

# Thermal Energy Storage by Poly(styrene-*co-p*-stearoylstyrene) Copolymers Produced by the Modification of Polystyrene

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**ABSTRACT:** A series of poly(styrene-*co-p*-stearoyl styrene) copolymers as novel polymeric solid–solid phase-change materials (SSPCMs) were synthesized by the modification of polystyrene with stearoyl chloride. The chemical structure and crystalline morphology of the synthesized copolymers were determined with Fourier transform infrared spectroscopy and polarized optical microscopy, respectively. The thermal energy storage properties and thermal stability of the SSPCMs were investigated with differential scanning calorimetry and thermogravimetric analysis, respectively. In addition, the thermal conductiv-

ity of the SSPCMs was measured with a thermal property analyzer. Moreover, thermal cycling tests showed that the copolymers had good thermal reliability and chemical stability after being subjected to 5000 heating/cooling cycles. The synthesized poly(styrene-*co-p*-stearoyl styrene) copolymers as novel SSPCMs 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:** copolymers; polystyrene; thermal properties

## INTRODUCTION

Thermal energy storage by latent heat of phase-change materials (PCMs) is a most attractive topic. PCMs have many potential applications in solar energy utilization,<sup>1,2</sup> waste heat recovery,<sup>3</sup> building air conditioning,<sup>4</sup> electric energy-storage kitchen utensils,<sup>5</sup> insulating clothing,<sup>6</sup> and thermal comfort<sup>7</sup> applications. However, PCMs need storage containers in energy storage applications because of a leakage problem during their melting processes. Form-stable or solid–solid phase-change materials (SSPCMs) are preferred to prevent seepage of PCMs. Such PCMs also have some other advantages, including a smaller volume change during the phase-change process, no leakage, no corrosion to the container, and long-term utility.<sup>8–11</sup> Form-stable PCMs are generally polymer composites, as SSPCMs can be molecular or polymeric. There are several defects in SSPCMs, including a too-high phase-transition temperature, low transition enthalpy, and unstable thermal properties.<sup>12</sup> All of these defects substantially limit their applications. Polymeric SSPCMs are at almost the starting point of develop-

ment, and they are very promising because of the expectation of easy formation of desired shapes.

Polymeric SSPCMs can be prepared by two general routes. The first one is the physical method, in which composite PCMs are obtained by the dispersal of PCMs into higher melting point polymeric matrices, which act as supporting materials. However, the dispersal of a PCM into a polymer matrix by physical interaction may result in phase segregations during repeated thermal cycles. The second route is to bind the PCMs onto supporting polymeric materials by chemical methods, such as chemical grafting, blocking, and crosslinking copolymerization. In this method, the PCMs lose their fluidity at higher temperatures than their melting point, and thus, the liquid leakage problem is overcome, and no encapsulation is needed. Furthermore, these kind of polymeric SSPCMs can be easily and directly prepared in their desired shapes.

Different polymeric SSPCMs, such as cellulose-graft-poly(ethylene oxide),<sup>12</sup> crosslinked poly(ethylene glycol) (PEG)/4,4'-diphenylmethane diisocyanate (MDI)/polyethylene copolymer,<sup>13</sup> polyurethane-graft-PEG,<sup>14,15</sup> cellulose diacetate-graft-PEG,<sup>16–18</sup> chlorinated polypropylene-graft-PEG,<sup>19</sup> cellulose-graft-PEG,<sup>20–22</sup> and poly(vinyl alcohol)-graft-PEG,<sup>23</sup> have been prepared and investigated in terms of their thermal energy storage characteristics.

In this study, poly(styrene-*co-p*-stearoyl styrene) copolymers with different stearoyl styrene contents were synthesized as novel polymeric SSPCMs and tested for their potential for use in thermal energy storage. By considering the previous literature survey,

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one can see clearly that PEGs with different molecular weights have been used as functional groups in the synthesis of polymeric SSPCMs. However, the analysis results show that SSPCMs, including PEG, did not show excellent phase-change properties unless the molecular weight of PEG was higher than 4000.<sup>24</sup> Moreover, subcooling behavior in most of these SSPCMs was observed because of the subcooling properties of PEG.<sup>14,15</sup> In addition, another disadvantage of polymeric SSPCMs, including PEG, is a too-high phase-transition temperature. These defects substantially limit the usage of PEG applications.

Polystyrene (PS) is an aromatic polymer and uses a renewable raw material manufactured from petroleum by the chemical industry. It is cheap, and therefore, many commercial applications, such as disposable cutlery, plastic models, smoke detector housings, packing materials, insulation, and foam drink cups, have been developed for PS.<sup>25,26</sup> The application fields of PS can be extended by grafting with fatty acids. The obtained polystyrenic materials can be considered as potential SSPCMs for thermal energy storage applications.

In these copolymers, the PS backbone serves as the skeleton, and *p*-stearoyl styrene is the segment carrying the energy storage units. The PS backbone restricts free movement of paraffinic side chains. The side chains form crystal domains at low crystal dimensions, and thermal treatment leads to these crystal domains becoming amorphous. The heat storage behavior of the copolymers was due to phase transformation between the crystalline and amorphous states of the paraffinic side chains.

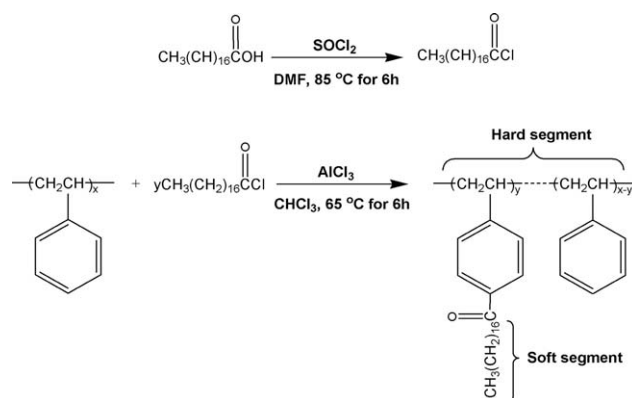
## EXPERIMENTAL

### Materials

Stearic acid [SA; CH<sub>3</sub>(CH)<sub>16</sub>COOH, 98% pure] was used as the soft segment in the preparation of the polystyrenic SSPCMs. It was obtained from Merck Co. PS, used as the hard segment, was purchased from Aldrich Co. Thionyl chloride (SOCl<sub>2</sub>), aluminum chloride (AlCl<sub>3</sub>), and dimethylformamide (DMF) were obtained from Merck. Analytical-grade toluene and chloroform were purchased from Merck, and they were used as solvents without further purification.

### Synthesis of the poly(styrene-*co-p*-stearoyl styrene) copolymers

Stearoyl chloride was preferred over SA because of the low reactivity of SA in the copolymerization reactions between PS and SA. Stearoyl chloride was prepared by the refluxing of SA (1 mol) and SOCl<sub>2</sub> (1 mol) at 85°C for 6 h in a reflux system. DMF was used as the catalyst in the reaction. Reaction moni-



**Figure 1** Synthesis scheme of the poly(styrene-*co-p*-stearoyl styrene) copolymers.

toring was done after the disclosure of hydrogen chloride. After the reaction, we removed the residual SOCl<sub>2</sub> and DMF by heating the mixture to 90°C for 1 h in a fume hood.

Polystyrenic SSPCMs, called *poly(styrene-co-p-stearoyl styrene) copolymers*, were prepared by the modification of PS. The synthesis scheme of the poly(styrene-*co-p*-stearoyl styrene)s is shown in Figure 1. We carried out the copolymerization reaction by placing calculated amounts of PS and stearoyl chloride (molar ratio = 4 : 1 styrene/stearoyl chloride) in chloroform in a reaction system equipped with a reflux condenser and a thermometer. AlCl<sub>3</sub> was used as the catalyst in this reaction. The reaction was continued at 65°C for 6 h, and reaction was monitored by observation of the color change of litmus paper during the reflux process. After the reaction was completed, the product was filtered and washed four times with deionized water including a weak alkaline. The same synthesis process was also applied with molar ratios of 4 : 2 and 4 : 3 of the number of PS repeating units to stearoyl chloride.

### Characterization

The chemical characterization of the synthesized copolymers was performed with Fourier transform infrared (FTIR) spectroscopy (Jasco model 430, Japan). The spectra of stearoyl chloride, PS, and poly(styrene-*co*-stearoyl styrene) copolymers were taken on KBr disks in the wave-number range 4000–400 cm<sup>-1</sup>. Polarized optical microscopy (POM) analyses were performed on a Leica DM EP model microscope, Germany equipped with a video camera.

### Determination of the thermal properties of the poly(styrene-*co-p*-stearoyl styrene) copolymers PCMs

The thermal properties, including the phase-transition temperature and enthalpy, of the poly(styrene-

*co-p*-stearoyl styrene) copolymers were measured by differential scanning calorimetry (DSC; Perkin Elmer TGA7, USA). The DSC analyses were carried out at a 5°C/min heating rate under a constant stream of argon at a flow rate of 60 mL/min. We tested reproducibility by conducting three measurements. To determine the thermal reliability of the copolymers, an accelerated thermal cycling test was conducted. The tests were performed for up to 5000 heating/cooling processes with a thermal cycler (BIOER model TC-25/H, China). The changes in the thermal properties after thermal cycling were evaluated with DSC analysis. In addition, the chemical and structural stability of the poly(styrene-*co-p*-stearoyl styrene) copolymers after thermal cycling was investigated with FTIR analysis.

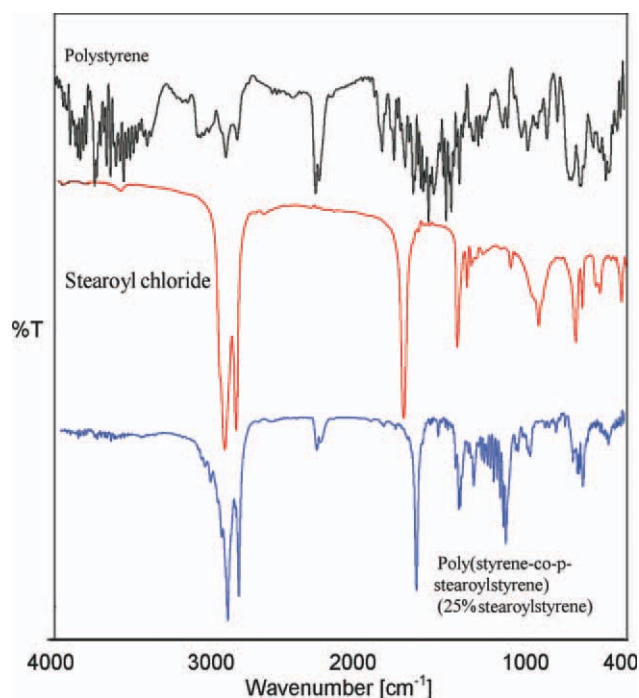
The thermal endurance limits of the copolymers were tested on a thermal analyzer (PerkinElmer TGA7). The measurements were performed between 25 and 600°C at a heating rate of 10°C/min under a static air atmosphere. The thermal conductivities of the copolymers were measured at room temperature with a KD2 thermal property analyzer, USA.

## RESULTS AND DISCUSSION

The chemical modification of PS has continued to attract much attention because the numerous applications of functionalized resins in areas as varied as ion exchange,<sup>24</sup> polymeric protecting groups,<sup>25</sup> peptide synthesis,<sup>26</sup> and other polymer supported reactions.<sup>27,28</sup> The chemical modification of polymers is generally an easy and economic way of producing new materials compared to the production of polymers from monomeric precursors.<sup>29</sup> In this study, PS was modified to carry a soft segment at different concentration levels, and the produced copolymers were characterized by available means.

### FTIR analysis

FTIR spectroscopy was used both for proving the reaction and to measure the thermal stability of the polymers after accelerated thermal cycling. Figure 2 shows the FTIR spectra for PS, stearoyl chloride, and poly(styrene-*co-p*-stearoyl styrene) copolymer (25% stearoyl stearate). The main difference of the PS spectrum from the other two was the carbonyl stretching peak, which was absent in the PS spectrum. The carbonyl peak was observed at 1799 cm<sup>-1</sup> in the stearoyl chloride spectrum and was seen at 1734 cm<sup>-1</sup> in the spectra of poly(styrene-*co-p*-stearoyl styrene) with 25, 50, and 75% stearoyl styrene. There was no shift in the carbonyl peaks of the copolymers because the carbonyl groups were all ester carbonyl in the copolymers. It was highly different in acyl chloride because it was completely a different group.



**Figure 2** FTIR spectra for PS, stearoyl chloride, and poly(styrene-*co-p*-stearoyl styrene) (25% *p*-stearoyl styrene) copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

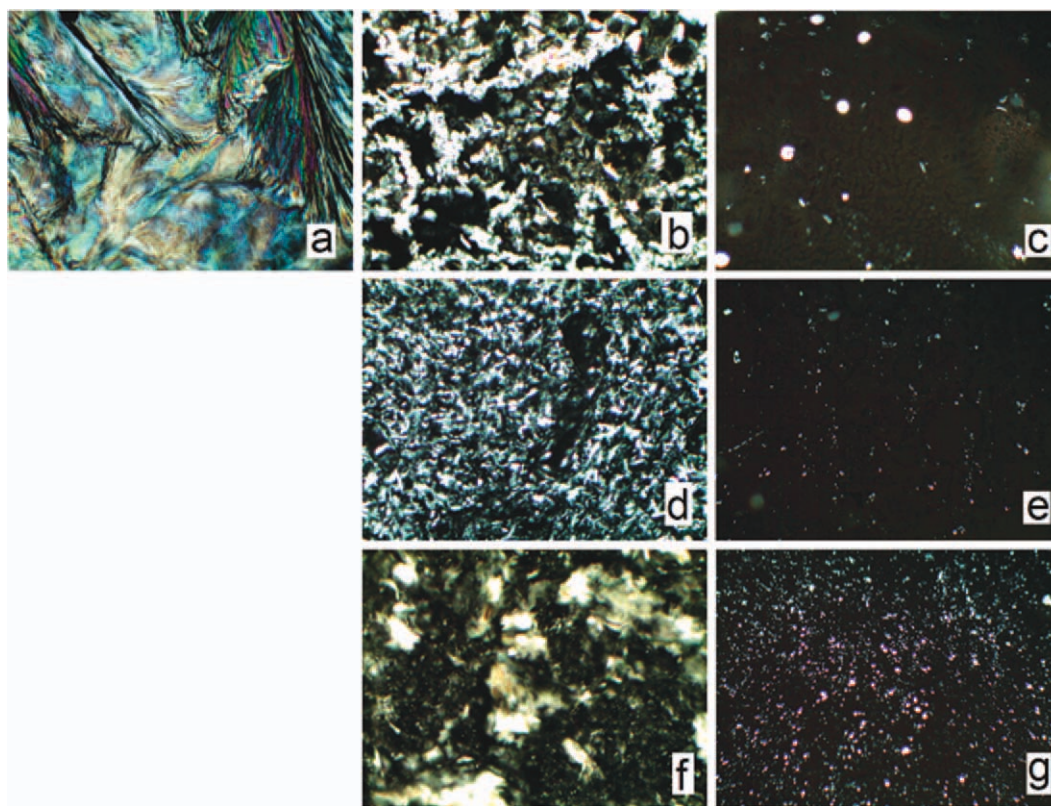
This result was also supported also by the shifting of aromatic C=C stretching bands at about 1500 cm<sup>-1</sup> on the aromatic rings of the copolymer chain.<sup>30</sup> The peaks observed at 2920 cm<sup>-1</sup> showed the asymmetric stretching of the C—H band of PS, as the peaks at 2923 and 2850 cm<sup>-1</sup> show the same groups for stearoyl styrene. The peaks at 717 and 678 cm<sup>-1</sup> corresponded to rocking vibrations and bending characteristics for the aliphatic chain of the stearoyl group.

### Crystalline morphology

During the solidification of some polymer melts, there may be some organization of the polymer chains if the polymer is crystalline in the solid state at its melting temperature. 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 white regions (spherulites) with distinct black extinction crosses.

Figure 3 shows the POM micrographs of the pure SA and poly(styrene-*co-p*-stearoyl styrene) copolymers at all stearoyl styrene compositions at temperatures lower and higher than its solid–solid phase-transition temperature. As shown in Figure 3(a,b), the pure SA and poly(styrene-*co-p*-stearoyl styrene) (25% stearoyl styrene) were crystalline below their phase-transition temperatures. The dimensions of





**Figure 3** POM micrographs of (a) pure SA at 15°C, (b) poly(styrene-*co-p*-stearoyl styrene) (25% *p*-stearoyl styrene) copolymer at 15°C, (c) poly(styrene-*co-p*-stearoyl styrene) (25% *p*-stearoyl styrene) copolymer at 35°C, (d) poly(styrene-*co-p*-stearoyl styrene) (50% *p*-stearoyl styrene) copolymer at 15°C, (e) poly(styrene-*co-p*-stearoyl styrene) (50% *p*-stearoyl styrene) copolymer at 35°C, (f) poly(styrene-*co-p*-stearoyl styrene) (75% *p*-stearoyl styrene) copolymer at 15°C, and (g) poly(styrene-*co-p*-stearoyl styrene) (75% *p*-stearoyl styrene) copolymer at 35°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

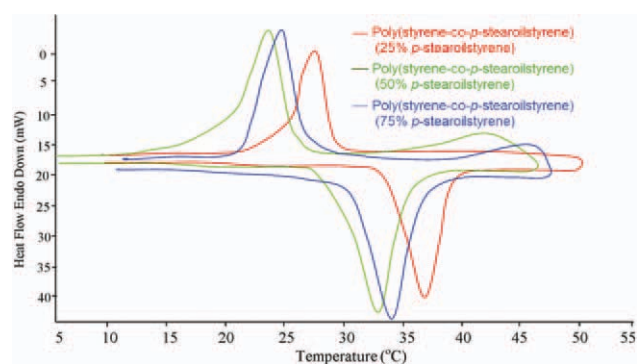
the crystals in the poly(styrene-*co-p*-stearoyl styrene) copolymers at any composition studied and represented in Figure 3(b,d,f) shrunk to a lower range; this could be attributed to the short-range interactions in the copolymers. Figure 3(c,e,g) show the amorphous morphologies of the copolymers above the phase-transition temperature.

The amorphous structures of the copolymers were slightly different than the amorphous phase structures of liquids because the chains were not fully freely moving; they were bonded to the PS backbone, and the PS backbone was not liquid at that temperature. To the best of our knowledge, the number of chain ends affected the mechanical properties drastically. Here, the free side chain ends behaved like the ends of a branch, and their number here was too high. This led the melting point of the PS to disappear. Unfortunately, there were no longer fatty acids easily available with higher chain lengths. Also, the modification of PS is naturally conducted randomly, and this made the copolymers random. If they became block copolymers, the physical properties of the blocks were almost preserved, and so, a second melting temperature was observed. These kinds of copolymers could be produced by means of

the direct copolymerization of the monomers. Our studies to improve the thermal and mechanical properties of these copolymers are ongoing.

### Thermal properties

DSC is an accepted method as convenient for PCM thermal property analysis because it prevents uncertainty about the phase-change temperatures, enthalpies, and subcoolings. Figure 4 shows the DSC curves



**Figure 4** DSC thermograms of the poly(styrene-*co-p*-stearoyl styrene) copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE I**  
**Thermal Properties of the Synthesized Poly(styrene-*co*-stearoylstyrene) [Poly(S-SS)]**  
**Copolymers before and after Thermal Cycling**

	Thermal properties			
	$T_{s-s,heating}$ (°C)	$\Delta H_{s-s,heating}$ (J/g)	$T_{s-s,cooling}$ (°C)	$\Delta H_{s-s,cooling}$ (J/g)
Before thermal cycling				
Poly(S-SS) (25% SS)	33.43	44.56	29.00	−32.55
Poly(S-SS) (50% SS)	24.84	50.43	29.05	−45.05
Poly(S-SS) (75% SS)	29.70	54.84	29.42	−46.33
After thermal cycling				
Poly(S-SS) (25% SS)	31.69	60.22	28.34	−48.53
Poly(S-SS) (50% SS)	31.09	70.81	28.39	−54.45
Poly(S-SS) (75% SS)	31.31	73.45	28.92	−63.98

Poly(S-SS): poly(styrene-*co-p*-stearoylstyrene), % SS: *p*-stearoylstyrene content, s-s: solid solid transition

of the poly(styrene-*co-p*-stearoyl styrene) copolymers at 25, 50, and 75 mol % compositions. The thermal properties obtained from the DSC curves are also summarized in Table I. As shown in Table I, the phase-transition temperatures of the poly(styrene-*co-p*-stearoyl styrene) copolymers did not differ considerably; this revealed that the paraffinic side of the stearoyl styrene segments produced crystalline domains at each of the 25, 50, and 75 mol % compositions in almost the same size. However, the phase-change enthalpies of the copolymers increased with the stearoyl styrene content. That is, the concentration of the crystalline domains increased with the molar percentages of the stearoyl styrene segments.

The latent heats of melting were found to be 44.56 J/g for poly(styrene-*co-p*-stearoyl styrene) with 25% stearoyl styrene, 50.43 J/g for poly(styrene-*co-p*-stearoyl styrene) with 50% stearoyl styrene, and 54.84 J/g for poly(styrene-*co-p*-stearoyl styrene) with 75% stearoyl styrene.

On the other hand, the phase-change temperatures and enthalpies of the copolymers were considerably lower than those of the corresponding fatty acid. The reason we did not get the same or similar phase-change temperatures was the decreased range of interactions. Some part of the side chain could not contribute to crystals because they were bonded to the PS backbone from one side, and there were some styrene segments between the stearoyl styrene segments, which prohibited the chains from getting close enough to form crystals. In this case, the SSPCM stored latent heat during its transition from a low entropy state to a high entropy state.<sup>22,23</sup> The thermal expansivities of the poly(styrene-*co*-stearoyl styrene) copolymers were also measured to show that the produced copolymers had very low volume changes upon temperature application. The expansivity of the copolymers tabulated in Table II were approximately 10 times the expansivity of PS; however, they were still low enough for thermal energy storage applications.

In our previous works, we synthesized several PCMs for different kinds of applications. Most were solid-liquid PCMs or shape-stabilized blends. Polymeric SSPCMs have all the advantages of shape-stabilized PCMs, direct applicability, and no phase separation upon utility.<sup>13–15</sup> In our previous work, palmitic acid was used instead of SA, and it was seen that the phase-change enthalpies of those polymers were much lower than that of poly(styrene-*co*-stearoylstyrene) copolymers.<sup>34</sup> Also poly(styrene-*co-p*-stearoyl styrene) copolymers should be considered for higher temperatures than poly(styrene-*co-p*-palmitoylstyrene) copolymers because of their high phase-change temperatures.

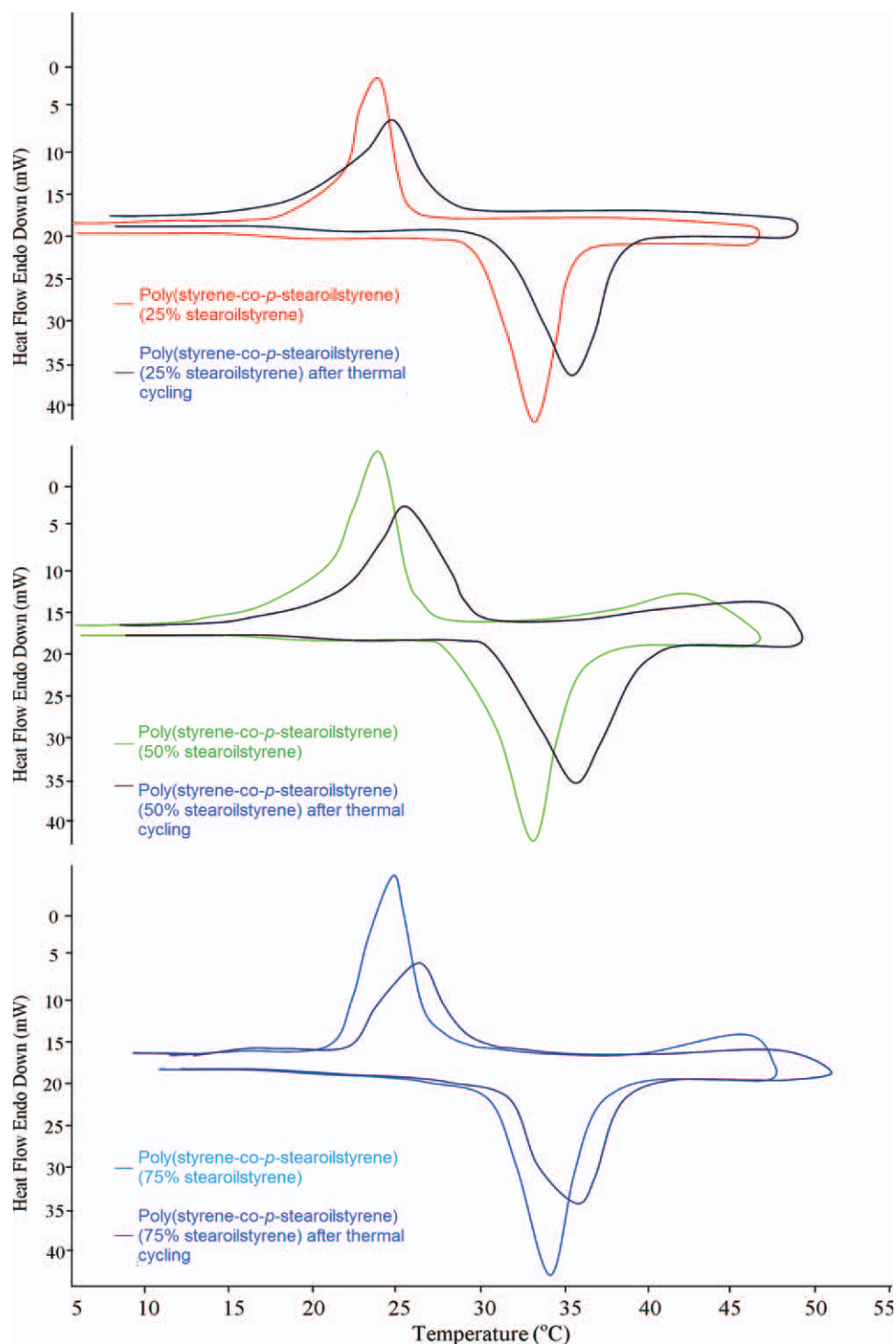
**Thermal reliability of the**  
**poly(styrene-*co-p*-stearoyl styrene) copolymers**

PCMs must be stable for long-term utility. Therefore, there should be no significant change in their thermal properties or chemical structures after repeated phase-transition processes. A thermal cycling test was conducted to determine the thermal reliability of the poly(styrene-*co-p*-stearoyl styrene) copolymers. Figure 5 shows the DSC curves for the copolymers before and after thermal cycling. The thermal properties obtained from the DSC curves are also given in Table I. As shown in Table I, the phase-change

**TABLE II**  
**Thermal Expansivities of the Poly(styrene-*co*-stearoylstyrene) [Poly(S-SS)] Copolymers**

	Thermal properties (°C <sup>−1</sup> )
PS	$1.50 \times 10^{-4}$
Poly(S-SS) (25% SS)	$4.57 \times 10^{-3}$
Poly(S-SS) (50% SS)	$3.19 \times 10^{-3}$
Poly(S-SS) (75% SS)	$3.39 \times 10^{-3}$

Poly(S-SS): poly(styrene-*co-p*-stearoylstyrene), % SS: *p*-stearoylstyrene content.

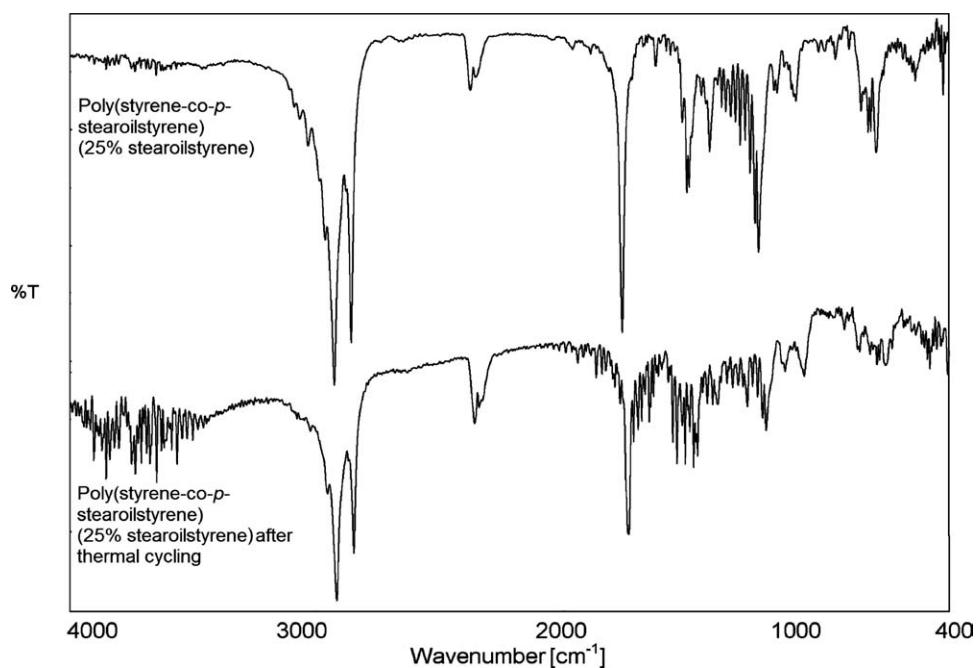


**Figure 5** DSC thermograms for the poly(styrene-co-*p*-stearoyl styrene) copolymers before and after thermal cycling. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

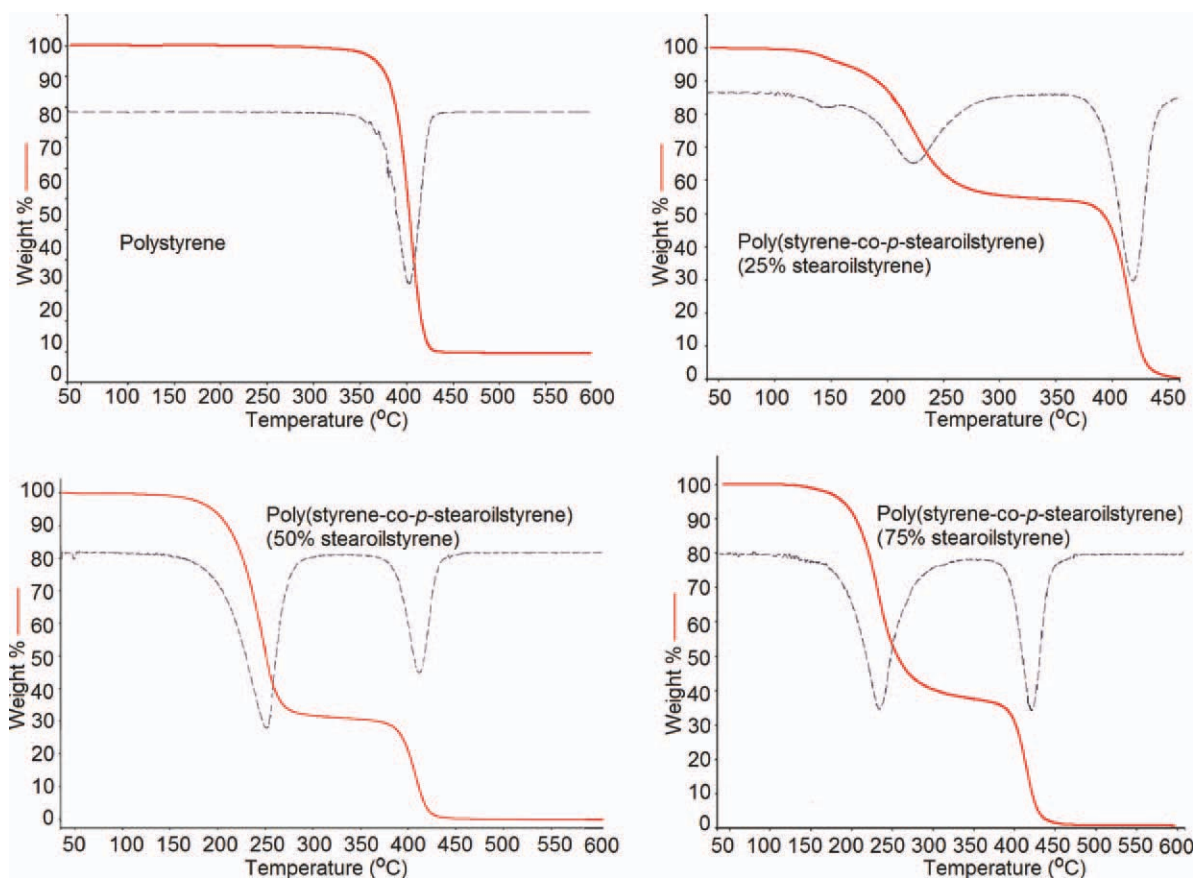
temperatures and enthalpies of the copolymers increased considerably after thermal cycling. It is well known that thermal treatment in polymer blends and composites results in phase segregation. In these materials, paraffinic side chains contributed to their phase, and the dimension of the crystallites increased. The copolymers gained high stability as a

result of accelerated thermal cycling because freely moving chain ends reached a consistent state, which gave rise to phase-change temperatures and enthalpy values. However, the phase-change temperatures and enthalpies were never as high as those of the corresponding fatty acids because the stearoyl styrene functional groups were bound to the





**Figure 6** FTIR spectra for the poly(styrene-*co-p*-stearoilstyrene) copolymer (25% *p*-stearoilstyrene) before and after thermal cycling.



**Figure 7** TGA curves of the PS and poly(styrene-*co-p*-stearoilstyrene) copolymer PCMs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE III**  
**TGA Data of the PS and Poly(styrene-*co*-stearoylstyrene)**  
**[Poly(S-SS)] Copolymers**

	Degradation interval (°C)	Mass loss (wt %)
PS	341–441	98.53
Poly(S-SS) (25% SS)	126–315 (one step)	44.41
	354–458 (two step)	53.71
Poly(S-SS) (50% SS)	133–305 (one step)	67.96
	357–445 (two step)	30.25
Poly(S-SS) (75% SS)	140–337 (one step)	61.43
	362–475 (two step)	36.24

backbone and only restricted movements of the paraffinic side chains were allowed. As a result, the poly(styrene-*co*-*p*-stearoyl styrene) copolymers were thermally reliable.

The chemical stability of the poly(styrene-*co*-*p*-stearoyl styrene) copolymers after repeated thermal cycling was investigated with FTIR spectroscopy. When the FTIR spectra of the poly(styrene-*co*-*p*-stearoyl styrene) copolymer with 25% stearoyl styrene before and after thermal cycling were compared (Fig. 6), we could see that not only the carbonyl peak of the polymer at  $1737.55\text{ cm}^{-1}$  but also the  $\text{CH}_2$  peaks at  $729\text{ cm}^{-1}$  and between  $2800$  and  $2900\text{ cm}^{-1}$  and their shapes were all consistent before and after thermal cycling. This meant that the chemical structure of the poly(styrene-*co*-*p*-stearoyl styrene) copolymers was retained at the end of thermal cycling.

#### Thermal stability of the synthesized SSPCMs

The endurance limits of the poly(styrene-*co*-*p*-stearoyl styrene) copolymers were investigated by thermogravimetric analysis (TGA). The thermal stability of PCMs is one of the most important parameters for thermal energy storage applications because PCMs should be stable at ambient temperatures. The TGA graphs are given in Figure 7, and the data from the graphs were tabulated in Table III. As shown in Figure 7, PS started to lose weight at approximately  $341^\circ\text{C}$ , and it completely lost its weight at  $441^\circ\text{C}$ . The degradation started around  $160^\circ\text{C}$  in the poly(styrene-*co*-*p*-stearoyl styrene) copolymers; this is acceptable for a polymeric PCM. The produced polymers had considerably low solid–solid phase-transition temperatures, and therefore, they could be used in cooling applications. The poly(styrene-*co*-*p*-stearoyl styrene) copolymers were very stable in the working temperature region and in the temperature range of phase transition for energy storage applications.

According to the TGA curves in Figure 7, PS decomposed in one clear and sharp step, whereas the poly(styrene-*co*-*p*-stearoyl styrene) copolymers decomposed in two distinct steps. The first step was

the thermal degradation of stearoyl styrene from the molecular chains. The second step was the thermal degradation of the PS main chains. The two-step degradation of the poly(styrene-*co*-*p*-stearoyl styrene) copolymers indicated the independent decomposition of the two components of the copolymer. Araki et al.<sup>35</sup> found similar results with another styrenic copolymer.

#### Thermal conductivity of the poly(styrene-*co*-*p*-stearoyl styrene) copolymers

The thermal conductivity of PCMs can be considered an important parameter in thermal energy storage applications as can their transition temperatures and latent heat. The thermal energy transfer ratio of PCMs depends on this parameter because it has a significant effect on the rates of energy storage and the release of PCM. The thermal conductivity of the synthesized SSPCMs were measured as  $0.13\text{ W m}^{-1}\text{ K}^{-1}$  for poly(-styrene-*co*-*p*-stearoyl styrene) with 25% stearoyl styrene,  $0.18\text{ W m}^{-1}\text{ K}^{-1}$  for poly(styrene-*co*-*p*-stearoyl styrene) with 50% stearoyl styrene, and  $0.25\text{ W m}^{-1}\text{ K}^{-1}$  for poly(styrene-*co*-*p*-stearoyl styrene) with 75% stearoyl styrene. These results indicate that the thermal conductivity of the copolymers increased with increasing molar percentage of stearoyl styrene.

## CONCLUSIONS

Poly(styrene-*co*-*p*-stearoyl styrene) copolymers were synthesized as novel polymeric SSPCMs by the modification of PS. The FTIR results confirmed that the stearoyl group was successfully added to the PS backbone as a pendant group. Thermal analyses of the copolymers conducted with DSC showed that the synthesized copolymers had typical solid–solid phase transition behavior with good energy storage density for thermal energy storage applications. In the copolymers, the PS backbone served as a hard segment, and the *p*-stearoyl styrene was the segment carrying functional side storage and releasing heat during the phase-transition process. The content of functional groups at the backbone increased the phase-change temperatures and enthalpy values.

The POM investigations proved that the crystalline phase of the functional group transformed into an amorphous phase during the solid–solid phase transition. The phase-change enthalpy of the copolymer PCMs could be adjusted through a change in the content of the functional segment (stearoyl styrene) in the copolymer. The TGA results show that the polystyrenic copolymers were stable up to considerably higher temperatures compared to possible ambient temperatures. In addition, FTIR spectroscopy showed that 5000 repeated thermal cycles did not cause any change in the chemical structure of



the copolymers, whereas the thermal reliability of the polymers was confirmed by DSC measurements before and after accelerated thermal cycling.

As a result, we concluded that the poly(styrene-*co-p*-stearoyl styrene) copolymers as SSPCMs have considerable potential for thermal energy storage and temperature-control applications.

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## References

1. Kurklu, A. *Renewable Energy* 1998, 13, 89.
2. Kenisarin, M.; Mahkamov, K. *Renewable Sustainable Energy Rev* 2007, 11, 1913.
3. Kaizawa, A.; Kamano, H.; Kawai, A.; Jozuka, T.; Senda, T.; Maruoka, N.; Okinaka, N.; Akiyama, T. *Isij Int* 2008, 48, 540.
4. Khudhair, A. M.; Farid, M. M. *Energy Convers Manage* 2004, 45, 263.
5. Kandasamy, R.; Wang, X. Q.; Mujumdar, A. S. *Appl Therm Eng* 2007, 27, 2822.
6. Wang, S. X.; Li, Y.; Hu, J. Y.; Tokura, H.; Song, Q. W. *Polym Test* 2006, 25, 580.
7. Alay, S.; Göde, F.; Alkan, C. *J Appl Polym Sci* 2011, 120, 2821.
8. Alkan, C.; Kaya, K.; Sari, A. *J Polym Environ* 2009, 17, 254.
9. Schossig, P.; Henning, H. M.; Gschwander, S.; Haussmann, T. *Sol Energy Mater Sol Cells* 2005, 89, 297.
10. Sari, A.; Alkan, C.; Karaipekli, A.; Uzun, O. *Sol Energy* 2009, 83, 1757.
11. Yang, R.; Xu, H.; Zhang, Y. *Sol Energy Mater Sol Cells* 2003, 80, 405.
12. Pielichowska, K.; Pielichowski, K. *Polym Adv Technol* 2010, 22, 1633.
13. Li, W. D.; Ding, E. Y. *Sol Energy Mater Sol Cells* 2007, 91, 764.
14. Su, J. C.; Liu, P. S. *Energy Convers Manage* 2006, 47, 3185.
15. Cao, Q.; Liu, P. S. *Eur Polym J* 2006, 42, 2931.
16. Guo, Y.; Tong, Z.; Chen, M.; Liang, X. *J Appl Polym Sci* 2003, 88, 652.
17. Ding, E. Y.; Jiang, Y.; Li, G. K. *J Macromol Sci Phys* 2001, 40, 1053.
18. Jiang, Y.; Ding, E. Y.; Li, G. K. *Polymer* 2002, 43, 117.
19. Zang, Y. N.; Ding, E. Y. *Chin Chem Lett* 2005, 16, 1375.
20. Liang, X. H.; Guo, Y. Q.; Gu, L. Z.; Ding, E. Y. *Macromolecules* 1995, 28, 6551.
21. Li, Y.; Liu, R.; Huang, Y. *J Appl Polym Sci* 2008, 110, 1797.
22. Yuan, X. P.; Ding, E. Y. *Chin Chem Lett* 2006, 17, 1129.
23. Zhang, M.; Na, Y.; Jiang, Z. *Chem J Chin Univ* 2005, 26, 170.
24. Xi, P.; Gu, X. H.; Cheng, B. *E-Polymers* 2008, 129, 1.
25. Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento* 1960, 15, 68.
26. Doroudiani, S.; Kortschot, M. T. *J Thermoplast Compos Mater* 2004, 17, 13.
27. Dorfner, K. *Ion Exchangers; Properties and Applications*; Ann Arbor Science: Ann Arbor, MI, 1972.
28. Frechet, J. M. J.; Eicler, E. *Polym Bull* 1982, 7, 345.
29. Ito, Y.; Fujii, H.; Imanishi, Y. *Biotechnol Prog* 1993, 9, 128.
30. Vinod Kumar, G. S.; Santhosh Kumar, K. *J Appl Polym Sci* 2005, 97, 8.
31. Sari, A.; Alkan, C.; Biçer, A.; Karaipekli, A. *Sol Energy Mater Sol C* 2011, 95, 3195.
32. Araki, J.; Wada, M.; Kuga, S. *Langmuir* 2001, 17, 21.