Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 651–655

MELTING BEHAVIOR OF POLY(TETRAHYDROFURAN)S AND THEIR BLENDS

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Abstract

Melting behavior of poly(tetrahydrofuran)s (PTHF) and their blend with different molecular masses has been studied by TM-DSC. PTHF and their blend show two endothermic peaks on their curve. The melting peak temperatures T_{m1} and T_{m2}, entropy of fusion ΔS_{f1} and ΔS_{f2}, and mean relaxation time for melting τ_{f1} and τ_{f2} have been estimated, and their dependence on the molecular mass has been examined. Plots of T_{m1} to the reciprocal of their molecular mass fit a simple equation ($T_m=a–b/M_n$). Plots of T_{m2} to their molecular mass also fit the equation with different factors. There seems to be a boundary around molecular mass 1200 in the molecular mass dependence of ΔS_f and τ_f. Effect of blending appeared on the τ_f and the non-reversing heat flow.

Keywords: melting behavior, molecular mass blend, molecular mass dependence, poly(tetrahydrofuran), TM-DSC

Introduction

Poly(tetrahydrofuran)(PTHF) is an important component in the preparation of polyurethane elastomers. For this purpose, amorphous or low melting temperature PTHF is preferred for keeping the softness of the elastomer. We have been studying on thermal behaviors of PTHF's oligomers and their blends, and reported that melting temperature of PTHF can be controlled by blending the different molecular mass PTHFs [1].

Some of the PTHF's oligomer and their blend show the multiple endothermic peaks on their DSC curves, and the behaviors depend on the average molecular mass and the thermal history. Such multiple endothermic peaks on DSC curves have been reported about Nylon [2]. Although relationship between the molecular mass of a polymer and the melting temperature have been generalized [3, 4], meaning of the relationship is not clear enough. In addition, the equations suppose the application to an equilibrium crystal of polymers, whereas our interest is on the imperfect crystal produced by quenching of a polymer melt.

We have studied the melting behavior of quenched PTHF and their blend by TM-DSC [5–7] to reveal the dependence on the molecular mass.

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Materials

Poly(tetrahydrofuran)s of molecular mass 650, 1000, 1400 and 2000 were purchased from Wako Pure Chemical Industries. Poly(tetrahydrofuran) of molecular mass 2900 was purchased from Sigma-Aldrich Co. Molecular mass blends of PTHF were prepared by mechanical mixing of PTHF1000 and PTHF2000 at 70°C. For DSC measurement, about 10 mg of the PTHF was placed in an aluminum pan, and the pan was crimped. Since some of the low molecular mass PTHFs was liquid at room temperature, the sample pan was not crimped. All the samples were quenched: each sample was pre-heated at 70°C and then cooled down to –30°C at the cooling rate 100 K min^{-1} in DSC.

Method

Perkin Elmer DSC 7 equipped with a DDSC kit obtained TM-DSC curves of both polymers and their blends. The measurements were carried out in the range from –10 to 50°C. The temperature was controlled by sawtooth modulation: an average heating rate was 1.0 K min^{-1}, amplitude of the modulation was 0.2 K, and the period was 24, 48, 60, 96 and 120 s. Baseline files for TM-DSC measurement were obtained using an empty pan. From the obtained heat-flow curves, the Complex C_p curve ($C(\omega)$), the real part ($C'(\omega)$ curve), the imaginary part ($C''(\omega)$ curve) and Total C_p curve were obtained [4]. The constant C_p and C_∞ were estimated from Cole-Cole's plots assuming that the distribution of relaxation time is unity. Component of reorganization during melting was estimated using the non-reversing components Φ_{non} at the melting peak temperatures [5, 7].

Results and discussion

DSC curves of quenched PTHF1400 measured at several scan rates are shown in Fig. 1. These curves show two endothermic peaks. In this paper, we name these peaks as the 1st peak (the lower temperature) and the 2nd peak (the higher temperature), respectively. We have reported that DSC curve of PTHF1400 stored at 20°C showed only single peak whereas the one quenched showed two peaks [1]. The faster the heating speed the lower the 2nd peak height, whereas the 1st peak does not depend on the heating rate. These phenomena are due to the formation of imperfect crystal: the 2nd peak corresponds to melting of reorganized PTHF crystal that is produced after the 1st melting. The reorganization process should depend on the nature of the polymer chain: flexibility, cohesion between polymer segments, number of end groups, and length of the polymer chain. The plot of the endothermic peak temperatures, T_{m1} and T_{m2}, of quenched PTHFs against the $1/M_n$ are shown in Fig. 2. The T_{m1} data fit on a straight line. The T_{m2} data fit on a different straight line with the same slope as the T_{m1}. Endothermic peak temperatures for an infinite molecular mass sample that is extrapolated from T_{m1} data are different from that of T_{m2}. Plots of entropy change of fusion ΔS_f *vs*. $1/M_n$ are shown in Fig. 3. There seems to be a boundary around molecular mass 1200.

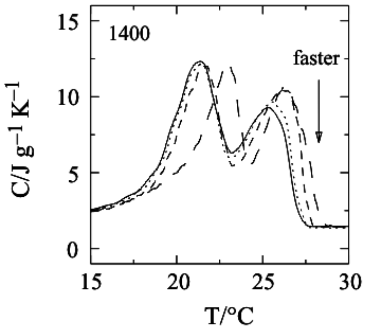

Fig. 1 Total C_p curves of quenched PTHF1400 recorded at the heating rate of 0.5, 0.75, 1.25 and 1.50 K min^{-1}

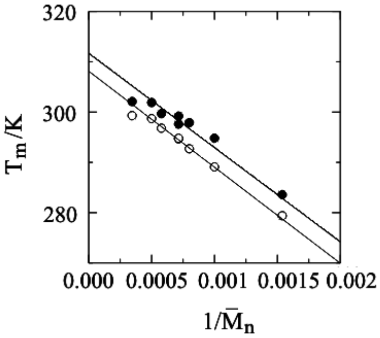

Fig. 2 Relationship between melting peak temperature and reciprocal of the molecular mass of quenched PTHF: o – the 1st peak; ● – the 2nd peak. Solid lines are the results of least mean square analysis, assumed the generalized relationship $(T_m=T_{m,o}-a/x)$ proposed by Wunderlich [3]

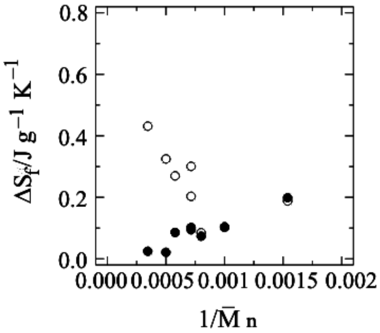

Fig. 3 Plots of entropy change of melting *vs*. reciprocal of the molecular mass. The blanked circle and the filled one denote the same peak as Fig. 2

Temperature modulation measurements also give us some information about the molecular mass dependence on melting process. Analytical methods of crystal melting by TM-DSC have been reported by several workers [6, 7]. Figure 4 shows the

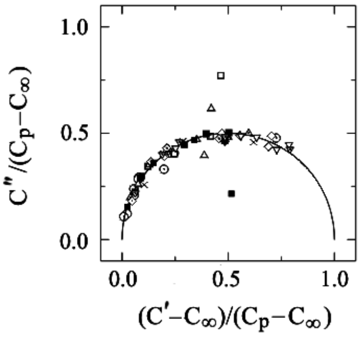

Fig. 4 Cole-Cole's plots of TM-DSC data for PTHF of various molecular masses: Here symbols ω, C_p and C_∞ denote the frequency of modulation, the heat capacity at limit ω=0, the heat capacity at limit ω=∞, respectively. Symbol τ denotes the mean relaxation time for melting

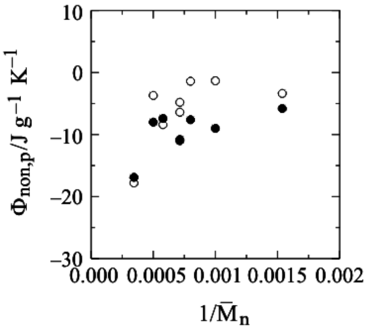

Fig. 5 Plots of non-reversing heat flow at melting peak temperatures *vs.* reciprocal of the molecular mass relations for quenched PTHF

Cole-Cole's plot of TM-DSC data. Most of the data fit on a curve that assumes a single relaxation time. Figure 5 shows molecular mass dependence of non-reversing heat flow at the melting peak temperatures. The exothermic component should be proportional to the heat of reorganization. The 2nd peak always shows larger non-reversing heat flow than the 1st peak. This result suggests that the crystal of the 2nd peak is still metastable, and can be reorganized to more stable structure. Figure 6 shows the plot of mean relaxation time for melting, τ_f, *vs.* $1/M_n$. This can also be divided to two regions at around 1200. This molecular mass, 1200, seems to have a special meaning on melting behavior of PTHF crystal. According to a structural study [8], length of one oxytetramethylene unit in the PTHF crystal is ca. 6 Å. If we can use this value for estimation of chain length of PTHF, chain lengths of PTHF1400 and PTHF1000 are 12 and 8 nm, respectively. These numbers are comparable to lamella thickness of polyethylene [9]. If chain folding of PTHF occurs at length of 10 nm, the chain of the longer PTHF must be folded during reorganization.

In most of the molecular masses, τ_f of the 1st peak is shorter than that of the 2nd peak. The relaxation time τ_{f1} of PTHF1400 is nearly equal to the corresponding mo-

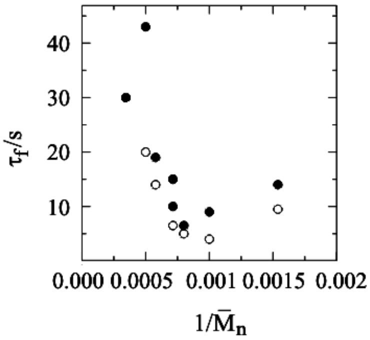

Fig. 6 Plots of mean relaxation time for melting *vs*. reciprocal of the molecular mass relations for quenched PTHF

lecular mass blend, so that this tendency is explained by the less organized structure of the 1st peak crystal.

Conclusions

DSC curve of quenched PTHF shows two endothermic peaks. The peak at higher temperature corresponds to melting of a reorganized polymer crystal. Relationship between melting temperature of quenched PTHF and reciprocal of their average molecular mass fit a simple equation ($T_m=a-b/M_n$). Influence of polymer dispersion to the deviation from the relationship is small. The influence appears on the mean relaxation time of the melting and the heat flow of reorganization. Concerning the molecular mass dependence of melting behavior of PTHF, there seems to be a boundary around molecular mass 1200.

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