet to best of our knowledge only limited work is done to explore this for TES. Some examples include random-copolymerization of poly(2-alkyloyloxyethylacrylate-co-methylacrylate) [23], and poly[(polyethylene glycol acrylate)-co-(methylmethacrylate)] [24] for

*An average 186 m² residential building has approximately 558 m² of interior surface area on the walls and ceiling, which do not actively participate in energy transfer within the building. Such large area in the building envelope provides a substantial room for thermal energy storage applications. For example, assuming an energy density of 100 kJ/kg and an energy storage material thickness of 1 cm, the envelope can store ~44 Ton-hours of thermal energy.

TES where they demonstrated effect of copolymerization of T_t . However in both these studies, energy density decreased significantly after copolymerization, which is understandable, as random-copolymers will have less crystalline structures compared to their homopolymer counterparts. To overcome this challenge of copolymerization we hypothesized that if the random copolymer is made from similar monomer functional groups, the overall change in crystallinity could be small and hence it should be feasible to lower the T_t without significantly impacting energy density. We hypothesized that the similar two monomer units on polymer backbone will co-crystallize to form crystal structure but not form amorphous/crystalline phase mixture like in normal mixing (or random copolymerization) system. Since the two units are slightly different, they would introduce defects in crystal structure resulting in low melting point of the copolymer.

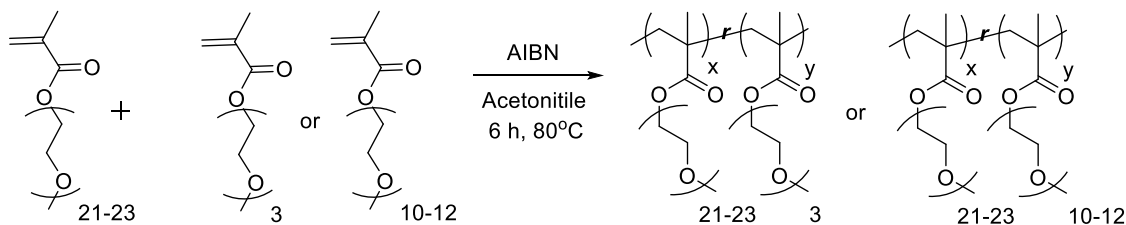
To test this hypothesis, polyethylene glycol (PEG) methyl ether methacrylate with two different molecular weight ($M_{n \text{ avg}}$ of 500 and 950 g/mol) and triethylene glycol methyl ether methacrylate were used to synthesize poly(polyethylene glycol methyl ether (950) methacrylate) (PPEGMA 950), poly[(polyethylene glycol methyl ether (950) methacrylate)-*random*-(polyethylene glycol methyl ether (500) methacrylate)] (COPOLYMER 950/500), and poly[(polyethylene glycol methyl ether (950) methacrylate)-*random*-triethylene glycol methyl ether methacrylate] (COPOLYMER 950/163). PEG based monomers were selected to study since PEG itself has been well studied for PCM due to their stability and relatively cheap materials. There were two copolymers with a fixed long PEG chain length (M_n of 950) mixed with medium PEG chain length (M_n of 500) or with short TEG (M_w of 163). The PEG 500 and TEG were introduced as impurity for tuning T_t of PEG 950 via copolymerization method. COPOLYMER 950/500 was expected to have higher crystallinity compared to COPOLYMER 950/163 according to the hypothesis. Also, the weight percentages of PEG 500 (0-40%) in COPOLYMER 950/500 were varied to show tunability of T_t values. The results including thermal properties of each polymer were discussed in this work. In addition, the effect of copolymerization on the melting point suppression was investigated by observing the change in crystal structure in different length scale levels from micron to nano size using optical microscope and x-ray techniques.

2. Experiments

All chemicals were purchased from commercial sources and used as received, unless otherwise mentioned. ^1H and ^{13}C NMR spectra were recorded by 500 MHz Bruker Avance II NMR spectrometer. Deuterated solvents peaks were used as internal standard peak. Molecular weight of polymer was characterized by gel permeation chromatography (GPC). TA-DSC2500 was used to collect differential scanning calorimetry (DSC) thermograms for all polymers. XRD patterns were recorded using Bruker-XRD D2 Phaser. Polarized optical images were taken by Nikon eclipse LV100 optical microscope. Small angle x-rays scattering (SAXS) was used to characterized the size of crystal.

2.1 Synthesis of poly(polyethylene glycol methyl ether (950) methacrylate) (PPEGMA 950)

1 g of polyethylene glycol methyl ether (950) methacrylate and 4 mg of azobisisobutyronitrile were dissolved in 2 mL of acetonitrile. The solution was degassed by purging with nitrogen for 15 min. The reaction was stirred at 75 °C for 6 h. The reaction was quenched by exposing to air. The crude polymer was dissolved in acetone and precipitated in hexane and the process was repeated 3 times. The polymer was further purification by dialysis (molecular weight cut off of 14,000 g/mol) in acetone. The polymer was obtained as white crystalline solid. ^1H NMR (CDCl_3): δ 4.39-3.88, 3.80-3.42, 3.41-3.25, 2.12-1.48, 1.22-0.44, GPC (THF) M_n 101,400 g/mol, D 2.34



Scheme 1. The synthesis of COPOLYMER 950/163 and COPOLYMER 950/500

2.2 Synthesis of poly[(polyethylene glycol methyl ether (950) methacrylate)-*random*-triethylene glycol methyl ether methacrylate] (10% COPOLYMER 950/163)

0.9 g of polyethylene glycol methyl ether (950) methacrylate, 0.1 g of triethylene glycol methyl ether methacrylate, and 4 mg of azobisisobutyronitrile were dissolved in 2 mL of acetonitrile. The polymerization and purification were done in the similar manner as reported in

the synthesis of PPEGMA 950 to give white crystalline solid. ^1H NMR (CDCl_3): δ 4.38-3.88, 3.81-3.42, 3.41-3.25, 2.12-1.48, 1.22-0.44, GPC (THF) M_n 101,800 g/mol, D 6.02

2.3 Synthesis of poly[(polyethylene glycol methyl ether (950) methacrylate)-*random*-polyethylene glycol methyl ether (500) methacrylate] (COPOLYMER 950/500)

COPOLYMER 950/500 was synthesized with different weight ratio of each monomer. The polymerization and purification were done in the same way as PPEGMA 950:

0.9 g of polyethylene glycol methyl ether (950) methacrylate, 0.1 g of polyethylene glycol methyl ether (500) methacrylate, and 4 mg of azobisisobutyronitrile (AIBN) in 2 mL of acetonitrile (ACN) for 10% COPOLYMER 950/500 as white crystalline solid. ^1H NMR (CDCl_3): δ 4.39-3.88, 3.81-3.42, 3.41-3.26, 2.12-1.48, 1.23-0.44, GPC (THF) M_n 101,800 g/mol, D 3.07. 13% weight of 500 PEG in the copolymer (by NMR)

0.8 g of polyethylene glycol methyl ether (950) methacrylate, 0.2 g of polyethylene glycol methyl ether (500) methacrylate, and 4 mg of azobisisobutyronitrile (AIBN) in 2 mL of acetonitrile (ACN) for 20% COPOLYMER 950/500 as white crystalline solid. ^1H NMR (CDCl_3): δ 4.39-3.88, 3.81-3.42, 3.41-3.25, 2.11-1.47, 1.22-0.45, GPC (THF) M_n 53,350 g/mol, D 6.02. 21% weight of 500 PEG in the copolymer (by NMR)

0.7 g of polyethylene glycol methyl ether (950) methacrylate, 0.3 g of polyethylene glycol methyl ether (500) methacrylate, and 4 mg of azobisisobutyronitrile (AIBN) in 2 mL of acetonitrile (ACN) for 30% COPOLYMER 950/500 as white crystalline solid. ^1H NMR (CDCl_3): δ 4.40-3.89, 3.80-3.42, 3.41-3.26, 2.12-1.48, 1.22-0.44, GPC (DMF) M_n 198,700 g/mol, D 7.21. 33% weight of 500 PEG in the copolymer (by NMR)

0.6 g of polyethylene glycol methyl ether (950) methacrylate, 0.4 g of polyethylene glycol methyl ether (500) methacrylate, and 4 mg of azobisisobutyronitrile (AIBN) in 2 mL of acetonitrile (ACN) for 40% COPOLYMER 950/500 as white crystalline solid. ^1H NMR (CDCl_3): δ 4.39-3.88, 3.80-3.42, 3.41-3.25, 2.13-1.48, 1.21-0.44, GPC (THF) M_n 475,900 g/mol, D 3.17. 45% weight of 500 PEG in the copolymer (by NMR)

2.4 Synthesis of crosslinked poly(polyethylene glycol methyl ether (950) methacrylate) and 30% COPOLYMER (XL-PPEGMA 950 and XL-30% COPOLYMER)

The polymerization and purification were done in the same way as PPEGMA 950 and 30% COPOLYMER with addition of pentaerythritol tetraacrylate as a crosslinker.

1 g of polyethylene glycol methyl ether (950) methacrylate, 4 mg of azobisisobutyronitrile (AIBN), and pentaerythritol tetraacrylate (1%, 2.5%, or 5% mole) in 2 mL of acetonitrile (ACN) for XL-PPEGMA 950 as white crystalline solid.

0.7 g of polyethylene glycol methyl ether (950) methacrylate, 0.3 g of polyethylene glycol methyl ether (500) methacrylate, 4 mg of azobisisobutyronitrile (AIBN), and pentaerythritol tetraacrylate (1%, 2.5%, or 5% mole) in 2 mL of acetonitrile (ACN) for XL-30% COPOLYMER 950/500 as white crystalline solid.

2.5 Small angle X-ray scattering

Transmission small angle X-ray scattering (SAXS) measurements were performed at room temperature at Advanced Light Source (beamline 7.3.3), Lawrence Berkeley National Laboratory (LBNL). The q range covered is between $6 \times 10^{-4} \text{ \AA}^{-1}$ and 0.3 \AA^{-1} ; here q is wave-vector and $q = 4\pi/\lambda \sin(\theta)$, λ is the wavelength and θ is half the scattering angle. The X-ray energy was 10 keV ($\lambda = 0.124 \text{ nm}$). Silver behenate (AgB) was used for calibration of sample-detector distance and beam center. SAXS essentially provides a fast Fourier transform (FFT) of electron density map of samples, depicting structural correlations in reciprocal space, on a 2-dimensional detector. Subsequent data reduction and analysis was performed using the Nika and Irena packages in Igor software respectively [25]. The 2D data is then accordingly reduced to a 1D plot representing Intensity (I) vs wave-vector (q) graph for sized-spacing analysis using Irena tool in Igor software [26]. In the Intensity versus q graph, the y-axis of intensity has been offset with 2 units for clarity purpose. The following equation is used to calculate d-spacing, where q_0 is peak position. All polymers were characterized in solid form.

$$d = \frac{2\pi}{q_0}$$

3. Results and discussion

3.1 Synthesis and thermal characterizations

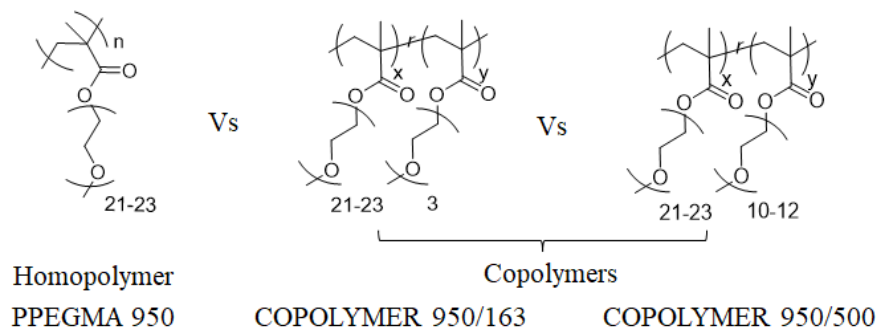


Figure 2. Homopolymer, PPEGMA 950, and copolymers, COPOLYMER 950/163 and COPOLYMER 950/500, structures for comparison studying between the homopolymer and random copolymer and the effect of polyethylene glycol chain length to melting temperature and heat energy storage.

A new approach for SS-PCM based on random copolymers of polyethylene glycol methyl ether methacrylate with different molecular weight was investigated. The polymer structures consisted of methacrylate-based backbone with polyethylene glycol methyl ether as side chains. This type of polymer was first introduced to thermal TES field in 2012 by S. Zhange and co-workers [27]. The design principle is to tie up PEG side chain onto the polymer backbone in order to increase rigidity of the materials. This resulted in solid-to-solid phase transition after copolymerization. The copolymers also remained stable after 100 cycles of heating and cooling.

Table 1. Melting temperature (T_{mp} peak and onset) and enthalpy of transition (ΔH_t) of PPEGMA 950, COPOLYMER 950/163, and COPOLYMER 950/500

Polymer	T_{mp} peak ($^{\circ}\text{C}$)	T_{mp} onset ($^{\circ}\text{C}$)	ΔH_t (J/g)
PPEGMA 950	39.9	35.6	118
COPOLYMER 950/163	34.2	30.0	99
COPOLYMER 950/500	35.2	31.3	108

Inspired by the results, we proposed to use copolymerization method based on the same design principle to tune transition temperature (T_t) of PCM. First, homopolymer PPEGMA 950 and copolymers, 10% COPOLYMER 950/163 and 10% COPOLYMER 950/500 (Figure 2) were synthesized to observe how the chain length of PEG side chain effect to T_t and enthalpy of transition (ΔH_t). The results were shown in Table 1. PPEGMA 950 showed T_{onset} at 35.6°C with ΔH_t of 118 J/g. Meanwhile, both 10% COPOLYMER 950/163 and 10% COPOLYMER 950/500 with approximately 10% weight of shorter PEG side chain as copolymer showed lowering of T_{onset} to 30.0°C and 31.3°C, respectively. As expected, the introduction of shorter PEG randomly into PPEGMA 950 can be used for lowering T_t of the polymers since they will lower the free energy of the resulting mixture by adding entropy to the non-crystalline phase and perhaps lowering the crystal lattice energy resulting in the depression of melting point. Interestingly, the change in ΔH_t of 10% COPOLYMER 950/500 (108 J/g) was less than that ΔH_t of 10% COPOLYMER 950/163 (99 J/g). The difference could be explained by looking at copolymer structure. Both copolymers were PEG based polymer with different molecular weight side chain. Since COPOLYMER 950/500 has smaller difference in PEG molecular weight in the copolymer than that of COPOLYMER 950/163, the structures similarity of COPOLYMER 950/500 was closer than COPOLYMER 950/163 when they were compared with the homopolymer. Due to the close in molecular structure of the copolymer, COPOLYMER 950/500 has potential to form high crystallinity solid resulting in a little change in ΔH_t .

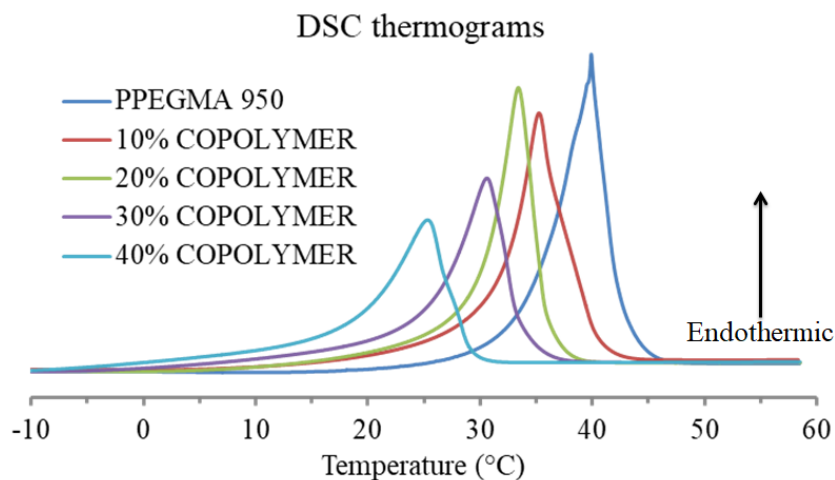


Figure 3. Differential scanning calorimetry (DSC) thermograms of COPOLYMER 950/500 with different percent weight ratio showing the melting point temperature tunability.

Table 2. Melting temperature (T_{mp} peak and onset), crystallization temperature (T_c onset) and enthalpy of transition (ΔH_t)

Polymer	T_{mp} peak (°C)	T_{mp} onset (°C)	ΔH_t (J/g)
PPEGMA 950	39.9	35.6	118
10% COPOLYMER	35.2	31.3	108
20% COPOLYMER	33.5	30.7	101
30% COPOLYMER	30.6	24.9	95
40% COPOLYMER	25.3	18.3	75

The random copolymerization method was successful to lower T_t of polymeric PCM and also the copolymer structure can affect to ΔH_t value. COPOLYMER 950/500 was further studied for possibility of T_t tunability with reasonable ΔH_t . The random copolymers with different in percent weight of PEG with molecular weight of 500 were synthesized. There were four different copolymers with 10%w, 20%w, 30%w, and 40%w. DSC thermograms were shown in Figure 3 and their thermal properties were summarized in Table 2. As expected, T_{onset} was decreased when the percentage of PEG 500 increase which were 31.3°C, 30.7°C, 24.9°C, and 18.3°C for 10%, 20%, 30% and 40% copolymer, respectively. This result confirmed that the random

copolymerization can be used to tune T_t of polymeric PCM. However, ΔH_t was also decreased when the amount of PEG 500 increase. This was not surprised since when there is more PEG 500 in the copolymer, the solid phase will become more disordered.

Table 3. Thermal properties of 30% COPOLYMER under thermal cycling

Thermal cycling number	T_{mp} peak (°C)	T_{mp} onset (°C)	ΔH_t (J/g)
0	30.6	24.9	95
50	30.6	25.1	94
100	30.6	25.1	94
150	30.5	25.2	92
200	30.5	25.2	92

30% COPOLYMER showed promising thermal properties as PCM for building envelop application with T_{onset} of 24.9°C and reasonable ΔH_t of 95 J/g. We further investigated its thermal stability. The polymer underwent 200 heating and cooling cycles with rate of 10°C/min. The thermal properties at 0, 50, 100, and 200 cycles were shown in Table 3. There was no significant change in T_t and ΔH_t showing high thermal stability of this material. It is known that T_t is a function of heating and cooling rate especially for crystallization temperature (T_c). The DSC thermogram of 30% COPOLYMER at cooling rate at 0.1°C/min and 10°C/min was shown in figure S1 showing the effect of cooling rate to T_c . Note that in daily, the heating and cooling rate is much slower when compared to 0.1°C/min (0.03°C/min for 2°C change in 1 hour). In order to demonstrate the effect of the heating and cooling rate at 0.03°C/min, isotherm (step scan) experiment was performed and the results were summarized in Figure S2.

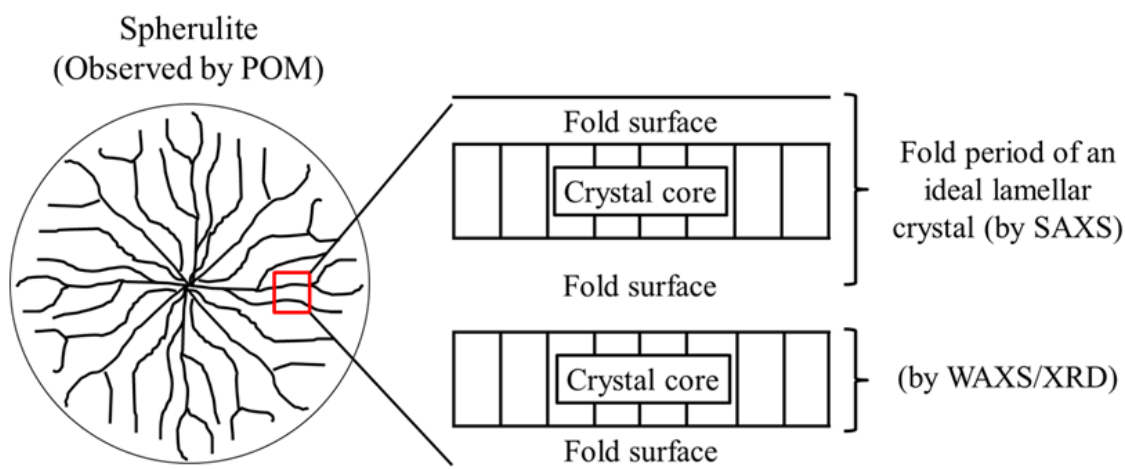


Figure 4. Illustration of spherulite and an ideal lamellar crystal structure consisting of two fold surfaces and a crystal core. To understand the impact of copolymerization on melting point suppression, the crystal structures were investigated. The sizes of spherulite were observed under polarized optical microscope (POM) and the thickness of lamellar and crystal core can be obtained from small angle x-ray scattering (SAXS) and x-ray diffraction (XRD) respectively.

3.2 Structural Characterizations

Structural characterization of the homopolymer and the copolymers were carried out using various techniques to understand the impact of copolymerization on different length scales (Figure 4). XRD was used to understand the crystal structure where length scale is in range of 0.1 – 2 nm, polarized optical microscopy (POM) was used to explore the size of spherulite (>10 μm), and SAXS was employed to probe lamellar thickness (length scale of 0.5 – 100 nm).

3.2.1 XRD analysis

XRD patterns of PPEGMA 950 and 20% COPOLYMER are shown in Figure 5. Both show similar diffraction pattern, displaying two sharp peaks at 19.1° and 23.3° , indicating that crystal structure did not change after copolymerization. In fact these XRD patterns are similar to that previously reported for PEG,[24] which implies that the crystalline nature of PEG was conserved after the synthesis and was not affected if PEG chains were free or tied up onto another polymer chain or randomly polymerized with other shorter PEG chain. However, the reduction in the intensity and broadening of the peak can be seen for 20% COPOLYMER

(Figure 5) suggesting overall decrease in the crystalline regions in 20% COPOLYMER when compared with that of PPEGMA 950.

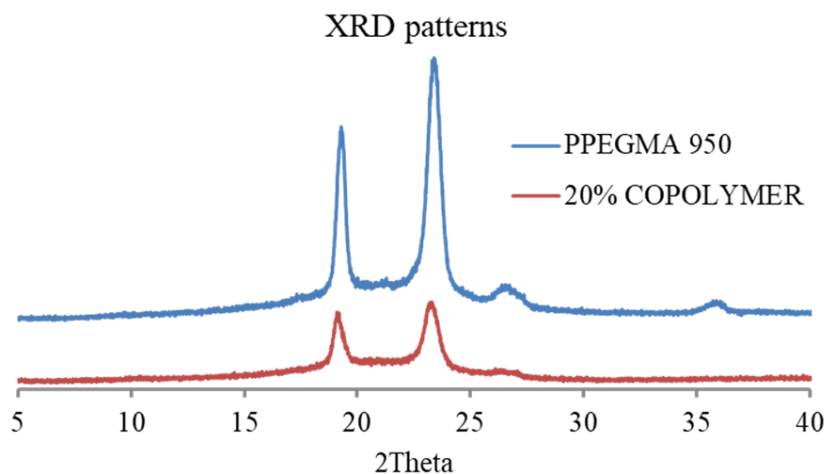


Figure 5. XRD patterns of PPEGMA 950 and 20% COPOLYMER confirming no change in crystal core structure.

3.2.2 Polarized Optical Microscopy

After analyzing the crystal structure using XRD, POM was used to investigate the size of crystalline domains in all the samples. POM can be used to observe an optically anisotropic specimen, which in this case is the crystalline domain in polymer. The POM images are shown in Figure 6. Distinct cross patterns were observed in all the samples indicating the presence of crystal spherulites. As expected, the size of spherulites became smaller when the weight fractions of the copolymer became larger. This was because the polymer structure became more disordered with increasing weight fraction of the random copolymer, thereby hindering crystallization process. This is in agreement with XRD data, which shows smaller degree of crystallization for the copolymer (Figure 5).

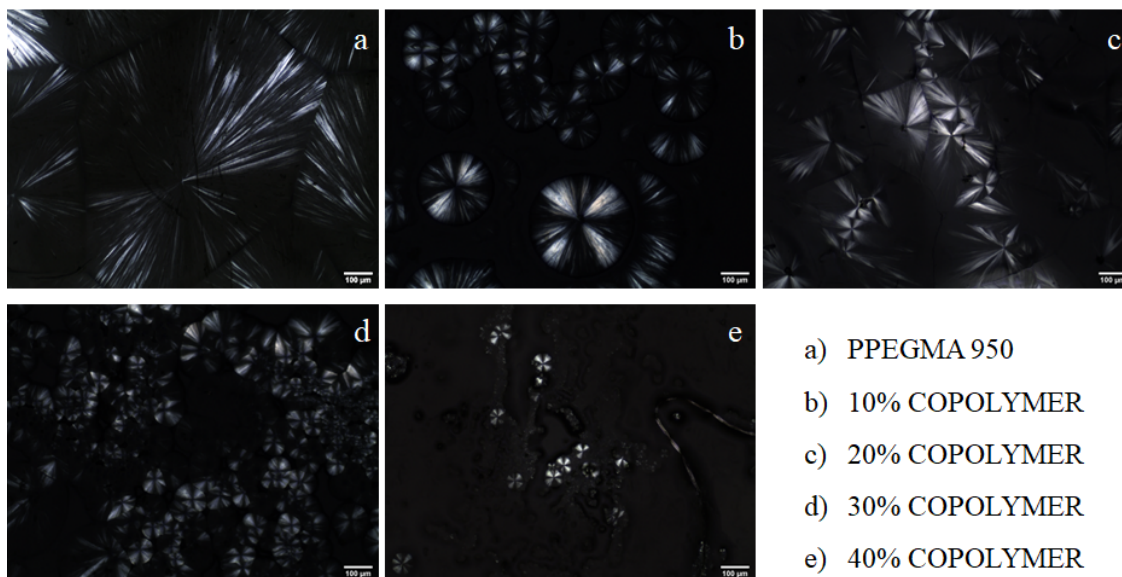


Figure 6. POM images for a) PPEGMA950, b) 10% COPOLYMER, c) 20% COPOLYMER, d) 30% COPOLYMER, and e) 40% COPOLYMER showing the decrease in both size and number of spherulite when the weight fraction of the copolymer increase.

3.2.3 SAXS Measurements

We used SAXS to gain insight into the physical nature of the melting point depression. 1D plot scattering profiles of PPEGMA 950 and all copolymers were shown in Figure 7 (left). The presence of peaks indicates a crystalline structure and we further notice that the peak position (q_0) (peak positions are marked with an asterisk symbol, “*”) shifted to lower q -values as the ratio of co-polymer increased. The decrease in q value corresponded to an increase in d -spacing ($d=2\pi/q_0$) with increasing copolymerization, which is summarized in Figure 7 (right, COPOLYMER was labeled as COP). Please note the d -spacing from SAXS [28] is usually referred as fold period of lamella thickness which consists of a crystal core and two fold amorphous surfaces (Figure 4) and is different from the d -spacing obtained from XRD pattern.

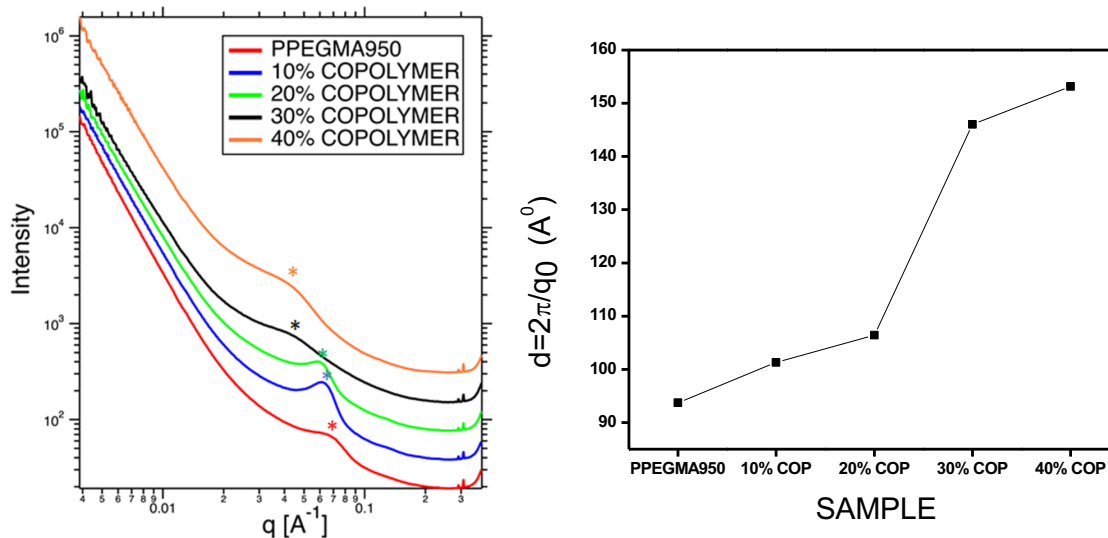


Figure 7. 1D scattering profile with asterisk marks indicating the maximum peak (q_0) (left) and d value graph (right) of PPEGMA and 10-40% COPOLYMER.

It has been shown that increasing d -spacing in SAXS is correlated with increasing melting point depression and decreasing crystallinity (ΔH_{melt}) [29], which is in agreement with our results. However, a previous study has shown an opposite effect in polyethylene, where the melting point increased with the increase in the lamella thickness (d -spacing) [30]. In this system, the increase in melting point was mainly due to the increase in the crystal core size in polyethylene, which resulted in thicker lamella. In our case, the crystal core sizes of our copolymer systems were almost constant according to XRD results. Thus, we believe that the increase in lamellar thickness was mainly corresponded to the increase in the size of the fold surfaces, which resulted in the reduction of crystallite density. We note that increase in d -spacing decreases crystallite density, lowering the crystallites characteristic phonon temperatures [31]. This is associated with an increase in free energy at a given temperature, thereby decreasing the crystallites melting temperature. Others have used Flory's theory of crystallization in copolymers to explain and quantify this trend [32], but the functional relationship does not fit our results, indicating that the melting point depression should not be attributed to steric factors.

3.3 Solidified PCM by crosslinking method

To further improve form stability of PCM, the crosslinking method was investigated. It is known that the rigidity of crosslinked polymer will be increased depending on crosslinking

degree which can improve the form stability of the materials. However, crystalline domains are also affected since high rigid structure will prevent crystallization growing process. Therefore, degrees of crosslink need to be optimized to improve the stability with less impact on crystallization domain. The thermal properties of XL-PPEGMA 950 and XL-30% COPOLYMER were summarized in Table 4.

Table 4. Thermal properties of XL-PPEGMA 950 and XL-30% COPOLYMER and their phase transition state

XL polymer	% mole of crosslinker	T _{mp} peak (°C)	T _{mp} onset (°C)	ΔH _t (J/g)	Phase transition
PPEGMA 950	0	39.9	35.6	118	solid to gel
	1	38.8	33.6	108	solid to gel
	2.5	42.5	33.0	108	solid to solid
	5	37.2	34.7	101	solid to solid
30% COPOLYMER	0	30.6	24.9	95	solid to gel
	1	33.6	29.8	87	solid to gel
	2.5	32.3	27.8	96	solid to gel
	5	28.0	24.1	79	solid to solid

As expected, the degree of crosslinking clearly affected to ΔH_t of both XL-PPEGMA 950 and XL-30% COPOLYMER. With 5% mole of crosslinker, the ΔH_t values were decreased by 14% and 17% for XL-PPEGMA 950 and XL-30% COPOLYMER, respectively. The phase transition of XL-PPEGMA 950 was found to be solid to solid transition if the crosslinker was 2.5% or higher. On the other hand, it was required up to 5% of crosslinker to improve the phase transition of XL-30% COPOLYMER to solid-solid transition. The requirement of higher crosslinking degree of XL-30% COPOLYMER to improve form stability could be due to the fact that the polymer structure was more disorder compared to the homopolymer leading to the loose packing and less rigidity.

4. Conclusions

We demonstrated that T_t can be precisely tuned by varying the copolymer content using copolymerization technique. The structure of the copolymer needed to be considered since it will directly affect to the overall ΔH_t of the materials. The phase transition was successfully improved from solid-liquid (PEGDME 1000) to solid-solid transition (PPEGMA 950) which implied that

there is no need of encapsulation methods while using these polymeric PCMs in building envelopes. In addition, the form stability of polymeric PCM can be further improved by optimizing crosslinking approach. By carrying out structural characterization at multiple length scales using XRD, SAXS and POM, we showed the effect of copolymerization on spherulite density and lamella thickness. We hope this work would give a complete understanding of a new design principle for polymeric SS-PCM possessing both high heat capacity and tunable transition temperature (T_t) as encapsulation-free thermal storage energy materials for sustainable energy usage of heat ventilation air conditioning (HVAC) systems in buildings. We also have an ongoing project to integrate these materials into prototype devices and test the entire device performance in a large calorimeter which will help demonstrate their practical thermal performances.

Acknowledgement

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Building Technologies Program, of the U.S. Department of Energy under Contract No. DEAC02-05CH11231. We thank to the Molecular Foundry for chemical structure analysis which was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We acknowledge use of Beamline 7.3.3 of the Advanced Light Source supported by the Director of the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

References

- [1] A. Sharma, V. V Tyagi, C.R. Chen, D. Buddhi, Review on thermal energy storage with phase change materials and applications, *Renew. Sustain. Energy Rev.* 13 (2009) 318–345. <https://doi.org/10.1016/j.rser.2007.10.005>.
- [2] B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, *Appl. Therm. Eng.* 23 (2003) 251–283. [https://doi.org/10.1016/S1359-4311\(02\)00192-8](https://doi.org/10.1016/S1359-4311(02)00192-8).
- [3] M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change

- energy storage: materials and applications, *Energy Convers. Manag.* 45 (2004) 1597–1615. <https://doi.org/https://doi.org/10.1016/j.enconman.2003.09.015>.
- [4] L. Miró, J. Gasia, L.F. Cabeza, Thermal energy storage (TES) for industrial waste heat (IWH) recovery: A review, *Appl. Energy.* 179 (2016) 284–301. <https://doi.org/https://doi.org/10.1016/j.apenergy.2016.06.147>.
- [5] Y. Guo, K. Li, C. Hou, Y. Li, Q. Zhang, H. Wang, Fluoroalkylsilane-Modified Textile-Based Personal Energy Management Device for Multifunctional Wearable Applications, *ACS Appl. Mater. Interfaces.* 8 (2016) 4676–4683. <https://doi.org/10.1021/acsami.5b11622>.
- [6] W. Zhang, R. Guo, J. Sun, L. Dang, Z. Liu, Z. Lei, Q. Sun, Textile carbon network with enhanced areal capacitance prepared by chemical activation of cotton cloth, *J. Colloid Interface Sci.* 553 (2019) 705–712. <https://doi.org/https://doi.org/10.1016/j.jcis.2019.06.048>.
- [7] W. Chalco-Sandoval, M.J. Fabra, A. López-Rubio, J.M. Lagaron, Use of phase change materials to develop electrospun coatings of interest in food packaging applications, *J. Food Eng.* 192 (2017) 122–128. <https://doi.org/https://doi.org/10.1016/j.jfoodeng.2015.01.019>.
- [8] L. Melone, L. Altomare, A. Cigada, L. De Nardo, Phase change material cellulosic composites for the cold storage of perishable products: From material preparation to computational evaluation, *Appl. Energy.* 89 (2012) 339–346. <https://doi.org/https://doi.org/10.1016/j.apenergy.2011.07.039>.
- [9] J.H. Johnston, J.E. Grindrod, M. Dodds, K. Schimitschek, Composite nano-structured calcium silicate phase change materials for thermal buffering in food packaging, *Curr. Appl. Phys.* 8 (2008) 508–511. <https://doi.org/https://doi.org/10.1016/j.cap.2007.10.059>.
- [10] N. Soares, J.J. Costa, A.R. Gaspar, P. Santos, Review of passive PCM latent heat thermal energy storage systems towards buildings' energy efficiency, *Energy Build.* 59 (2013) 82–103. <https://doi.org/https://doi.org/10.1016/j.enbuild.2012.12.042>.

- [11] A. Waqas, Z. Ud Din, Phase change material (PCM) storage for free cooling of buildings—A review, *Renew. Sustain. Energy Rev.* 18 (2013) 607–625. <https://doi.org/https://doi.org/10.1016/j.rser.2012.10.034>.
- [12] F. Kuznik, D. David, K. Johannes, J.-J. Roux, A review on phase change materials integrated in building walls, *Renew. Sustain. Energy Rev.* 15 (2011) 379–391. <https://doi.org/https://doi.org/10.1016/j.rser.2010.08.019>.
- [13] R. Baetens, B.P. Jelle, A. Gustavsen, Phase change materials for building applications: A state-of-the-art review, *Energy Build.* 42 (2010) 1361–1368. <https://doi.org/https://doi.org/10.1016/j.enbuild.2010.03.026>.
- [14] S. HIMRAN, A. SUWONO, G.A.L.I. MANSOORI, Characterization of Alkanes and Paraffin Waxes for Application as Phase Change Energy Storage Medium, *Energy Sources.* 16 (1994) 117–128. <https://doi.org/10.1080/00908319408909065>.
- [15] L. Weinstock, R.A. Sanguramath, M.S. Silverstein, Encapsulating an organic phase change material within emulsion-templated poly(urethane urea)s, *Polym. Chem.* 10 (2019) 1498–1507. <https://doi.org/10.1039/C8PY01733F>.
- [16] S.N. Gunasekara, R. Pan, J.N. Chiu, V. Martin, Polyols as phase change materials for surplus thermal energy storage, *Appl. Energy.* 162 (2016) 1439–1452. <https://doi.org/https://doi.org/10.1016/j.apenergy.2015.03.064>.
- [17] A. Sari, C. Alkan, A. Biçer, Synthesis and thermal properties of polystyrene-graft-PEG copolymers as new kinds of solid–solid phase change materials for thermal energy storage, *Mater. Chem. Phys.* 133 (2012) 87–94. <https://doi.org/https://doi.org/10.1016/j.matchemphys.2011.12.056>.
- [18] X. Du, H. Wang, X. Cheng, Z. Du, Synthesis and thermal energy storage properties of a solid–solid phase change material with a novel comb-polyurethane block copolymer structure, *RSC Adv.* 6 (2016) 42643–42648. <https://doi.org/10.1039/C6RA02559E>.
- [19] D.-H. He, Y.-Y. Di, Z.-C. Tan, F.-F. Yi, W.-Y. Dan, Y.-P. Liu, Crystal structures and thermochemistry on phase change materials $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4(\text{s})$ ($n=14$ and 15),

- Sol. Energy Mater. Sol. Cells. 95 (2011) 2897–2906.
<https://doi.org/https://doi.org/10.1016/j.solmat.2011.06.014>.
- [20] W. Li, D. Zhang, T. Zhang, T. Wang, D. Ruan, D. Xing, H. Li, Study of solid–solid phase change of $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$ for thermal energy storage, *Thermochim. Acta.* 326 (1999) 183–186. [https://doi.org/https://doi.org/10.1016/S0040-6031\(98\)00497-3](https://doi.org/https://doi.org/10.1016/S0040-6031(98)00497-3).
- [21] K. Nishioka, N. Suura, K. Ohno, T. Maeda, M. Shimizu, Development of Fe Base Phase Change Materials for High Temperature Using Solid-Solid Transformation, *ISIJ Int.* 50 (2010) 1240–1244. <https://doi.org/10.2355/isijinternational.50.1240>.
- [22] A. Fallahi, G. Guldentops, M. Tao, S. Granados-Focil, S. Van Dessel, Review on solid–solid phase change materials for thermal energy storage: Molecular structure and thermal properties, *Appl. Therm. Eng.* 127 (2017) 1427–1441.
<https://doi.org/https://doi.org/10.1016/j.applthermaleng.2017.08.161>.
- [23] C. Alkan, Ö.F. Ensari, D. Kahraman, Poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-co-methylacrylate) comblike polymers as novel phase-change materials for thermal energy storage, *J. Appl. Polym. Sci.* 126 (2012) 631–640.
<https://doi.org/10.1002/app.36646>.
- [24] S. Sundararajan, A.B. Samui, P.S. Kulkarni, Synthesis and characterization of poly(ethylene glycol) acrylate (PEGA) copolymers for application as polymeric phase change materials (PCMs), *React. Funct. Polym.* 130 (2018) 43–50.
<https://doi.org/https://doi.org/10.1016/j.reactfunctpolym.2018.05.012>.
- [25] J. Ilavsky, Nika: software for two-dimensional data reduction, *J. Appl. Crystallogr.* 45 (2012) 324–328. <https://doi.org/10.1107/S0021889812004037>.
- [26] J. Ilavsky, P.R. Jemian, Irena: tool suite for modeling and analysis of small-angle scattering, *J. Appl. Crystallogr.* 42 (2009) 347–353.
<https://doi.org/10.1107/S0021889809002222>.
- [27] B. Tang, Z. Yang, S. Zhang, Poly(polyethylene glycol methyl ether methacrylate) as novel solid-solid phase change material for thermal energy storage, *J. Appl. Polym. Sci.* 125

- (2012) 1377–1381. <https://doi.org/10.1002/app.35287>.
- [28] J.-I. Wang, I.R. Harrison, 6.2 Crystallite Size and Lamellar Thickness by X-Ray Methods, in: R.A.B.T.-M. in E.P. Fava (Ed.), *Polymers (Basel)*, Academic Press, 1980: pp. 128–184. [https://doi.org/https://doi.org/10.1016/S0076-695X\(08\)60757-7](https://doi.org/https://doi.org/10.1016/S0076-695X(08)60757-7).
- [29] L. Mandelkern, A.S. Posner, A.F. Diorio, D.E. Roberts, Low-Angle X-Ray Diffraction of Crystalline Nonoriented Polyethylene and Its Relation to Crystallization Mechanisms, *J. Appl. Phys.* 32 (1961) 1509–1517. <https://doi.org/10.1063/1.1728386>.
- [30] J.J. Weeks, Melting Temperature and Change of Lamellar Thickness with Time for Bulk Polyethylene, *J. Res. Natl. Bur. Stand. Sect. A, Phys. Chem.* 67A (1963) 441–451. <https://doi.org/10.6028/jres.067A.046>.
- [31] M. Pyda, M. Bartkowiak, B. Wunderlich, Computation of Heat Capacities of Solids Using a General Tarasov Equation, *J. Therm. Anal. Calorim.* 52 (1998) 631–656. <https://doi.org/10.1023/A:1010188110516>.
- [32] S. Matsuoka, The effect of pressure and temperature on the specific volume of polyethylene, *J. Polym. Sci.* 57 (1962) 569–588. <https://doi.org/10.1002/pol.1962.1205716545>.