

THE DOUBLE ENDOTHERMIC PHENOMENON OF POLYTETRAHYDROFURANS IN THE MELTING TEMPERATURE REGION

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A double endothermic peak appears in the DSC curve of a PTHF oligomer. In order to investigate this phenomenon, a two-component blend of PTHF was prepared with a number average molecular mass of $M=1400$, and the double endothermic phenomena were investigated by TM-DSC. The larger the amount of the long chain component in the PTHF blend, the smaller the difference between the C_p-T curve and the normal DSC curve. The amounts of endothermic energy $\Delta H_{\text{endo},1}$, $\Delta H_{\text{endo},2}$ and exothermic energy $\Delta H_{\text{exo},1}$, $\Delta H_{\text{exo},2}$ in each peak at infinite modulation frequency were estimated.

Keywords: double endotherm, molecular mass blend, polytetrahydrofuran, TM-DSC

Introduction

Polytetrahydrofuran (PTHF), similar to nylon, shows double endothermic peaks on the differential scanning calorimetry (DSC) curve depending on the thermal history [1–3]. This phenomenon may be attributed to the reorganisation processes of the polymer chain. The thermal behaviours of a molar mass blend can be expected to provide information regarding this phenomenon because the kinetic behaviour of each of the oligomers depends on the chain length. We studied the relationship between the mean relaxation time (τ_f) of these endothermic peaks and the average molecular mass of oligomers, and reported that the molecular mass dependence of τ_f changed at $M_n=1200$ [4].

In order to clearly understand this change, we prepared the molar mass blends and studied their thermal behaviours by temperature-modulated DSC (TM-DSC). On the basis of the frequency dependence of TM-DSC curves, we were able to identify the endothermic and exothermic parts in a curve [5, 6]. The endothermic/exothermic parts of PTHF1400 curves, which were different from the TM-DSC curves, displayed one peak on each curve. On the other hand, double peaks appeared in the conventional DSC curve of this oligomer. The results of molar mass blends differ from those of PTHF1400 with regard to curves. The conventional DSC as well as the endothermic/exothermic curves obtained from TM-DSC displayed double peaks in the melting temperature region.

Experimental

Materials

Polytetrahydrofurans with molar masses of 650, 1000, 1400 and 2000 were purchased from Wako Pure Chemical Industries. Those with molecular masses of 250 and 2900 were purchased from Sigma Aldrich Co. A pair of PTHF oligomers was melted at 70°C and mechanically mixed to prepare a molecular mass blend. The mixture ratio of the two components was adjusted such that the number average molecular mass for each of these components was set as 1400. The mass composition of the prepared PTHF blends is summarised in Table 1.

Method

DSC and TM-DSC were performed using Perkin-Elmer DSC7 equipped with a DDSC kit. Approximately 10 mg of the PTHF blend was placed in an aluminium pan and covered with an aluminium lid. All the samples were quenched by preheating at 70°C; they were then cooled down to –30°C at a cooling rate of 100 K min⁻¹ in DSC. The measurements were conducted in the range from –10 to 50°C. In the TM-DSC experiments, the temperature was controlled by sawtooth modulation without cooling. The average heating rate was 1.0 K min⁻¹ and the amplitude of modulation was 0.2 K. Using our equipment, the modulation periods, which are a combination of the programming rate and amplitude, were selected as 24, 48, 60, 96 and 120 s [5–7]. Baseline files for modulations were obtained using an empty pan.

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Table 1 Composition and calculated molar masses of PTHF molar mass blends

Sample	M_w	M_n	M_w/M_n	X_{long}	PTHF				
					250	650	1000	2000	2900
1	1583	1412	1.12	0.41			0.59	0.41	
2	1730	1413	1.22	0.57		0.43		0.57	
3	1844	1411	1.31	0.22			0.78		0.21
4	1895	1407	1.35	0.66	0.34			0.66	
5	2208	1404	1.57	0.34		0.66			0.34
6	2635	1408	1.87	0.44	0.56				0.44

Analysis

The analysis method employed in TM-DSC is the same as that employed in previous reports [4, 7]. The heat capacity (C_p) and heat capacity at high modulation frequencies (C_∞) were calculated by the least-squares method from the Cole–Cole plot at each of the experimental temperatures [7]. An exothermic component, F_{exo} , was estimated by subtracting C_p from the total C_p at the melting temperature [5, 6]. The amount of endotherm in a double endotherm phenomenon was calculated by subtracting C_∞ from C_p . The crystallisation temperature and the heat of crystallisation of each sample were estimated by DSC.

Results and discussion

Figure 1 shows the curves of the PTHF oligomers and their molecular mass blends obtained from the TM-DSC data. Figure 1d shows an exotherm, F_{exo} , with a double endotherm phenomenon that is observed across all samples. The onset temperature of the total C_p curve, $T_{1,onset}$, of blend samples was 2°C lower than that of F_{exo} curve, $T_{exo,1,onset}$. On the other hand, both onset temperatures were almost equal for one component sample. The F_{exo} of sample 1 increased discontinuously at the 1st endothermic peak temperature of the total C_p curve. Such a change was not observed in the case of pure PTHFs. This suggests that the reorganisation process is induced by the lower molecular mass component of the blended sample after the melting process. This may be explained on the basis of the amount of the amorphous portion and the motility of each component.

The size of a fine crystal is known to depend on the crystallisation temperature. The relationship between $T_{1,onset}$ and $T_{c,onset}$ of PTHFs is shown in Fig. 2. A linear relationship between the crystallisation and melting temperatures is observed when the blend contains a long-chain component. This result suggests that a crystal in a blend containing PTHF2900 is larger than that in a blend containing PTHF2000, provided the crystal has been crystallised at the same temperature.

Moreover, since the data points of pure PTHF1400 fall on the correlation straight line of blends containing PTHF2000, the blends containing PTHF2000 are suitable for investigating PTHF1400. Although the relationship between T_c and X_{long} may be approximated by a linear equation, the data points of pure PTHFs are far away from the line.

Table 2 summarises the enthalpy change of PTHF blends during the double endothermic peak analysis. It is revealed that the sum of endotherms and exotherms in a melting process balances the heat of crystallisation in a majority of samples, including pure PTHF. The value of 76 J g⁻¹ for $\Delta H_{endo,1}$ of PTHF1400 is superfluous to ΔH_c . It is believed that the amount of heat required for this phenomenon, i.e. $\Delta H_{endo,1} + \Delta H_c$, is equivalent to the heat of fusion of the crystal produced at the 1st endothermic peak and is in excess. Since the sum of all heats falls within the experimental error limit, all the crystals produced at the 2nd endothermic peak are assumed to melt at the 2nd endothermic peak temperature.

Table 2 The enthalpy change in PTHF blends during the double endothermic peaks obtained by TM-DSC

Sample	ΔH_c	$\Delta H_{endo,1}$	$\Delta H_{exo,1}$	$\Delta H_{endo,2}$	$\Delta H_{exo,2}$
1	-89	94	-38	96	-61
2	-90	85	-38	91	-55
3	-85	75	-44	100	-59
4	-89	169	-92	41	-18
5	-91	95	-57	91	-57
6	-85	225	-164	53	-35
PTHF1400	-107	183	-98	38	-14

ΔH in J g⁻¹

The 2nd peak of the double endotherm phenomenon may appear as a result of the following: (1) when a sufficiently large crystal is created by reorganisation and (2) when different-sized crystals are present from the start. In case (1), the sum of $\Delta H_{endo,1}$ and ΔH_c should be smaller than $-\Delta H_{exo,1}$ because large crystals that are generated by reorganisation do not melt in

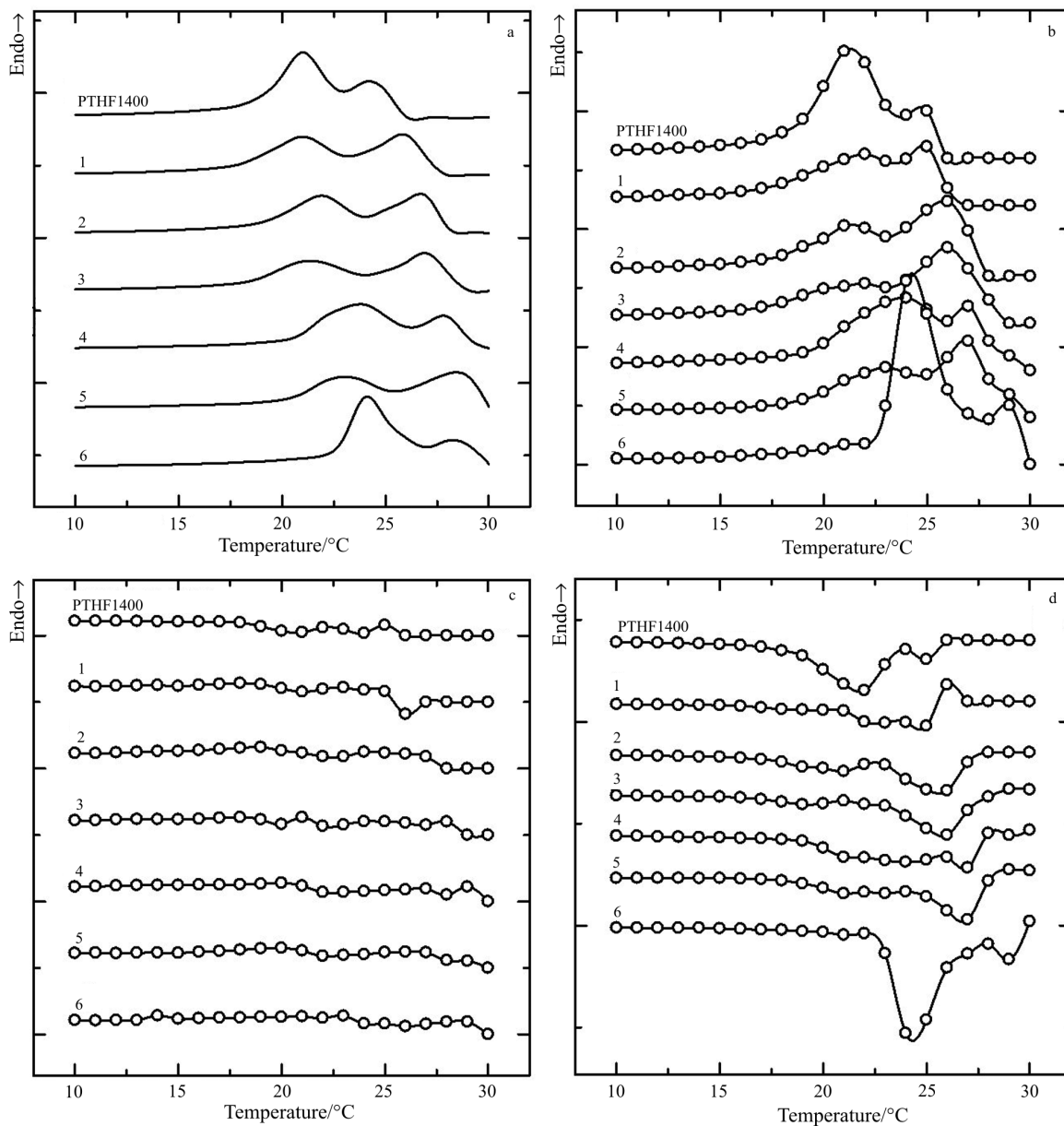


Fig. 1 The curves and molecular mass blends of the PTHF oligomers obtained from the TM-DSC data: a – total C_p curves, b – C_p curves, c – C_s curves, d – F_{exo} curves. The numbers presented on the left hand side of each line correspond to the sample numbers in Table 1

the 1st endothermic peak. The results presented in Table 2 support (1) as the double endotherm phenomenon is observed with PTHF and its blend.

Figure 3 shows the relationship between the fraction of exotherm over the endotherm in the 1st endothermic peak and X_{long} of the blended PTHF. This figure also shows that the long-chain component in the molar mass blend is strongly associated with reorganisation.

In the case of samples 1, 2 and 5, the absolute values of ΔH_c and $\Delta H_{\text{endo},1}$ are almost equal; further, the value of $\Delta H_{\text{exo},1}$ is not very large. This suggests that the reorganisation of these samples is not very active at

the 1st endothermic peak. In the case of sample 1, F_{exo} is discontinuously increased near the end temperature of the 1st endothermic peak. We have already reported that the melting relaxation time of pure PTHF2000, which is of the long-chain component of sample 1, is slower than that of PTHF1000 [4]. This discontinuous increase in F_{exo} , observed in sample 1, is considered for reorganisation to receive restriction by slow relaxation of the molecular chain of PTHF2000.

The sum of $\Delta H_{\text{endo},2}$ and $\Delta H_{\text{exo},2}$ as well as the sum of ΔH_c , $\Delta H_{\text{endo},1}$ and $\Delta H_{\text{exo},1}$ must be equal to the heat of fusion of the crystal that exists below the onset temperature of the 2nd endothermic peak of the total

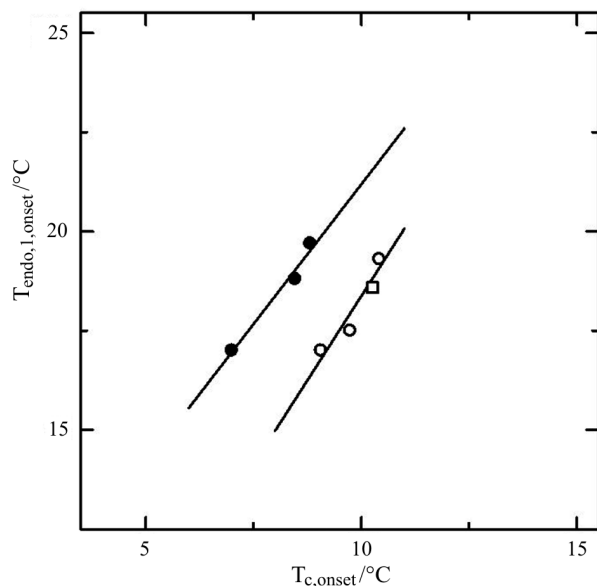


Fig. 2 Relationship between the crystallisation temperature and the melting temperature: ● – PTHF2900 blend, ○ – PTHF2000 blend, □ – PTHF1400 blend

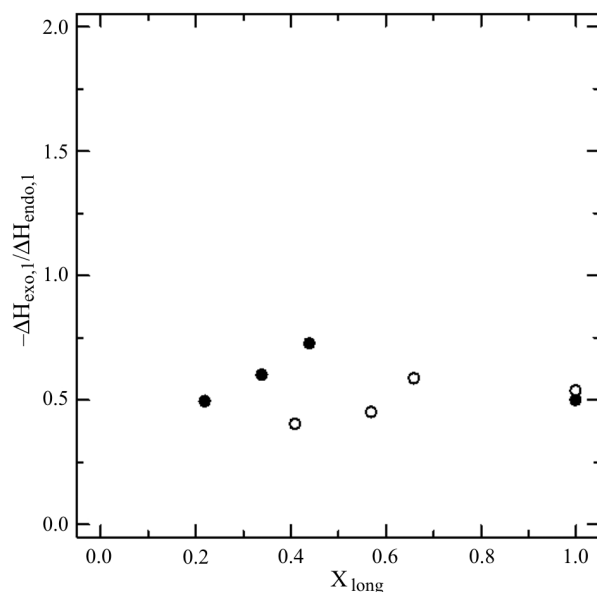


Fig. 3 Relationship between $(-\Delta H_{\text{exo},1}/\Delta H_{\text{endo},1})$ and mass fraction of the long-chain component in PTHF blend: ● – PTHF2900 blend; ○ – PTHF2000 blend

C_p curve. Figure 4 shows the relationship between the amount of heat in each peak, which is estimated from TM-DSC data, and the amount of endotherm obtained from the total C_p curve. The endotherm obtained from the total C_p curve is in good correlation with these quantities. This suggests that the 2nd peak of a total C_p curve directly represents the heat of fusion and degree of perfection of a crystal that is created at the 1st peak.

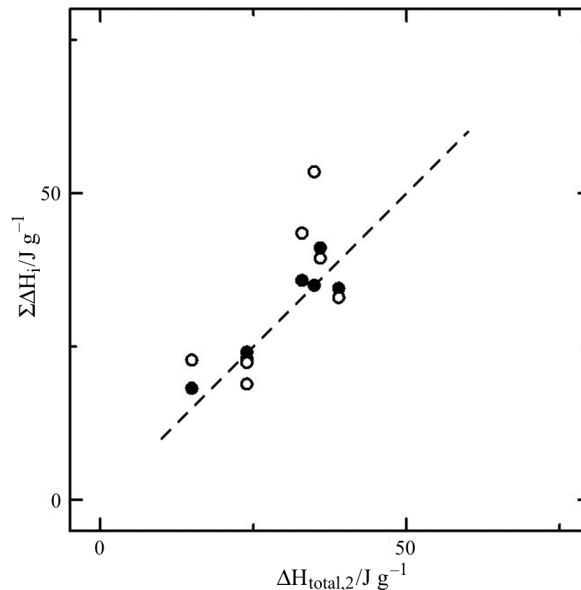


Fig. 4 The relation between the amount of heat in each peak estimated from TM-DSC data and the amount of endotherm obtained from a total C_p curve: ● – $(-\Delta H_{\text{endo},2} + \Delta H_{\text{exo},2})$, ○ – $(-\Delta H_c + \Delta H_{\text{endo},1} + \Delta H_{\text{exo},1})$

Conclusions

Double endothermic peak appears on the DSC curve of PTHF due to reorganisation of the polymer chain that occurs superfluously rather than by the melting of tiny crystals. The 2nd endothermic peak observed at non-modulated temperature during the DSC measurement corresponds to the melting temperature of a large crystal that is formed at the temperature of the 1st peak. A long-chain component in blended samples interferes with the reorganisation process of the PTHF chain. The double endotherm phenomenon appearing on the DSC curve of PTHF1400 is the result of the ability of the PTHF chain to move easily in the melt and form a crystal with a high degree of perfection.

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