DSC STUDIES ON POLYTETRAHYDROFURANS WITH VARIOUS MOLECULAR MASSES, THEIR BLENDS AND THEIR CURED SAMPLES

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Abstract

DSC studies are given for polytetrahydrofurans with molecular masses equal to 650, 1400, and 2900, for their blends, and for their cured samples. The samples were stored, annealed, and quenched to obtain the samples with different thermal histories.

Two or more endothermic peaks appear in the DSC curves for the stored samples, even for the non-blended samples. A hyperbolic curve forced the plot of the highest melting temperature *vs.* the molecular mass to asymptote to about 50°C. The relationship between the highest melting temperature and the composition for the blended samples is suitable to linear or Fox's relation. A peak and a shoulder appear in the DSC curves of the cured samples. As the samples are cooled at the faster rates in the thermal treatment, the shoulder appears at the lower temperatures.

Keywords: blends, DSC, melting temperature, molecular mass, polytetrahydrofuran

Introduction

Polytetrahydrofuran (PTHF), synthesized by ring-opening cationic polymerization of tetrahydrofuran (THF) [1, 2], is important to industries of rubber, foam, and etc., to become urethane prepolymer with excellent elasticity by being cured with diisocyanate. Curing is conducted in the molten state a little bit over the melting temperature [3]. Therefore, the elasticity is affected by the melting temperature and the chain length between urethane bonds. Accordingly, the molecular mass dependence of the melting temperature is of industrial interest. The melting points of polymers are independent of the molecular masses. However, the molecular masses of PTHF used frequently are in the range of those of oligomers, and influence the melting temperature. In our previous works [4–6], the solution properties and the thermal degradation behaviors of PTHF were elucidated.

In the present paper, DSC studies, particularly, discussion on melting peaks obtained from DSC curves, are given for polytetrahydrofurans with molecular masses

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of 650 (PTHF650), 1400 (PTHF1400), and 2900 (PTHF2900). They were used for this study after blending, curing with isophorondiisocyanate (IPDI), or not treating.

DSC curves (particularly, in vicinity of the glass transition temperature) are dependent on the thermal history of sample [7–9]. The stored, annealed, and quenched samples were used for elucidation of relationship between the thermal history and the DSC behavior.

Experimental

PTHF (Terathane, DuPont product) and IPDI were purchased from Aldrich Chemical Co. and were used without further purification. These melt viscosities (60°C) were obtained using an Ubbelohde viscometer. The blend samples with various compositions were obtained by manually stirring PTHF650 and PTHF2900 in a glass tube by a glass rod at 60°C. The cured samples were obtained by storing 0.0017 mmol of PTHF2900 with 0.00275 or 0.0034 mmol of IPDI in a flame-sealed glass tube for two weeks at 60°C. The former and the latter are called PTHFc 1 and PTHFc 2, respectively. The samples in DSC sample pans were stored, annealed, or quenched under various conditions. The storing was conducted in a thermostat. Annealing and quenching were conducted by use of the DSC apparatus.

The DSC measurements were performed using a Perkin Elmer DSC 7. The temperature was calibrated with indium standard.

Results and discussion

Dependence of melting temperature on molecular mass and thermal history

Figures 1, 2, and 3 show representative DSC curves for PTHF650, PTHF1400, and PTHF2900, stored and quenched. All the peaks are endothermic peaks. These are considered to be melting temperatures. A single endothermic peak appears at about 25°C in the DSC curves for quenched PTHF1400 and PTHF2900 samples. The DSC curves for the stored samples show an extra endothermic peak at a higher temperature. The temperature depends on the molecular mass as shown in Fig. 4. Generally, polymers with molecular masses up to about 1000–2000 show asymptotic increase in melting temperature with increasing molecular mass [10]. The hyperbolic curve tentatively drawn in Fig. 4 is asymptotic to about 50°C that seems to be the melting temperature of THF polymers with a large molecular mass [11].

Two or more peaks on fusion were observed for some crystalline polymers [12, 13]. Gray and Casey [13] showed DSC curves with multiple peaks on fusion of ethylene(94%)/butene(6%) copolymer samples annealed stepwise at various temperatures in vicinity of the melting temperature. They explained this in terms of crystallite size distribution induced by thermal treatment, and not difference in crystallization mechanisms. While it is known for solvent crystallization of polymers that lamellar thickness decreases with the increasing difference in temperature between crystallization and melting [14]. The difference in DSC behavior between the stored and the

quenched samples may reflect difference in period for growth of lamellae: perhaps intramolecular (short period) and intermolecular (long period) crystallization. The crystal structure of PTHF is two essentially planar zigzag chains running through the c-axis [15]. This makes the intermolecular crystallization possible when two planar zigzag chains are different molecules.
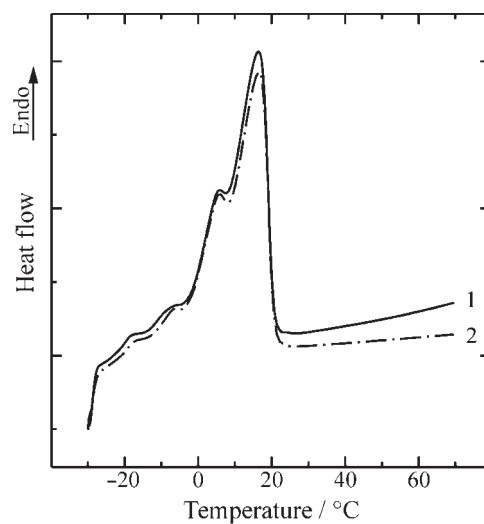

Fig. 1 DSC curves recorded at the heating rate of $10°C$ min^{-1} for PTHF650, 1 – stored at 25°C for 2 weeks and 2 – quenched at –30°C

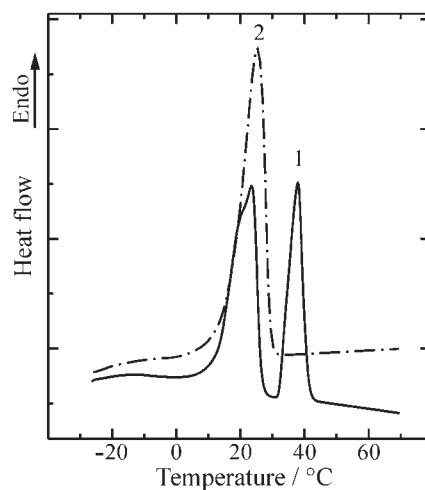**Fig. 2** DSC curves recorded at the heating rate of $10°C$ min^{-1} for PTHF1400, 1 – stored at 25°C for 2 weeks and 2 – quenched at –30°C

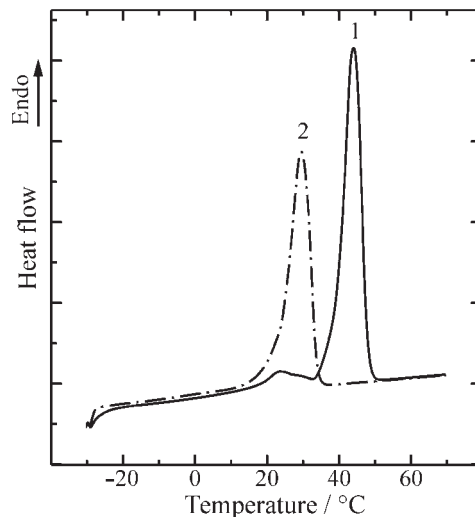**Fig. 3** DSC curves recorded at the heating rate of 10°C min^{-1} for PTHF2900, 1 – stored at 25°C for 2 weeks and 2 – quenched at –30°C
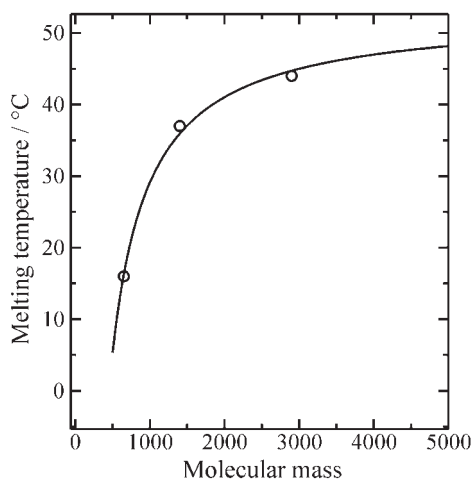

Fig. 4 Plots of the highest melting temperature (T_m) *vs.* the molecular mass (*M*) for the stored samples. The solid line was drawn by use of the equation:
$$T_m = 53 - 24050 \, M$$

Melting temperature vs. composition relations for blends of PTHF's with different molecular masses

Figure 5 shows the composition dependence of the highest melting temperature determined from the DSC curves for the samples stored for periods exceeding 3 months at 25°C. Melting temperature *vs.* composition curves are classified to two types for copolymers (copolyamides) in the literature [16, 17].
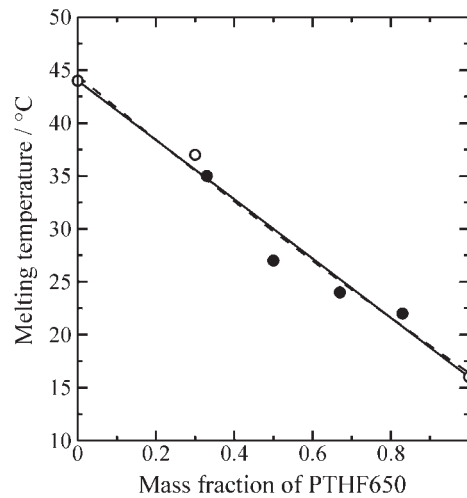
Fig. 5 Melting temperature *vs.* composition relations for PTHF650/PTHF2900 blends. The solid and the broken lines express a linear and a Fox's relations, relatively. The black and the blank circles denote 'blended' and 'not blended'

(a) The relation is approximately explained by the equation for the freezing-point depression:

$$T_m = T_{m_1} (1 + (RT_{m_1}/\Delta H) \ln X_1) \qquad (1)$$

$$T_m = T_{m_2} (1 + (RT_{m_2}/\Delta H) \ln X_2) \qquad (2)$$

where X is the mole fraction, and 1 and 2 denotes component 1 and 2, respectively.

The larger the mole fraction, the lower the melting temperature for both components 1 and 2. Therefore, the plots of the melting temperature *vs.* the composition show a minimum value.

(b) The relation is termed polymer isomorphism by analogy with the more common isomorphism existing among monomeric organic and inorganic crystals. The relationship between melting temperature and composition is linear and the crystal lattice changes with composition.

The (b) type relation is favorable to the present results. This composition dependence is similar to that of the glass transition temperature of compatible polymer blends [18, 19]. The Fox equation [20] are effectively used for the relationship between melting temperature and composition in Fig. 5.

DSC curves of the cured samples

Figure 6 shows DSC curves of PTHFc 2. The samples are cooled to –30°C at various rates, in analogy with a DSC technique for enthalpy relaxation studies [9]. The curves in Figure 6 has a peak independent of the cooling rate and a shoulder of which the temperature lowers with increasing cooling rate. The peak and the shoulder seem to be attributed to fusion of the main crystal and the incomplete crystal recrystallized
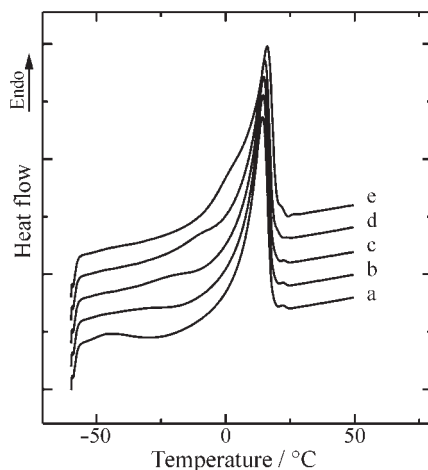
Fig. 6 DSC curves of PTHF2900, cured with IPDI of twice the mole and cooled at various rates: a – 20.0, b – 10.0, c – 5.0, d – 2.0, e – 0.5°C min^{-1}, respectively

due to enthalpy of the main crystallization, respectively [21]. The DSC behaviors of PTHFc 1 are similar to those of PTHFc 2.

Conclusions

The main results obtained from the present study are summarized as follows:

1. Two or more endothermic peaks due to fusion appear in the DSC curves of polytetrahydrofurans with molecular masses equal to 650, 1400, and 2900 and of their blends and their cured samples. This is remarkable for the stored samples. A hyperbolic curve forced the plot of the highest melting temperature *vs.* the molecular mass to asymptote about 50°C.

2. The melting temperature *vs.* composition dependence suitable to a linear or a Fox's relation suggests that the polymers in blends are very compatible.

3. A peak and a shoulder appear in the DSC curves of the cured samples. As the samples are cooled at the faster rates in the thermal treatment, the shoulder appears at the lower temperatures.

In conclusion, these results suggest that the thermal history dependence of DSC behaviors for the polymers, their molecular mass blends, and their cured samples.

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