

Poly(polyethylene glycol methyl ether methacrylate) as Novel Solid-Solid Phase Change Material for Thermal Energy Storage

Bingtao Tang, Zhenyu Yang, Shufen Zhang

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China

Received 4 March 2011; accepted 18 July 2011

DOI 10.1002/app.35287

Published online 13 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Poly(polyethylene glycol methyl ether methacrylate) as novel solid–solid phase change materials (PCMs) for thermal energy storage was prepared via the facile bulk polymerization of polyethylene glycol methyl ether methacrylate and was characterized by Fourier transform infrared, ^{13}C -NMR, X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis measurements. Based on the results, it is indicated that the poly (polyethylene glycol methyl ether methacrylate) as novel

PCM showed solid–solid properties with suitable transition temperature, high transition enthalpy, and good thermal stability, which was apt to crystallize due to the flexibility of long polyether side chain. This novel PCMs have advantages for the potential application in energy storage. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1377–1381, 2012

Key words: bulk polymerization; phase behavior; phase change material; polyethers; thermal properties

INTRODUCTION

In recent years, phase change materials (PCMs) have become one of the most attractive functional materials,^{1–3} because they can store and release thermal energy in large quantities at nearly constant temperature during the phase change process.⁴ Therefore, the PCMs have been widely used in energy-saving construction,⁵ recovery of waste heat,⁶ and smart textiles.⁷

During the melt process of solid–liquid PCMs, the PCMs need to be encapsulated to prevent leakage. Therefore, polymeric solid–solid PCMs were well developed due to their attractive advantages.^{8–11} Two kinds of polymeric solid–solid PCMs have been reported. One kind is solid–liquid PCMs/polymeric supporting material composites.^{12,13} The other is synthesized polymeric PCMs, which were mainly obtained by grafting or crosslinking solid–liquid PCMs—polyethylene glycol (PEG) onto polymers.¹⁴ The second approach is advantageous in the development of covalent bond between solid–liquid PCM and polymer, which endows with excellent solid–

solid performance. However, the graft reaction is difficult when the molecular weight of PEG is over 1000 owing to the reduction of reactivity and steric hindrance effect. Here, we present new materials and facile approach to overcome the limitations of previous methods by the bulk polymerization of polyethylene glycol methyl ether methacrylate.

Polyethylene glycol methyl ether methacrylates (mP, 'm' means monomer) are kind of polymerizable monomers,^{15–17} which are easy to form homopolymers or copolymers. At the same time, they have the similar structure and good crystallinity as PEG. Therefore, the novel solid–solid PCMs developed in this work are the poly(polyethylene glycol methyl ether methacrylates) (PP), which were obtained by the bulk polymerization of polyethylene glycol methyl ether methacrylates (mP). The long polyether side chain (PEG chain) is used as working substances for the heat storage, and the polymeric main chain restricted the free movement of suspended polyether; hence at temperatures above the polyethylene glycol methyl ether methacrylate phase melting transition, the whole system always remains in the solid state. Therefore, the PP has high transition enthalpy and good solid–solid properties.

Correspondence to: S. Zhang (zhangshf@dlut.edu.cn).

Contract grant sponsor: National Natural Science Funds of China; contract grant number: 20804007.

Contract grant sponsor: Doctoral Fund of Ministry of Education of China; contract grant number: 200801411032.

Contract grant sponsor: State Key Program of National Natural Science Foundation of China; contract grant number: 20836001.

EXPERIMENTAL

Materials

Polyethylene glycol methyl ether methacrylate (mP11, $M_n = 1100$; mP20, $M_n = 2080$, from Aldrich),

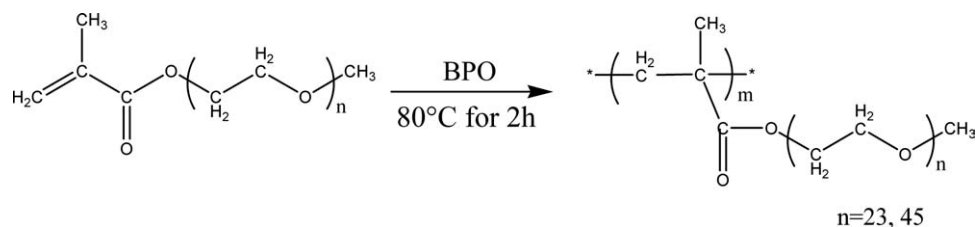


Figure 1 The synthetic route of PP.

benzoyl peroxide (BPO) was recrystallized from methanol.

Synthesis of PP(EGMA)

PP11 and PP20 were prepared by free-radical bulk polymerization of mP11 and mP20, respectively. The polymerization was conducted at 80°C for 2 h and 0.9 wt % BPO was used as initiator. The polymers were obtained by washing several times with acetone and were further purified by Soxhlet extraction for 72 h with acetone. They were finally dried overnight in a vacuum oven at 70°C and 5 mbar until constant weight. The yields were 82 and 86%, respectively.

Characterization of PP(EGMA)

The FTIR Spectra were recorded on a Nicolet Nexus 870 from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} using film and nujol mull methods, which were used to confirm the polymerization of polyethylene glycol methyl ether methacrylate.

^{13}C -NMR spectra of mP11 and mP20 were recorded on a Bruker AVANCE 400 spectrometer (400 MHz); Solid-state ^{13}C magic angle spinning

(MAS) NMR spectra of PP11 and PP20 were recorded at 100.5 MHz on the Varian Infinityplus-400 spectrometer using a 4 mm ceramic probe and spinning speed of 8 kHz.

DSC and TGA were performed in nitrogen atmosphere by using a Perkin-Elmer DSC7 DSC module at a heating rate of 5°C/min. XRD patterns of the samples were obtained using an X-ray diffractometer (D/max-III A, Japan). The thermal conductivity of mP20 and PP20 were measured using DRL-III Thermal conductivity tester.

RESULTS AND DISCUSSION

Synthesis and FTIR spectroscopy analysis of PP

PP was obtained by bulk polymerization of mP. This polymerization process was carried out by a simple heating process under the presence of BPO (Fig. 1), which was used as initiator. Therefore, the preparation of PP was facile, and the polymerization reaction was characterized by FTIR spectroscopy method.

Figure 2a and b show the FTIR spectra of mP11 by the film method and nujol mull method, respectively, and the FTIR spectrum of PP11 is shown in

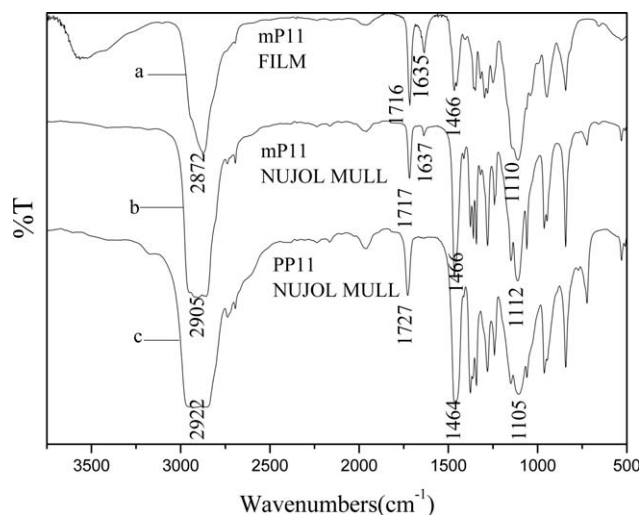


Figure 2 FTIR spectra of mP11 FILM (a), mP11 NUJOL MULL (b) and PP11 NUJOL MULL (c).

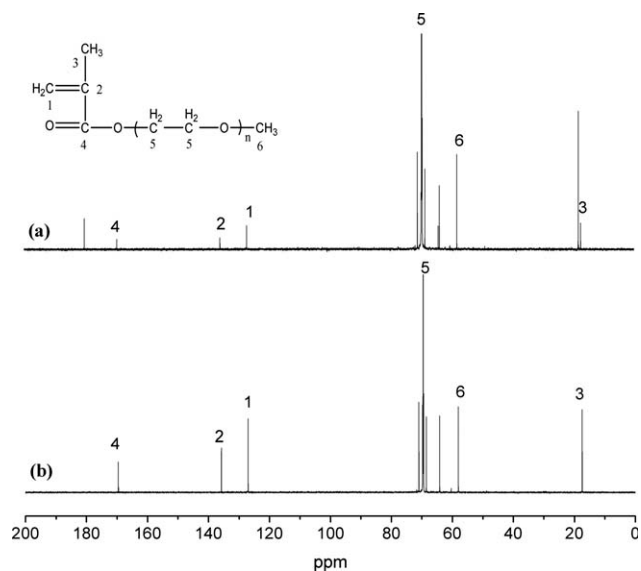


Figure 3 ^{13}C NMR spectra of mP11 (a) and mP20 (b).

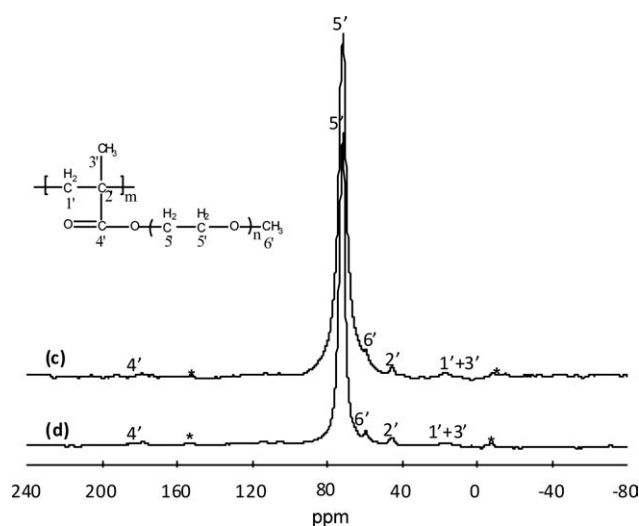


Figure 4 ^{13}C MAS NMR spectra of PP11 (c) and PP20 (d).

Figure 2(c) by nujol mull method. It was clear from the Figure 2 that C=C stretching vibration (1635 cm^{-1}) in mP disappeared when PP was obtained, which showed the polymerization reaction took place. The peak of C—O—C stretching peak at 1110 cm^{-1} was not obviously changed, when the PP was formed.

^{13}C -NMR analysis of mP and PP

To verify further the FTIR analysis results, the ^{13}C -NMR and ^{13}C MAS NMR analysis was performed. Figures 3 and 4 show the ^{13}C -NMR spectrum of mP and the ^{13}C MAS NMR spectrum of PP, respectively. All chemical shifts were expressed in parts per million (d) relative to the solvent signal. The chemical shifts of C atom in mP ($d1 = 127.0$, $d2 = 135.7$, $d3 = 17.4$, $d4 = 169.5$, $d5 = 69.6$, $d6 = 58.1$) and PP ($d1'$, $d3'$

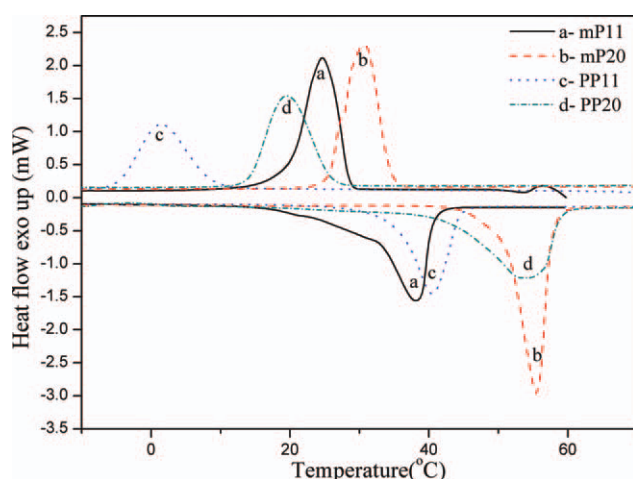






Figure 5 The DSC curves of mP11, mP20, PP11 and PP20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Transition Temperature and Transition Enthalpy of mP and PP

Sample	Phase transition (70°C)	ΔH_m (J/g)	ΔH_c (J/g)	T_m (°C)	T_c (°C)
mP11		138.0	138.1	32.5	20.2
mP20		156.5	141.2	51.5	26.7
PP11		99.7	94.5	35.8	1.4
PP20		132.5	118.6	44.7	14.4

T_m , melting temperature; T_c , crystallization temperature; ΔH_m , heat latent of fusion; ΔH_c , heat latent of crystallization.

$= 17\text{--}20$, $d2' = 46$, $d4' = 178\text{--}179$, $d5' = 72$, $d6' = 60$) could be clearly observed. The analyses results of the ^{13}C -NMR and ^{13}C MAS NMR spectrum verify further prove that PP has been successfully prepared.

DSC thermal analysis and solid–solid performance of PCM

Figure 5 presents the thermal characteristics of mP and PP in the heating and subsequent cooling in between -20°C and 80°C at the rate of 5°C min^{-1} . From the DSC curves of mP and PP, the endothermic and exothermic enthalpy values were given in Table I. mP had high transformation enthalpy of 156.5 J/g . The phase change enthalpy of PP copolymer reached 132.5 J/g , which meant that its endothermic and exothermic capacity had been weakened after polymerization. The enthalpy reduction may be attributed to partial suppression of the arrangement and orientation of the long polyether side chain, while the PP still had higher heat storage capacity over 132 J/g compared with some other solid–solid PCMs reported in previous works.^{14,18}

The key idea of this work is the generation of solid–solid phase change of PP in which the free

TABLE II
Thermal Properties of PP20 Under Thermal Cycling

Thermal cycling number	ΔH_m (J/g)	ΔH_c (J/g)	T_m (°C)	T_c (°C)
0	132.5	118.6	44.7	14.4
50	126.6	127.2	48.5	14.4
100	127.5	128.3	47.7	16.4

T_m , melting temperature; T_c , crystallization temperature; ΔH_m , heat latent of fusion; ΔH_c , heat latent of crystallization.

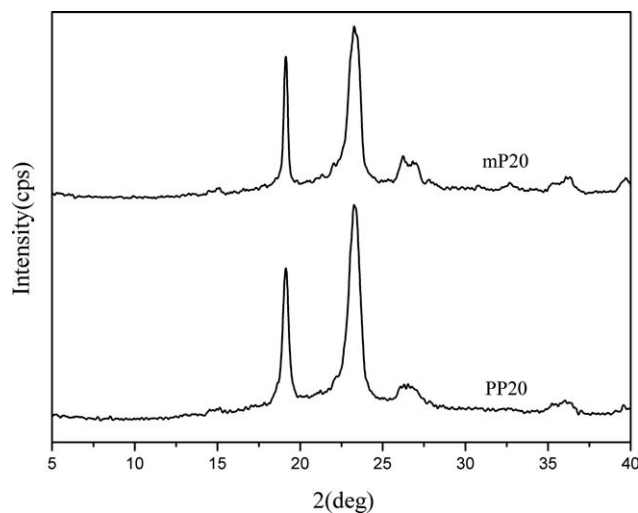


Figure 6 XRD spectra of mP20 and PP20.

movement of the long polyether side chain is restricted by the polymeric main chain structure,¹ at temperatures above the mP phase melting transition, the whole system always remains in the solid state. PP is heated in a piece of glass directly, no liquid is observed in the heating process and still appear white, even if the temperature is up to 70°C. It indicates that the PP11 and PP20 kept solid state during the temperature range of transition (from the Table I). It can be concluded that PP has a good energy storage effect and solid–solid performance.

Thermal cycling test of PCM

In this experiment, PP20 was chosen to test its thermal reliability after 50 and 100 times thermal cycling. Thermal properties after thermal cycling were showed in Table II. After repeated 50, 100 times of thermal cycling, the melting temperatures of PP20 changed by 3.8 and 3.0°C, and the crystallization temperature changed by 0.0 and 2.0°C,

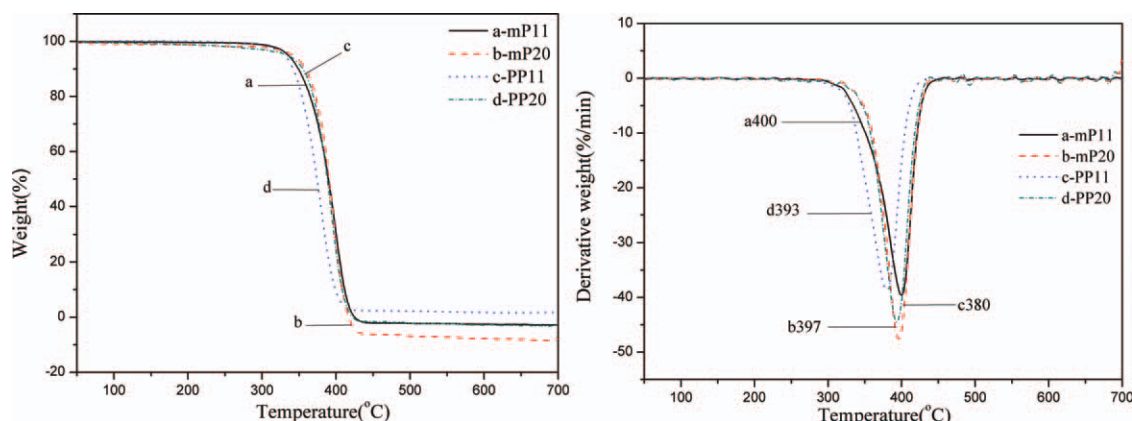


Figure 7 TGA (left) and DTGA (right) curves of mP and PP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE III
XRD Parameter of mPEGMA and PPEGMA Samples

Samples	Type of phase change	2θ (°)	D (nm)	Crystallinity (%)
mP20	Solid–liquid	19.1	4.6	86.1
PP20	Solid–solid	19.1	4.6	78.7

respectively. The latent heat of melting changed by 4.5% and 3.8%, whereas the latent heat of crystallization changed by 7.2% and 8.2%, respectively. The results showed the temperature had a little change, It also could be seen that the solid–solid composite PCM had good thermal reliability in terms of the latent heat value.

XRD analysis of PCM

Figure 6 presents powder X-ray diffraction (XRD) patterns of the prepared samples from mP20 and PP20. The data is summarized in Table III. Sharp and intense diffraction peaks at 19.14° and 23.28° were observed for the fresh mP20 and PP20 samples, indicating that the mPEG on the support was present in the crystalline state. It is obviously seen that pure mP and PP show diffraction angle, crystal plane distance and the degree of crystallization are nearly the same. The crystallization of mP in the PP was disturbed by the polymeric main chain, which results in the crystallinity decreases. These results imply that crystal structure of mP does not changed during the synthesis, and PP still has good crystalline properties.

Thermal stability analysis and Thermal conductivity of PCM

The thermal stability of mP and PP were determined by TGA and differential thermogravimetric analysis (DTGA). The corresponding results are shown in Figure 7. According to Figure 7, the thermal stability is essentially the same for all four materials.

Corresponding to the degradation process, the sharp weight loss within the temperature around 390°C is ascribed to the decomposition of the ethylene glycol side chains' degrading. Therefore, the TGA results indicate that the novel solid–solid PCMs will have a broad applicable temperature range for its good heat-resistant performance. The thermal conductivity of mP20 and PP20 are $0.287 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.228 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The decrease of the thermal conductivity was most likely because of the new polymeric main chain structure covering the ethylene glycol chains.

CONCLUSIONS

In summary, PP as novel PCMs for thermal energy storage was successfully obtained by the facile bulk polymerization of mP. The structure and properties of PP have been extensively investigated. IR, ^{13}C -NMR and ^{13}C MAS NMR spectra indicate that the polymerization of mP takes place. The analysis results of DSC, XRD, and TGA indicate that PP is solid–solid PCMs with good thermal stability and has large enthalpy value (132 J/g). Therefore, PP has extensively potential applications for thermal energy storage and temperature control.

References

1. Xi, P.; Gu, X. H.; Cheng, B. W.; Wang, Y. F. *Energy Convers Manage* 2009, 50, 1522.
2. Li, W. D.; Ding, E. Y. *Mater Lett* 2007, 61, 4325.
3. Alkan, C.; Kaya, K.; Sari, A. *Mater Lett* 2008, 62, 1122.
4. Sari, A.; Alkan, C.; Karaipekli, A.; Onal, A. *Energy Convers Manage* 2008, 49, 373.
5. Khudhair, A. M.; Farid, M. M. *Energy Convers Manage* 2004, 45, 26.
6. Zhu, D. S.; Wu, H. J.; Wang, S. W. *Int J Therm Sci* 2006, 45, 804.
7. Mondal, S. *Appl Therm Eng* 2008, 28, 1536.
8. Chen, C. Z.; Wang, L. G.; Huang, Y. *Mater Lett* 2009, 63, 569.
9. Sari, A.; Alkan, C.; Kolemen, U.; Uzun, O. *J Appl Polym Sci* 2006, 101, 1402.
10. Alkan, C.; Sari, A. *Sol Energy* 2008, 82, 118.
11. Sari, A.; Akcay, M.; Soylak, M.; Onal, A. *J Sci Ind Res India* 2005, 64, 991.
12. Sari, A. *Energy Conv Manage* 2004, 45, 2033.
13. Karaipekli, A.; Sari, A. *Sol Energy* 2009, 83, 323.
14. Li, Y. X.; Wu, M.; Liu, R. G.; Huang, Y. *Sol Energy Mater Sol C* 2009, 93, 1321.
15. Gu, B. H.; Armenta, J. M.; Lee, M. L. *J Chromatogr A* 2005, 1079, 382.
16. Zou, X. P.; Kang, E. T.; Neoh, K. G. *Surf Coat Technol* 2002, 149, 119.
17. Kim, M. K.; Park, I. S.; Dal Park, H.; Wee, W. R.; Lee, J. H.; Park, K. D.; Kim, S. H.; Kim, Y. H. *J Cataract Refr Surg* 2001, 27, 766.
18. Jiang, Y.; Ding, E. Y.; Li, G. K. *Polymer* 2002, 43, 117.