

# Poly(2-alkyloxyethylacrylate) and Poly(2-alkyloxyethylacrylate-co-methylacrylate) Comblike Polymers as Novel Phase-Change Materials for Thermal Energy Storage

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**ABSTRACT:** A series of poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-co-methylacrylate) polymers as novel polymeric phase-change materials (PCMs) were synthesized starting from 2-hydroxyethylacrylate and fatty acids. The chemical structure and crystalline morphology of the synthesized copolymers were characterized with Fourier transform infrared and <sup>1</sup>H-NMR spectroscopy and polarized optical microscopy, respectively, and their thermal energy storage properties and thermal stability were investigated with differential scanning calorimetry and thermogravimetric analysis, respectively. The thermal conductivities of the PCMs were also measured with a thermal property

analyzer. Moreover, thermal cycling testing showed that the copolymers had good thermal reliability and chemical stability after they were subjected to 1000 heating/cooling cycles. The synthesized poly(2-alkyloxyethylacrylate) polymers and poly(2-alkyloxyethylacrylate-co-methylacrylate) copolymers as novel PCMs have considerable potential for thermal energy storage and temperature-control applications. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** addition polymerization; copolymers; differential scanning calorimetry (DSC); FT-IR; polymer synthesis and characterization

## INTRODUCTION

Latent heat thermal energy storage (LHTES) is a popular method for thermal energy storage because it provides high-energy storage density and small temperature variation from storage to retrieval.<sup>1,2</sup> In this method, thermal energy is stored by a phase-change material (PCM) during the phase-change process, and the stored energy is released when it turns back. Recently, a great variety of inorganic and organic compounds and mixtures as PCMs for LHTES systems have been investigated.<sup>3,4</sup> Interest in developing polymer-based PCMs as novel LHTES materials has been growing in recent years.<sup>5–10</sup> The shape of the material is stabilized in polymer-based PCMs because solid–liquid PCMs are encapsulated or bound in polymer matrices. Therefore, polymer-based materials are called *form-stable PCMs*. Form-

stable PCMs have many advantages. For example, melted PCMs do not ooze during heating, and the thermal resistance caused by the capsule shell is eliminated. In addition, polymer-based PCMs do not need additional containers, and therefore, they are cost effective. Also, they can easily be prepared in one's required dimensions.

Polymeric solid-solid phase change materials (SSPCMs), such as cellulose-*graft*-poly(ethylene oxide),<sup>11</sup> crosslinked poly(ethylene glycol) (PEG)/methylene diisocyanate (MDI)/Pentaerytritol polymer,<sup>12</sup> polyurethane-*graft*-PEG,<sup>13,14</sup> cellulose diacetate-*graft*-PEG,<sup>15–17</sup> chlorinated polypropylene-*graft*-PEG,<sup>18</sup> cellulose-*graft*-PEG,<sup>19–21</sup> and poly(vinyl alcohol)-*graft*-PEG,<sup>22</sup> have been prepared and investigated in terms of their thermal energy storage characteristics.

Acrylic and methacrylic vinyl esters can be readily polymerized by free-radical polymerization to form linear, branched, or network copolymers.<sup>23</sup> The copolymers of acrylic/methacrylic esters have been used for various industrial applications.<sup>24</sup> Phenyl acrylate polymers are relatively newly developed materials compared to commercial polymers, such as vinylics, acrylamides, and alkylacrylates.

Recently, the acrylate family of polymers has been used successfully as membranes for potentiometric ion sensors<sup>25–27</sup> without the use of a plasticizer. Since then, the application of this class of plasticizer-

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free polymers has been extended to optical ion sensors, particularly membranes based on crosslinked dodecyl acrylate<sup>28</sup> and decyl methacrylate.<sup>29</sup> Also, different types of hydrogels made up of acrylic copolymers have been studied.<sup>30</sup>

In this study, poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers with three different monomer feed ratios were synthesized as novel polymeric SSPCMs, and they were characterized with Fourier transform infrared (FTIR) spectroscopy, <sup>1</sup>H-NMR spectroscopy, and polarized optical microscopy (POM). The thermal properties and thermal stability of the polymeric SSPCMs were determined with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermal reliabilities of the polymeric SSPCMs were determined after 5000 heating/cooling cycles. In addition, the thermal conductivities of the PCMs were measured by a thermal property analyzer.

## EXPERIMENTAL

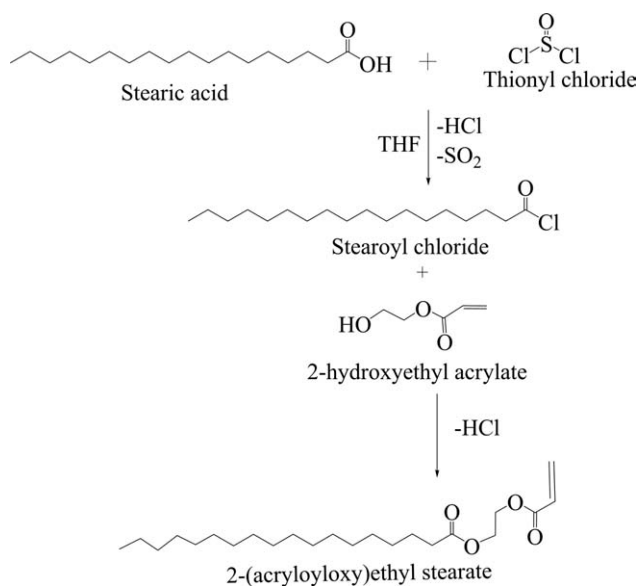
### Materials

Myristic, palmitic, and stearic acids (MA, PA, and SA respectively) were analytical grade and were obtained from Merck Co. They were also purified to remove trace water. 2-Hydroxyethylacrylate (HEA) from Acros Co. was used after the purification of the inhibitor. Commercial HEA contains impurities, such as ethylene glycol, acrylic acid, and ethylene glycol diacrylate. The presence of diacrylate leads to crosslinking, and that of acrylic acid may inhibit the polymerization. Therefore, the polymerizations of unpurified or poorly purified monomer may be incomplete and slow or may lead to insoluble solids. HEA was dissolved in water (25 vol %), and the solution was extracted 10 times with hexane to remove diacrylates. The aqueous solution was then salted with 200 g of NaCl/L, and the monomer was separated from the aqueous phase by ether extraction (four times) to remove acrylic acid. Finally, a drying agent, MgSO<sub>4</sub> at 3 wt %, was used to remove traces of water before the evaporation of the ether phase in a rotary evaporator. The purified monomer was distilled *in vacuo* immediately before use in the polymerizations.<sup>31</sup>

Acyl chlorides of MA, PA, and SA were prepared by a reported procedure<sup>32</sup> and reacted with purified HEA to produce 2-alkyloxyethylacrylate monomers.

### Synthesis of the monomers and homopolymerization and copolymerization of the monomers in solution

The 2-alkyloxyethylacrylate monomers were synthesized from HEA and the MA, PA, and SA and



**Figure 1** Synthesis of SEA from SA and HEA (THF = tetrahydrofuran).

were named 2-myristoyloxyethylacrylate (MEA), 2-palmitoyloxyethylacrylate (PEA), and 2-stearoyloxyethylacrylate (SEA), respectively. The poly(2-alkyloxyethylacrylate) homopolymers produced from these monomers were poly(2-myristoyloxyethylacrylate) [poly(MEA)], poly(2-palmitoyloxyethylacrylate) [poly(PEA)], and poly(2-stearoyloxyethylacrylate) [poly(SEA)]; as copolymers, these were called poly(2-myristoyloxyethylacrylate-*co*-methylacrylate) [poly(MEA-*co*-MA)], poly(2-palmitoyloxyethylacrylate-*co*-methylacrylate) [poly(PEA-*co*-MA)], and poly(2-stearoyloxyethylacrylate-*co*-methylacrylate) [poly(SEA-*co*-MA)]. The synthetic routes for the monomers are shown in Figure 1.

Poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers with 1/3, 1/1, and 3/1 monomer feed ratios were synthesized in toluene solution with 2,2'-azobisisobutyronitrile as a free-radical initiator. Methylacrylate monomer was double-distilled before use to remove monomethyl ether hydroquinone as an inhibitor. Appropriate quantities of the monomer (and comonomer in the copolymers), toluene, and 2,2'-azobisisobutyronitrile were placed in a three-necked balloon, and the polymerization was performed under a nitrogen atmosphere at 70°C. The copolymer was precipitated by pouring the reaction mixture into excess methanol. It was filtered and dried *in vacuo* at 40°C.

### Characterization

The synthesized monomers, homopolymers, and copolymers were characterized structurally with a Jasco 430 model FTIR (Tokyo, Japan) spectrophotometer and a Bruker AVANCE III 400-MHz <sup>1</sup>H-NMR

instrument. FTIR measurements were performed on KBr disks, and  $^1\text{H-NMR}$  spectra were recorded with trimethylsilane as an internal reference. The morphology of the polymers was investigated with a polarized optical microscope (Leica model, Wetzlar, Germany). The microscopy investigation of the samples were conducted with  $100\times$  magnification.

The thermal properties, such as the melting and crystallization points and latent heats, of poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers with three different molar ratios were measured with the DSC technique (PerkinElmer Jade DSC instrument, Shelton, USA). The analyses were carried out at  $5^\circ\text{C}/\text{min}$  heating rate under a constant stream of nitrogen at a flow rate of  $20\text{ mL}/\text{min}$ . The reproducibility was tested with three measurements, and the mean deviation was  $\pm 0.04^\circ\text{C}$  in phase-change temperature and  $\pm 1.40\text{ J}/\text{g}$  in latent heat capacity.

To determine the thermal reliability of the form-stable PCMs, an accelerated thermal cycling test was conducted with an experimental procedure reported in the literature.<sup>32</sup> The samples were subjected to a melting/freezing process. In the thermal cycling, the samples were heated from  $20$  to  $100^\circ\text{C}$  and were cooled back to  $20^\circ\text{C}$  1000 times with a BIOER-TC-25/H thermal cycling instrument.

The thermal stability of the PCMs was investigated with FTIR spectroscopy and DSC measurements after thermal cycling. The thermal properties of the PCMs were measured with the DSC instrument.

TGA was carried out on a PerkinElmer TGA7 thermal analyzer (Shelton, USA), which was calibrated with calcium oxalate from  $25$  to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in a static air atmosphere.

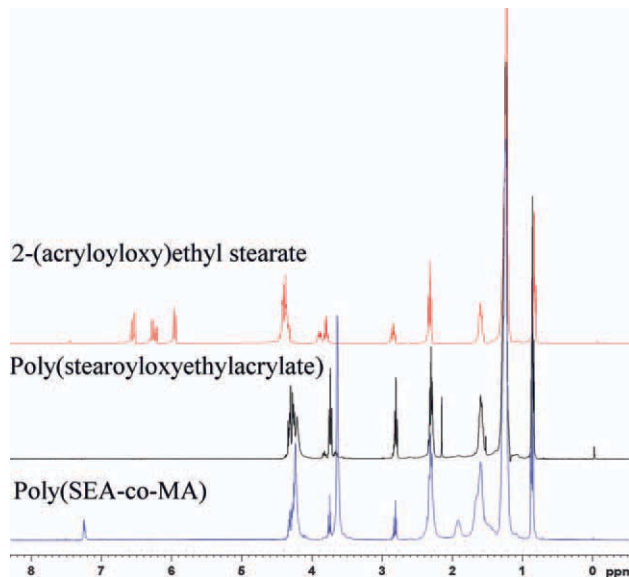
The thermal conductivities of the copolymers were measured at room temperature with a KD2 thermal property analyzer.

## RESULTS AND DISCUSSION

The poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers at three different molar ratios were soft and elastic materials; this indicated an amorphous morphology. This preliminary characteristic of the polymers could be valuable in combination with the data produced with sophisticated instruments.

### $^1\text{H-NMR}$ analysis

Figure 2 shows  $^1\text{H-NMR}$  spectra for SEA, poly(SEA), and poly(SEA-*co*-MA) as a sample of  $^1\text{H-NMR}$  characterization of the acrylic polymers and copolymers produced in this study. The main important point in the  $^1\text{H-NMR}$  spectra was the disappearing signals of the vinyl protons of 2-alkyloxyethylacrylate around



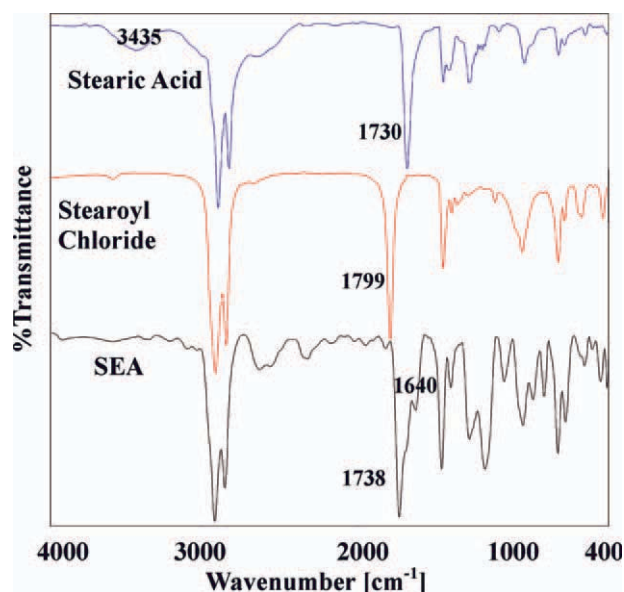
**Figure 2**  $^1\text{H-NMR}$  spectra of SEA, poly(SEA), and poly(SEA-*co*-MA) (1/1) copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$6\text{ ppm}$ . The difference in the spectra of the copolymers from the homopolymers was the  $\text{CH}_3$  protons at  $3.60\text{ ppm}$  and  $\text{CH}_2$  peak intensity at  $1.25\text{ ppm}$ .

### FTIR analysis

FTIR spectroscopy was used to prove the reaction and to examine the thermal stability of the homopolymers and the copolymers after accelerated thermal cycling. Figure 3 shows the FTIR spectra for SA, stearoyl chloride, and SEA, and Figures 4 and 5 show the FTIR spectra of poly(SEA) and poly(SEA-*co*-MA) (1/1), respectively, before and after thermal cycling. According to Figure 3, the main difference in the SA spectrum with stearoyl chloride was the carbonyl stretching peak, which drastically shifted from  $1730$  to  $1799\text{ cm}^{-1}$ . The carbonyl peak was observed at  $1738\text{ cm}^{-1}$  in the spectrum of SEA. Also, the broad peak caused by H bonding in SA disappeared in stearoyl chloride; this showed the purity of stearoyl chloride. The carbonyl peaks kept up with their position in poly(SEA) and poly(SEA-*co*-MA) because the carbonyl peaks of the polymers were all ester carbonyls. The disappearance of the band at  $3435\text{ cm}^{-1}$  indicated the formation of the polymers. The FTIR results were similar to the results Patel<sup>33</sup> obtained from another acrylic copolymer.

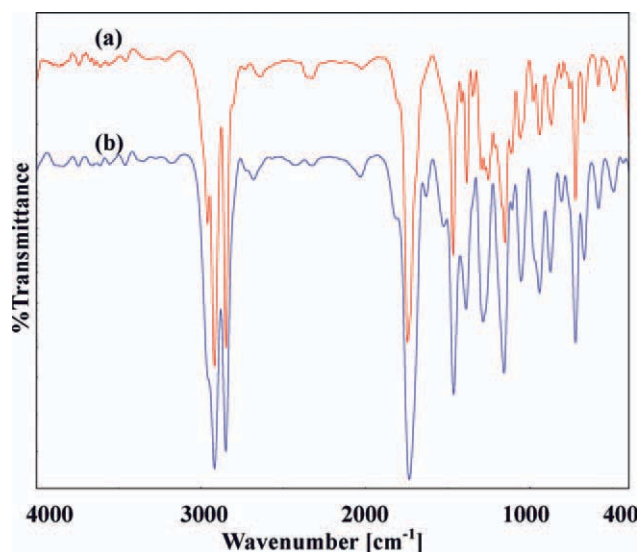
The FTIR spectra confirmed the structures of the homopolymers and copolymers. The band at  $2988\text{--}2946\text{ cm}^{-1}$  was attributed to C—H stretching vibrations of methyl and methylene groups. The bands at  $1382$  and  $1481\text{ cm}^{-1}$  were also assigned due to the C—H bending vibrations of the methyl and



**Figure 3** FTIR spectra of SA, stearoyl chloride, and SEA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

methylene groups. The strong absorption around  $1738\text{ cm}^{-1}$  was due to C=O stretching vibrations in the ester group, whereas the strong absorption at  $1228\text{ cm}^{-1}$  was attributed predominantly to C—O stretching.

The chemical stability of the poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers after repeated thermal cycling was investigated by FTIR analysis. The FTIR spectra of poly(SEA) and poly(SEA-*co*-MA) (1/1) copolymer before and after thermal cycling are given



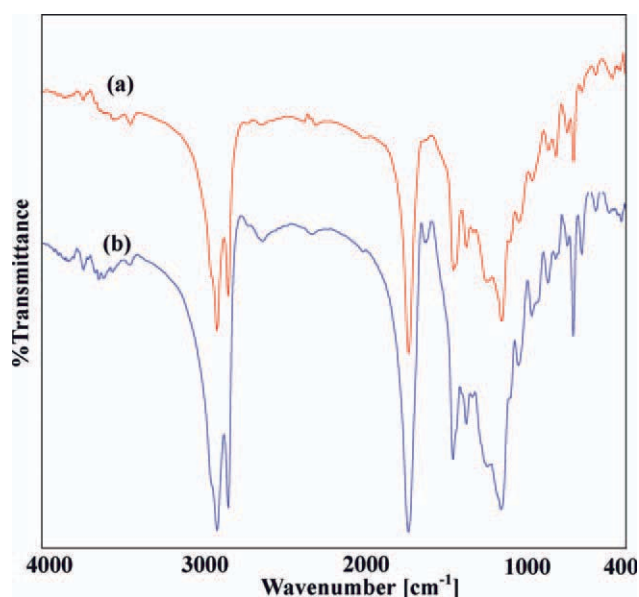
**Figure 4** FTIR spectra of poly(SEA) (a) before and (b) after the accelerated thermal cycle. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

as examples in Figures 4 and 5. From these figures, one can see that the peak positions and shapes were consistent after thermal cycling, except for the comparatively small peaks that arose at  $1636$  and  $1652\text{ cm}^{-1}$  in the spectra of poly(SEA) and poly(SEA-*co*-MA) (1/1) copolymer, respectively. That is, the chemical structures of the poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers did not change too much at the end of thermal cycling.

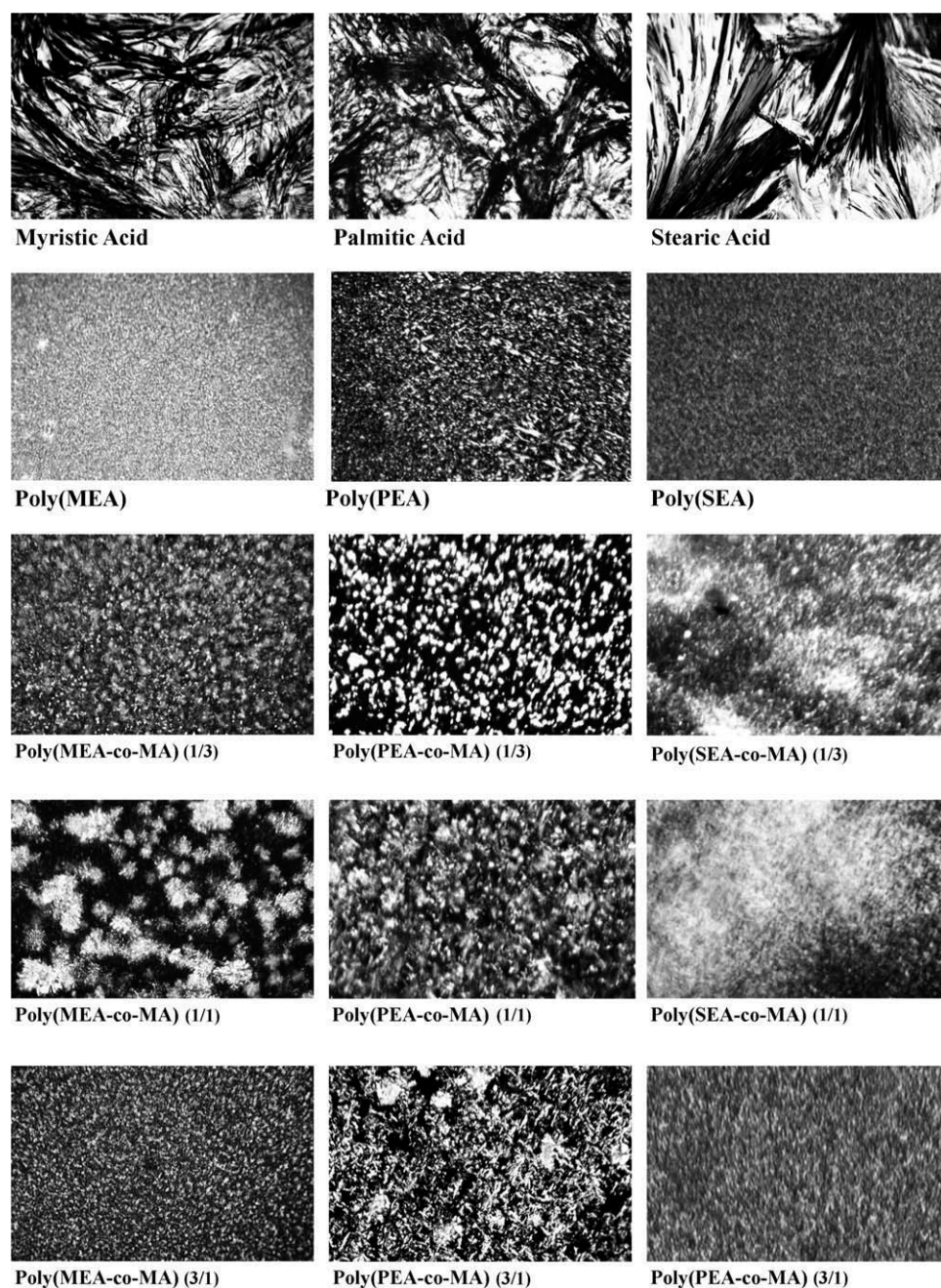
### Crystalline morphology

During solidification of crystalline polymer melts, some arrangements occur in the polymer chains in its solid state. When nucleation occurs in these polymers, the chains arrange themselves tangentially, and the solidified regions grow radially. Crossed polarized illumination makes it possible to observe as white regions the spherulites, with distinct black extinction crosses.<sup>11–22</sup> Polymers produced from fatty acids are somewhat different.<sup>34</sup> Figure 6 shows the POM micrographs of pure fatty acids, poly(2-alkyloxyethylacrylate), and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers.

As shown in Figure 6, the pure fatty acids, poly(2-alkyloxyethylacrylate), and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers were crystalline below their phase-transition temperatures. Above their phase-transition temperatures, the crystalline morphology was replaced with an amorphous, irregular appearance. Also, the dimensions of the crystals in the poly(2-alkyloxyethylacrylate)



**Figure 5** FTIR spectra of poly(SEA-*co*-MA) (1/1) copolymer (a) before and (b) after the accelerated thermal cycle. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** POM micrographs of the fatty acids, poly(2-alkyloxyethylacrylate), and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers at 100 $\times$  magnification.

and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers at all compositions of the monomers shrank to lower domains. This was attributed to the short-range interactions in the polymers. In this case, the polymer morphology was spherulite-like.

The amorphous structures of the polymers were slightly different than the amorphous phase structures of liquids because the chains were not fully freely moving. They were bonded to the polymer backbone, and the poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymer backbones were not liquid at that tem-

perature. To the best of our knowledge, the number of chain ends affected the mechanical and thermal properties drastically. Here, the free side chain ends behaved like the end of a branch, and their number here was too high. This led the melting point of the poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers to disappear. Also, poly(2-alkyloxyethylacrylate-*co*-methylacrylate) copolymers occur naturally randomly. If they are produced as block copolymers, the physical properties of the blocks would almost be preserved, and so, a second melting temperature

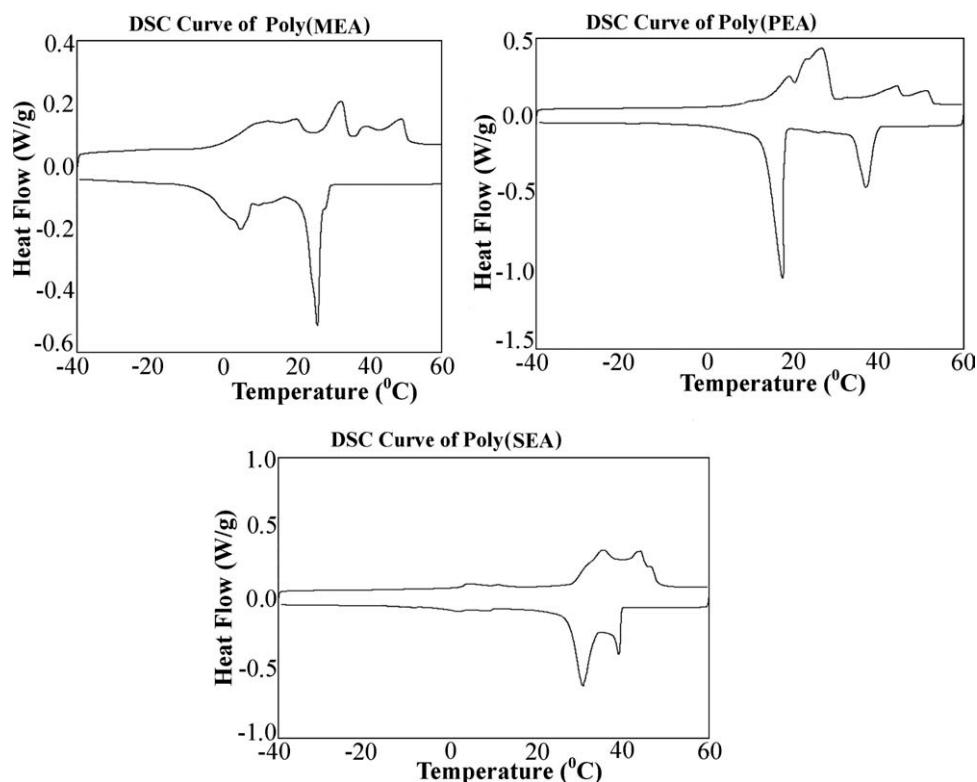


Figure 7 DSC curves of the poly(MEA), poly(PEA), and poly(SEA) polymers.

is observed for the polymethylacrylate (PMA) block. These kinds of copolymers can be produced by means of the atom transfer radical polymerization of the monomers. For this reason, our studies to improve the thermal and mechanical properties of these copolymers are ongoing.

### Thermal properties

DSC is one of the most widely used methods for analyzing the thermal properties of PCMs and revealing the phase-change temperatures, enthalpies, and subcoolings.<sup>35</sup> Figure 7 shows the DSC curves of poly(MEA), poly(PEA), and poly(SEA) polymers. Figure 8 shows the poly(PEA-*co*-MA) polymers at 1/3, 1/1, and 3/1 PEA compositions. The thermal properties obtained from the DSC curves of all of the polymers produced are also summarized in Table I.

As shown in Figure 7 and Table I, there were several transitions in the poly(MEA), poly(PEA), and poly(SEA) polymers, which were all overlapping solid–solid phase transitions. The starting point of the first transitions are tabulated in Table II. The thermograms were reproducible, so all of the transitions were reversible. In this case, it is not possible to discuss overcooling because of the overlapping of some of the transitions. From Table II, we concluded that as the length of the side groups increased, the transition temperatures increased. The total enthalpy

values of the poly(MEA), poly(PEA), and poly(SEA) polymers also increased with the length alkyl side group, except for poly(SEA).

DSC thermograms of the poly(PEA-*co*-MA) copolymers produced with three different monomer feed compositions are given as examples of DSC thermograms of poly(2-alkyloxyethylacrylate-*co*-methylacrylate) copolymers. Like the homopolymers, there were several different reversible solid–solid phase transitions in the copolymers.

As shown in Table I, despite exceptions, the phase-transition temperatures and enthalpies of the poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers did not differ considerably after the thermal cycling treatment. This meant that the segments with paraffinic side groups in the poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers produced crystalline domains at each of the 1/3, 1/1, and 3/1 molar monomer feed ratios. The phase-change enthalpies of the copolymers increased with the 2-alkyloxyethylacrylate content. That is, the concentration of the crystalline domains increased with the molar percentage of 2-alkyloxyethylacrylate segments. When the number of segments at the domain was not enough, the crystallization of the whole number of segments declined, so the enthalpy decreased. If the number of 2-alkyloxyethyl acrylate segments at the domain was enough, it tangled together and impeded to form well-defined crystals.

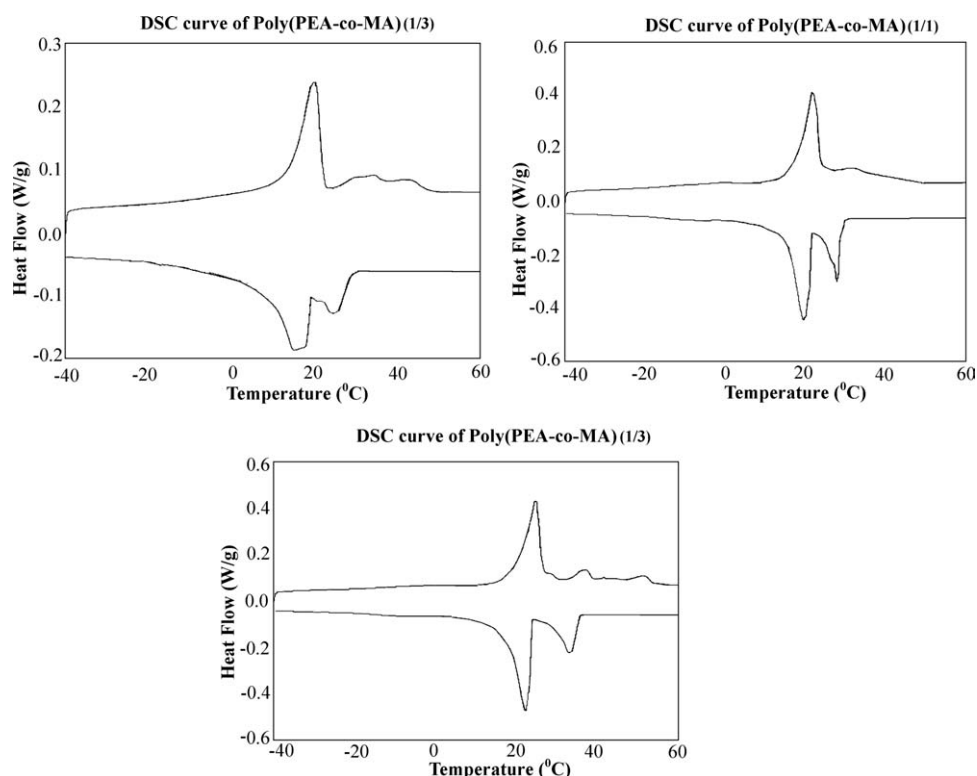


Figure 8 DSC curves of the poly(PEA-co-MA) copolymers.

Therefore, the two factors (concentration and length of 2-alkyloxyethylacrylate) worked together and led the crystallinity and the enthalpy reach the maxima.

On the other hand, the phase-change temperatures and enthalpies of the copolymers were considerably lower than the corresponding fatty acids. The reason we did not get the same or similar phase-change temperatures was the decreased range of interactions. Some part of the side groups could not contribute to crystals because the polymer had randomly distributed 2-alkyloxyethyl acrylate segments, which led the distances between these groups at the backbone to be irregular and too long to contribute crystal domains.

In the poly(2-acryloyloxyethylacrylate) polymers and poly(2-acryloyloxyethylacrylate-co-methylacrylate) copolymers, the acrylic backbone served as a hard segment, and the 2-alkyloxyethylacrylates were the segments carrying functional side groups storing and releasing heat during the phase-transition processes. The hard segment restricted the free movement of the molecular chains of the soft segment above the phase-transition temperatures. The heat storage of the copolymers was due to phase transformation between the crystalline and amorphous states of the soft segments bonded to the acrylic backbone at 1/3, 1/1, and 1/3 molar ratios. In this case, the

SSPCM stored latent heat during its transition from a low entropy state to a high entropy state.<sup>21,22</sup>

PCMs must be stable for long-term utility. Therefore, there should be no significant change in their thermal properties and chemical structures after repeated phase-transition processes. Thermal cycling testing was conducted to determine the thermal reliability of the poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-co-methylacrylate) polymers. As shown in Table I, the phase-change temperatures and enthalpies of the copolymers changed only slightly. The copolymers reached a more stable state because the phase-change temperatures were more stable, as the phase-change enthalpies of the copolymers were due to the aggregation of alkyl groups caused by increasing thermal treatment according to the increasing amount of 2-alkyloxyethylacrylate. Therefore, it can be said that the polyalkyloxyethylacrylate and poly(2-alkyloxyethylacrylate-co-methylacrylate) polymers had good thermal reliability in terms of the changes in their phase-transition temperatures.

#### Thermal stability of the synthesized SSPCMs

TGA has been used widely to investigate the thermal decompositions of acrylate and methacrylate vinyl ester polymers.<sup>33,35</sup> The endurance limits of the poly(2-alkyloxyethylacrylate) and poly(2-

**TABLE I**  
**DSC Data of the Poly(2-alkyloxyethylacrylate) Homopolymers and Poly(2-alkyloxyethylacrylate-co-methylacrylate) Copolymers before and after Thermal Cycling**

Polymer	Solid–solid phase-change temperature (heating; °C)	Solid–solid phase-change enthalpy (heating; J/g)	Solid–solid phase-change temperature (cooling; °C)	Solid–solid phase-change enthalpy (cooling; J/g)
Homopolymers before thermal cycling				
Poly(MEA)	5.9	121.2	23.2	–161.1
Poly(PEA)	14.2	186.9	15.4	–179.7
Poly(SEA)	37.3	161.1	37.4	–130.7
Homopolymers after thermal cycling				
Poly(MEA)	6.6	95.3	10.9	–111.0
Poly(PEA)	14.4	180.3	17.0	–185.8
Poly(SEA)	37.9	143.7	37.6	–127.0
Copolymers before thermal cycling				
Poly(MEA-co-MA) 1/3	–5.8	48.5	19.3	–71.6
Poly(MEA-co-MA) 1/1	0.9	87.6	3.3	–110.4
Poly(MEA-co-MA) 3/1	1.4	110.8	4.5	–148.6
Poly(PEA-co-MA) 1/3	14.1	74.9	18.7	–54.5
Poly(PEA-co-MA) 1/1	18.0	99.3	19.8	–111.1
Poly(PEA-co-MA) 3/1	20.7	97.2	21.3	–126.2
Poly(SEA-co-MA) 1/3	26.8	97.5	31.0	–90.5
Poly(SEA-co-MA) 1/1	33.1	112.8	33.6	–117.8
Poly(SEA-co-MA) 3/1	15.1	100.9	29.0	–114.8
Copolymers after thermal cycling				
Poly(MEA-co-MA) 1/3	–9.2	91.3	20.5	–69.0
Poly(MEA-co-MA) 1/1	1.8	104.4	3.5	–130.6
Poly(MEA-co-MA) 3/1	–0.6	154.1	44.3	–145.2
Poly(PEA-co-MA) 1/3	14.0	99.8	18.2	–61.6
Poly(PEA-co-MA) 1/1	16.6	103.5	19.7	–112.4
Poly(PEA-co-MA) 3/1	19.6	107.5	20.7	–117.1
Poly(SEA-co-MA) 1/3	27.9	74.9	30.3	–77.8
Poly(SEA-co-MA) 1/1	31.3	112.9	33.4	–112.1
Poly(SEA-co-MA) 3/1	42.0	95.9	38.8	–108.9

alkyloxyethylacrylate-co-methylacrylate) polymers were also investigated by TGA. The thermal stability of PCMs is one of the most important parameters in thermal energy storage applications because PCMs should be stable at ambient temperatures. The TGA and derivative thermogravimetry (DTG) graphs for the poly(SEA) and poly(SEA-co-MA) polymers are given as examples of the synthesized polymeric SSPCMs in Figures 8 and 9, and the data from the TGA graphs are tabulated in Table II.

The poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-co-methylacrylate) polymers decomposed in two distinguishable steps. However, the primary decomposition steps in the homopolymers were probably due to alkyloyl groups, as shown in Figure 9, as the first degradation step in the copolymers could have been due to repeating units containing stearoyl groups because the weight loss percentage increased with 2-alkyloxyethylacrylate content. In the polyalkyloxyethylacrylate polymers, the first step was the decomposition step for the thermal degradation of 2-alkyloxyethylacrylate from the molecular chains, and the second step was due to the thermal degradation of the

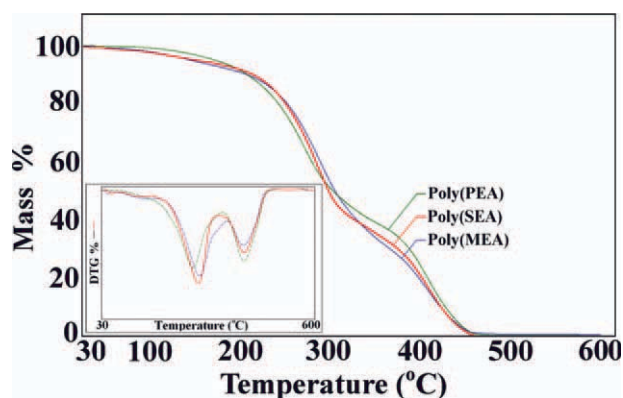
methylacrylate main chains. The degradation in two steps for the poly(2-alkyloxyethylacrylate-co-methylacrylate) polymers indicated the independent decomposition of the two components of the

**TABLE II**  
**TGA Data of the Poly(2-alkyloxyethylacrylate) and Poly(2-alkyloxyethylacrylate-co-methylacrylate) Polymers**

Polymer	DTG <sub>max</sub> 1 (°C)	Mass loss (%)	DTG <sub>max</sub> 2 (°C)	Mass loss (%)
Poly(MEA)	275	60.34	411	39.66
Poly(PEA)	292	67.99	410	32.01
Poly(SEA)	289	61.22	412	38.78
Poly(MEA-co-MA) 1/3	270	34.00	417	66.00
Poly(MEA-co-MA) 1/1	272	47.00	414	53.00
Poly(MEA-co-MA) 3/1	277	54.66	412	45.34
Poly(PEA-co-MA) 1/3	280	25.04	418	74.96
Poly(PEA-co-MA) 1/1	278	40.74	416	59.26
Poly(PEA-co-MA) 3/1	290	54.61	415	45.39
Poly(SEA-co-MA) 1/3	275	14.72	413	85.28
Poly(SEA-co-MA) 1/1	287	14.31	413	85.69
Poly(SEA-co-MA) 3/1	289	23.92	412	76.08

DTG<sub>max</sub> is the peak at differential thermal gravimetry graphs for the first degradation step





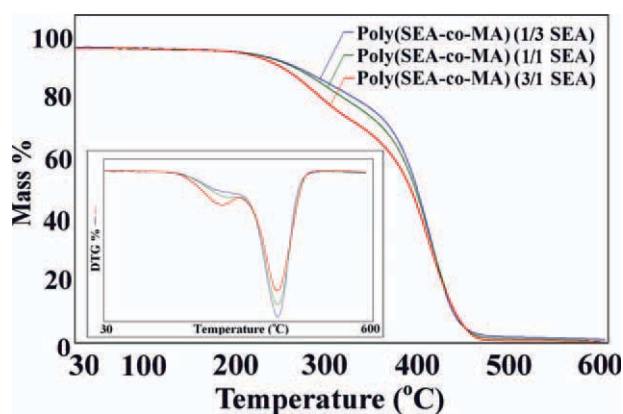
**Figure 9** TGA and DTG graphs of the poly(2-alkyloxyethylacrylate) polymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

copolymer. Senthilkumar et al.<sup>36</sup> found similar results for another acrylic copolymer.

As shown in Figures 9 and 10, degradation started after 200°C in the poly(2-alkyloxyethylacrylate)s and poly(2-alkyloxyethylacrylate-*co*-methylacrylate)s; this was considerably higher than possible utility temperatures in cooling, heating, and air-conditioning applications. The poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers were very stable in the working temperature region and in the temperature range of phase transition for energy storage applications.

#### Thermal conductivity of the poly(2-alkyloxyethylacrylate) and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers

The thermal conductivity of PCMs can be considered an important parameter in thermal energy storage applications as can their transition temperatures and latent heat. Most thermal energy storage materials



**Figure 10** TGA and DTG graphs of the poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE III**  
Thermal Conductivity Data for the Polymers and Fatty Acids

	Thermal conductivity (W m <sup>-1</sup> C <sup>-1</sup> )
PMA	0.22
MA	0.17
PA	0.16
SA	0.17
Poly(MEA)	0.20
Poly(PEA)	0.20
Poly(SEA)	0.22
Poly(MEA- <i>co</i> -MA) 1/3	0.17
Poly(MEA- <i>co</i> -MA) 1/1	0.18
Poly(MEA- <i>co</i> -MA) 3/1	0.18
Poly(PEA- <i>co</i> -MA) 1/3	0.19
Poly(PEA- <i>co</i> -MA) 1/1	0.18
Poly(PEA- <i>co</i> -MA) 3/1	0.19
Poly(SEA- <i>co</i> -MA) 1/3	0.19
Poly(SEA- <i>co</i> -MA) 1/1	0.19
Poly(SEA- <i>co</i> -MA) 3/1	0.19

are based on the use of PCMs with high storage capacities, and among them, organic PCMs attract considerable attention because of their variable application temperatures and high enthalpy values. However, organic materials have, in general, very low thermal conductivities so that techniques to enhance heat transfer are under investigation.<sup>37–39</sup>

The response time of PCMs, which is considerably important for applications, depends on the thermal conductivity. The thermal conductivities of the synthesized SSPCMs are tabulated in Table III. The thermal conductivity of PMA is 22 W m<sup>-1</sup> K<sup>-1</sup>, and the thermal conductivities of the fatty acids used to produce polymers with solid–solid phase changing properties are around 0.17 W m<sup>-1</sup> K<sup>-1</sup>. Poly(MEA), poly(PEA), and poly(SEA) had thermal conductivities higher than 0.20 W m<sup>-1</sup> K<sup>-1</sup>. Also, the thermal conductivities of the copolymers increased very slightly with increasing side-group length but did not change considerably with monomer constitution. As a result, the thermal conductivity data of the PCMs were at an acceptable level for organic SSPCMs and showed that they could be used for LHTES applications.

## CONCLUSIONS

2-Alkyloxyethylacrylate monomers, polyalkyloxyethylacrylate polymers, and poly(alkyloxyethylacrylate-*co*-methylacrylate) copolymers with 1/3, 1/1, and 3/1 monomer feed ratios were synthesized from fatty acids and HEA. FTIR and <sup>1</sup>H-NMR spectroscopy methods confirmed the chemical structures of the synthesized products.

POM investigations proved the crystalline phases of the soft segments to be transformed to amorphous phases at the end of phase transitions. Thermal analyses of the copolymers conducted with DSC showed that the synthesized polymers had more than one solid–solid phase transition with good total energy storage density for thermal energy storage applications.

The phase-change enthalpy values of the polymers and copolymer PCMs could be adjusted through changing the content of the soft segment 2-alkyloxyethylacrylate in the copolymer. In conclusion, the results show that the phase-transition temperatures and enthalpies of the poly(2-alkyloxyethylacrylate)s increased with the length of the alkyl side group as they increased in the copolymers with the length and molar percentages of 2-alkyloxyethylacrylate repeating units in the poly(2-alkyloxyethylacrylate-*co*-methylacrylate) copolymers.

TGA revealed that the poly(2-alkyloxyethylacrylate)s and poly(2-alkyloxyethylacrylate-*co*-methylacrylate) polymers were stable up to considerable temperatures. They degraded in two distinguishable steps at conveniently higher temperatures than the expected ambient temperatures. In addition, FTIR spectroscopy proved the structural consistency after 1000 repeated thermal cycles, whereas the thermal energy storage properties of the polymers and copolymers determined with DSC confirmed the stability of the polymers after thermal cycling.

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## References

- Abhat, A. *Sol Energy* 1983, 30, 313.
- Dinçer, I.; Rosen, M. A. *Thermal Energy Storage. Systems and Applications*; Wiley: New York, 2002.
- Kenisarin, M.; Mahkamov, K. *Renew Sustainable Energy Rev* 2007, 11, 1913.
- Mehling, H.; Cabeza, L. F. *Heat and Cold Storage with PCM—An Up to Date Introduction into Basics and Applications*; Springer: Berlin, 2008.
- Alay, S.; Alkan, C.; Göde, F. *Thermochim Acta* 2011, 518(1–2), 1.
- Xiao, M.; Feng, B.; Gong, K. C. *Energy Convers Manage* 2002, 43, 103.
- Shuo, P.; Fuchs, A.; Wirtz, R. A. *J Appl Polym Sci* 2004, 93, 1240.
- Hong, Y.; Xin-Shi, G. *Sol Energy Mater Sol Cells* 2000, 64, 37.
- Demirel, Y.; Paksoy, H. Ö. *Thermochim Acta* 1993, 23, 211.
- Pielichowski, K. *Eur Polym J* 1999, 35, 27.
- Pielichowska, K.; Pielichowski, K. *Polym Technol* 2011, 22, 1633.
- Li, W. D.; Ding, E. Y. *Sol Energy Mater Sol Cells* 2007, 91, 764.
- Su, J. C.; Liu, P. S. *Energy Convers Manage* 2006, 47, 3185.
- Cao, Q.; Liu, P. S. *Eur Polym J* 2006, 42, 2931.
- Guo, Y.; Tong, Z.; Chen, M.; Liang, X. *J Appl Polym Sci* 2003, 88, 652.
- Ding, E. Y.; Jiang, Y.; Li, G. K. *J Macromol Sci B* 2001, 40, 1053.
- Jiang, Y.; Ding, E. Y.; Li, G. K. *Polymer* 2002, 43, 117.
- Zang, Y. N.; Ding, E. Y. *Chin Chem Lett* 2005, 16, 1375.
- Liang, X. H.; Guo, Y. Q.; Gu, L. Z.; Ding, E. Y. *Macromolecules* 1995, 28, 6551.
- Li, Y.; Liu, R.; Huang, Y. *J Appl Polym Sci* 2008, 110, 1797.
- Yuan, X. P.; Ding, E. Y. *Chin Chem Lett* 2006, 17, 1129.
- Zhang, M.; Na, Y.; Jiang, Z. *Chem J Chin U* 2005, 26, 170.
- Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991; p 198.
- Kine, B. B.; Nivak, R. W. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1986.
- Heng, L. Y.; Chern, L. H.; Ahmad, M. *Sensor* 2003, 2, 339.
- Heng, L. Y.; Hall, E. A. *Anal Chem* 2000, 72, 42.
- Heng, L. Y.; Hall, E. A. *Electroanalysis* 2000, 12, 178.
- Peper, S.; Tsagkatakis, I.; Bakker, E. *Anal Chim Acta* 2001, 442, 25.
- Ambrose, T. M.; Meyerhoff, M. E. *Anal Chim Acta* 1999, 378, 119.
- Çaykara, T.; Birlik, G. *Macromol Mater Eng* 2005, 290, 869.
- Vargün, E.; Usanmaz, A. *J Polym Sci Part A: Polym Chem* 2005, 43, 3957.
- Canik, G.; Alkan, C. *Sol Energy* 2010, 84, 666.
- Patel, M. G.; Patel, H. J.; Patel, K. H.; Patel, R. M. *Malays Polym J* 2008, 3, 14.
- Sarı, A.; Alkan, C.; Biçer, A.; Karaipekli, A. *Sol Energy Mater Sol Cells* 2011, 95, 3195.
- Chang, T. C.; Chen, H. B.; Ho, S. Y.; Chiu, Y. S. *Polym Degrad Stab* 1995, 57, 7.
- Senthilkumar, U.; Ganesan, K.; Reddy, B. S. R. *J Polym Res* 2003, 10, 21.
- Watanabe, T.; Kikucki, H.; Kanzawa, A. *Heat Recovery Systems CHP* 1993, 13, 57.
- Mehling, H.; Hiebler, S.; Ziegler, F. *Latent heat storage using a PCM-graphite composite material*, Proceedings of TERRA-STOCK 2000, Stuttgart, Germany, 2000.
- Cabeza, L. F.; Mehling, H.; Hiebler, S.; Ziegler, F. *Appl Therm Energy* 2002, 22, 1141.