Fabrication and Properties of Poly(Diethylene Glycol N-alkyl Ether Vinyl Ethers) as a Phase Change Material

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ABSTRACT

Diethylene glycol n-alkyl ether vinyl ethers (C\textsubscript{m}E\textsubscript{2}VEs) (m=14,16,18) were synthesized using diethylene glycolmonovinylether (E\textsubscript{2}VE) and brominated alkanes as raw materials. Furthermore, they were cationic polymerized to form a comb-like polymeric phase change material-poly(diethylene glycol n-alkyl ether vinyl ethers) (PC\textsubscript{m}E\textsubscript{2}VE). The structure, composition, molecular weight, phase transition behavior, thermal stability and crystallization behavior of PC\textsubscript{m}E\textsubscript{2}VE were investigated using Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Both the melting and crystallizing enthalpy of (PC\textsubscript{m}E\textsubscript{2}VE) are more than 90 J/g; and the measured thermal decomposition temperatures (5% mass loss) of PC\textsubscript{14}E\textsubscript{2}VE, PC\textsubscript{16}E\textsubscript{2}VE, and PC\textsubscript{18}E\textsubscript{2}VE were 259 ºC, 307 ºC and 315 ºC, respectively. It increased rapidly with increasing the number of carbon atoms in the side chain.

INTRODUCTION

Thermal energy storage (TES) containing sensible heat and latent heat which can bridge between energy requirements and energy use is the temporary storage of high or low temperature energy for later use. Phase change materials (PCMs) can be used to achieve the temporary storage of thermal energy, due to they can be kept at...
almost isothermal conditions for a period of time and their availability at wide range of phase transitions [1-2]. The first comb-like polymer poly(n-alkyl acrylate)s[3] were synthesized by Rehberg and Fisher, which were prepared by radical polymerization. After then, many different kinds of comb-like polymers were also prepared, such as poly(n-alkyl methacrylate)s, poly(n-alkyl vinyl ester)s, poly(n-alkyl vinyl ether)s, poly(n-alkyl acrylamide)s, poly(1-alkylethylene)s, poly(1-alkylethylene oxide)s, poly(polyethylene glycol octadecyl ether methacrylate) poly(diethylene glycol hexadecyl ether acrylate) and poly(n-alkyl itaconate)s, etc. [4]. In order to improving the regularity of the main chain, we have designed polyethylene chain as the main chain of comb-like polymers, in order to reduce the frustrated crystallization of side chain, the ester bond between main chain and side chain has been replaced by polyethylene glycol segment. Up to now, we have successfully prepared a series of comb-like polymers poly(polyethylene glycol n-alkyl ether vinyl ethers) (PCmE2VE) through living cationic homopolymerization [5]. In this paper, we will focus on introducing the design, synthesis and characterization of the novel polyethylene glycol n-alkyl ether vinyl ethers (CmE2VE), and poly(polyethylene glycol n-alkyl ether vinyl ethers) (PCmE2VE) (m=14,16,18).

EXPERIMENTAL

Materials

1-Bromooctadecane (C18H37Br), 1-Bromohexadecane (C16H33Br), 1-Bromotetradecane (C14H29Br), were purchased from Aldrich and used after refining. Diethylene glycol monovinyl ether (E2VE) (TCI; > 96.0%) and isobutyl vinyl ether (IBVE) (TCI; > 99.0%) were washed with an 0.1M aqueous alkaline solution and then with water, then monomers were distilled twice over calcium hydride and stored in a brown ampule under dry nitrogen in refrigerator. Solvents and added bases (hexane, dimethyl sulfoxide, and ethyl acetate) were purified by the usual methods and distilled at least twice over CaH2 and metallic sodium (for hexane) just before use. EtAlCl2 (Aldrich; 25wt% in hexanes) was used as commercially supplied. 1-(isobutoxy) ethyl acetate (CH3CH(OiBu)OCOCH3 [IBEA]), as a cationogen, was prepared by addition reaction of isobutyl vinyl ether and acetic acid and distilled over CaH2 under reduced pressure[6]. Sodium hydroxide (NaOH), tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were purchased from Tianjin Sailboat Chemical Reagent Co., Ltd., and used as received.

Preparation of Diethylene Glycol N-alkyl Ether Vinyl Ethers (CmE2VE)

Monomers C14E2VE, C16E2VE, and C18E2VE were produced according to the methods of the published literature[7-9]. Taking the fabrication process of C18E2VE as an example, the experimental process is as follows: 6 grams of NaOH
was added into 200 mL of anhydrous DMSO, and the mixture solution was stirred at 30 °C for 3 h under nitrogen gas, and then, 0.1 mol of ethylene glycol monovinyl ether (E2VE) was added by dry medical syringe, and the compound was continuously stirred for 2-3 h, followed by the addition of 0.1 mol of bromooctadecane under stirring using dry medical syringe. The mixture solution was washed twice with deionized water. After that, crude C18E2VE was purified by column chromatography elution with the mixture solution of petroleum ether and ethyl acetate, the synthetic processes of other CmE2VEs (m=14,16,18) were similar to that of C18E2VE.

**Synthesis of Poly(DiethyleneGlycol N-alkyl Ether Vinyl Ether)**

The polymerization of diethylene glycol n-alkyl ether vinyl ether (CmE2VE) were carried out at 30 °C under a dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock baked at 250 °C for 20 min before use. The polymerization reaction was initiated by addition of EtAlCl2-toluene solution into a mixture of a monomer, an added base, the cationogen IBEA in hexane at the polymerization temperature (20~30 °C) by a dry medical syringe. After a predetermined interval, the polymerization was quenched with 0.3 wt % ammoniac methanol. The quenched mixtures were sequentially washed with dilute hydrochloric acid and water to remove the initiator residues[10]. Scheme 1 gives the reaction process of CmE2VEs and PCmE2VEs. In this paper, PCmE2VEs (m=14, 16, 18) were successfully prepared.
RESULTS AND DISCUSSION

Structural Characterization of Monomers

Fig. 1 shows FTIR spectra of monomers as follows: A: $C_{14}H_{29}Br$ (a), $C_{14}E_2VE$ (b), B: $C_{16}H_{33}Br$ (a), $C_{16}E_2VE$ (b); C: $C_{18}H_{37}Br$ (a), $C_{18}E_2VE$ (b). From Fig. 1, it can be found that the bands at 1621 cm$^{-1}$ and 1204 cm$^{-1}$, 1126 cm$^{-1}$ are assigned to the C=C, C-O-C stretching vibration bands of $C_mE_2VE$s, while in brominated alkanes there is no absorption peak in these bands. The bands at 730 cm$^{-1}$/719 cm$^{-1}$ are assigned to the (CH$_2$)$_n$ (n>4) rocking bands, which are existed in both brominated alkanes and diethylene glycol n-alkyl ether vinyl ether. The above contents prove that $C_mE_2VE$s have been synthesized and exists in orthorhombic crystal at room temperature.
The $^1$H NMR and $^{13}$C NMR spectra of $C_{18}E_2$VEs are shown in Fig. 2. For $C_{18}E_2$VE, as shown in Fig. 2b, the chemical shift at 0.88 ppm (a) is characteristic of the CH$_3$ group derived from the alkyl side chain, and the methylenes in C$_{17}$H$_{34}$ are located at 1.26 (b), 1.60 (c), and 3.47 (d) ppm. The chemical shifts at 3.65 ppm (e) and 3.83 ppm (f), 3.89 ppm (g) and 3.91 ppm (h) are characteristic of the CH$_2$ groups in O-CH$_2$CH$_2$-O; 6.50 ppm(k) is the representative of the H atom of C=CHO; and 4.20 ppm (i) and 4.01 ppm (j) are characteristic of the H atoms in CH$_2$=C. Further, Fig. 2b’ shows the $^{13}$C NMR spectra of $C_{18}E_1$VE. The chemical shift of 14.1 ppm (a) is assigned to -CH$_3$ group in the side chain, and the peaks at 22.7 (b), 26.1 (c), 29.3 (d), 29.6 (e), 31.9 (f), and 70.1 (i) ppm are characteristic of the C atoms of the CH$_2$ groups in the alkyl side chain. The chemical shifts at 67.3 ppm (g) and 69.0 ppm (h, i, j, k) are characteristic of methylene carbon atoms between two ether bonds, and the C atoms of C=C are located at 86.5 ppm (l) and 151.8 ppm (m). The nuclear magnetic spectra as further evidence that monomers $C_mE_2$VEs have been prepared successfully.
Structural Characterization of Poly(Diethylene Glycol N-alkyl Ether Vinyl Ether)

The FTIR spectrum of PC\textsubscript{18E2VE} is shown in Fig. 3. From Fig. 3, there are no peaks near about 1621 cm\textsuperscript{-1} in the spectrum of PC\textsubscript{18E2VE}, which suggests that no monomers exist in the product. The strong and broad bands of the ether bond at 1123 cm\textsuperscript{-1} have replaced the three sharp bands at 1216 cm\textsuperscript{-1}, 1156 cm\textsuperscript{-1} and 1141 cm\textsuperscript{-1}. These results prove that the cationic polymerizations of PC\textsubscript{18E2VE} have been successfully completed. The characteristic absorption band at 720 cm\textsuperscript{-1} is attributed to the rocking vibrations of (CH\textsubscript{2})\textsubscript{n} groups (n > 4) in PC\textsubscript{18E2VE}, which indicates that the crystal form of alkyl side chain has changed from orthorhombic crystal in monomer to hexagonal crystalline polymers.

Figure 2. \textsuperscript{1}H NMR spectra of C\textsubscript{18E2VE}(b), and \textsuperscript{13}C NMR spectra of C\textsubscript{18E2VE}(b').

Figure 3. FTIR spectrum of PC\textsubscript{18E2VE}. Fig. 4. \textsuperscript{13}C NMR spectrum in CDCl\textsubscript{3} of PC\textsubscript{18E2VE}. 

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Fig. 4 shows the 13C NMR spectrum of PC18E2VE. Through a polymerization reaction, the C=C has been turned into a single bond, so the chemical shift values of the carbon atoms in the main chain have changed from the low field (51.8 ppm and 86.5 ppm) to the high field (for a: 74.2-67.9 ppm; for b: 74.1-70.1 ppm). The chemical shift values of other carbon atoms in side chains nearly didn’t change.

The number-average molecular weight (Mn) and molecular weight distribution (MWD) of PCmE2VE (m=14,16,18) are shown in Fig. 5. The characteristic data of polymers are listed in Table 1. It is well-known that only when the length of the side alkyl chain is beyond a certain value does the sidechain crystallization behavior appear. It is worth noting that only the part of side-chains away from the polymeric backbones can participate in the formation of crystals, and the crystallization enthalpy depends upon the length of the side chains. To further analyze the ordered packing mode of sidechain crystals according to eqn (1), the k is the contribution of each added CH2 group to enthalpy, and \( \Delta H_m \), \( e \) is a constant reflecting the contribution of chain end to enthalpy. In order to calculate the crystalline degree of side-chain and the crystallizable carbon atoms per side-chain, eqn (1), (2) and (3), are used[11,12]. The number of crystallizable CH2 groups (Nc) and the crystallinity (Xc) of the polymers PCmE2VE are listed in Table 1.

\[
\Delta H_m = nk + \Delta H_{m_e}
\]  
(1)

\[
N_c = \frac{\Delta H_m}{k}
\]  
(2)

\[
X_c = \frac{(N_c \times 14.026)}{M_{\text{unit}}}
\]  
(3)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( M_n ) (GPC) ( \times 10^4 )</th>
<th>( M_w/M_n )</th>
<th>( \Delta H_m ) (J/mol)</th>
<th>( X_c ) (%)</th>
<th>( N_c )</th>
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<tr>
<td>PC_{14}E_2VE</td>
<td>1.7</td>
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<td>94</td>
<td>33</td>
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<td>PC_{16}E_2VE</td>
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<td>103</td>
<td>36</td>
<td>9.2</td>
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<td>PC_{18}E_2VE</td>
<td>1.3</td>
<td>1.57</td>
<td>103</td>
<td>36</td>
<td>9.9</td>
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As shown in Table 1, \( N_c \) increases from 7.7 to 9.9 and \( X_c \) increases from 33% to 36% with n changing from 14 to 18. It is concluded that only when the carbon atoms of side chains are over 7 or 8 does the side-chain crystallization behavior for PC_mE_2VE can appear.
Thermal Behavior of Poly(Diethylene Glycol N-alkyl Ether Vinyl Ether)

Fig. 6 presents the DSC curves of PCmE2VEs (m=14, 16, 18) in the heating and cooling process. With increasing of the side-chain length from 14 to 18, the melting temperature (Tm) and the freezing temperature (Tc) exhibit a linear change, changing from 25.8 to 52.9 °C and from 15.8 to 42.4 °C, respectively. The increasing melting enthalpy (ΔHm) or crystallization enthalpy (ΔHc) from 92 to 102 J/g for PCmE2VEs (m=14 to 18), proving that the side alkylchains formed the ordered crystal structures surrounded by polymer backbones. Some thermal parameters (Tmo, Tmp, ΔHm, Tco, Tcp, ΔHc) of monomers and polymers PCmE2VEs (m=14, 16, 18) are listed in Table 2. The single peak in the PCmE2VEs DSC curves demonstrates that there is only one packing form for the side chains, which should be hexagonal structure.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>ΔHm (J/g)</th>
<th>ΔHc (J/g)</th>
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<tr>
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<td>19.8</td>
<td>15.8</td>
<td>93</td>
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<td>PC16E2VE</td>
<td>37.4</td>
<td>35.2</td>
<td>30.8</td>
<td>103</td>
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<tr>
<td>PC18E2VE</td>
<td>48.9</td>
<td>46.4</td>
<td>42.4</td>
<td>103</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tm a (°C)</th>
<th>Tm b (°C)</th>
<th>Tc c (°C)</th>
<th>Tc d (°C)</th>
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<tr>
<td>PC14E2VE</td>
<td>22.1</td>
<td>25.8</td>
<td>19.8</td>
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<tr>
<td>PC16E2VE</td>
<td>37.4</td>
<td>41.9</td>
<td>35.2</td>
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<tr>
<td>PC18E2VE</td>
<td>48.9</td>
<td>52.9</td>
<td>46.4</td>
<td>42.4</td>
</tr>
</tbody>
</table>

* onset temperature of melting point
* peak temperature of melting point
* onset temperature of crystallization point
* peak temperature of crystallization point

Figure 5. M_n and MWD of PC14E2VE, PC16E2VE, PC18E2VE, obtained using IBEA/EtAlCl_2 in n-hexane ethyl acetate as added base at 30 °C: [monomer]=0.1 M; [IBEA]=4.0 mM; [EtAlCl_2]=20 mM; [added base]=1.0 M, in n-hexane, 1-2 h.
Thermal Stability of Poly(Diethylene Glycol N-alkyl Ether Vinyl Ether)

The TGA curves of C14E2VE, C16E2VE, and C18E2VE, and corresponding polymers PCmE2VEs (m=14, 16, 18) are shown in Fig. 7. It’s clearly that the thermal stabilities of the polymers show a very obvious enhancement than the corresponding monomers. The thermal decomposition temperatures (5% mass loss) of PC14E2VE, PC16E2VE, and PC18E2VE were 259ºC, 307ºC and 315ºC, respectively, and the corresponding monomers were 214 ºC, 232 ºC and 237ºC, respectively. The relatively high thermal decomposition temperatures show that the polymers were thermally stable.

CONCLUSIONS

Diethylene glycoln-alkylether vinyl ether CmE2VEs (m=14,16,18) have been synthesized successfully, and then PCmE2VEs (m=14, 16, 18) were obtained by living cationic polymerization. The melting temperatures of PC14E2VE, PC16E2VE and PC18E2VE are 25.8 ºC, 41.9 ºC and 52.9 ºC, and the crystallization temperatures are 15.8 ºC, 30.8 ºC, and 42.4 ºC, respectively. In addition, the enthalpy values of PC14E2VE, PC16E2VE and PC18E2VE are 93 J/g, 103 J/g, and 103 J/g, respectively. They exhibit relatively high thermal decomposition temperatures (5% mass loss), they are 259ºC, 307ºC, and 315ºC, respectively. These new phase change materials can be applied in heat storage, energy conservation, and environmental protection.

Figure 6. DSC curves of PCmE2VEs (m=14,16,18).
Figure 7. TGA (A) and DTG (B) curves of C\textsubscript{m}E\textsubscript{2}VEs and PC\textsubscript{m}E\textsubscript{2}VEs (m=14,16,18).

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (No. 2016YFB0303000) and the New Materials Research Key Program of Tianjin (No. 16ZXCLGX00090).

REFERENCES

