

MOLAR-MASS DEPENDENCE OF APPARENT RELAXATION TIME IN MELTING REGION OF POLY(OXYTETRAMETHYLENE)GLYCOL

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Melting behaviours of poly(oxytetramethylene)glycols (POTMGs) with different molar masses were investigated by temperature-modulated differential scanning calorimetry (TMDSC) and relaxation times within the melting range were estimated from the modulation-frequency dependence of phase angle δ . An Arrhenius plot of the relaxation times exhibited a plateau in the lower melting peak region of POTMGs with molar masses of 1400, 1000 and 650. This plot was compared with the standard DSC curve. The apparent activation energy was estimated from the relaxation time in the upper and lower sides of a melting temperature region: slight dependence on the molar mass was observed for the former region whereas the maximum value was obtained for a molar mass 1400 for the latter region.

Keywords: poly(oxytetramethylene)glycol, polytetrahydrofuran, relaxation time, temperature dependence, TMDSC

Introduction

The properties of a polymer solid are influenced by the crystallinity, thermal history and molar mass [1]. In particular, oligomers are influenced by the molar mass. The crystallization process of a polymer is expected to be dependent on the molar mass. On the other hand, a multiple endothermic phenomenon has occasionally been observed within the melting temperature range of crystalline polymers [2–5]. Since this phenomenon can be attributed to a variety of reasons, it is important to identify its mechanism in order to understand the crystallization and melting processes of a polymer.

Pak *et al.* studied the supercooling phenomena of linear polymers by temperature-modulated differential scanning calorimetry (TMDSC), and determined the critical number of backbone atoms required for molecular-nucleation-induced supercooling [6]. TMDSC can be used to determine the complex heat capacity, which depends on the modulation frequency. Therefore, the modulation-frequency dependence determined by TMDSC provides kinetic information such as the relaxation time. This technique may directly yield information about the motion of segments in macromolecules [7].

The author *et al.* have been studying the melting behaviours of poly(oxytetramethylene)glycol having a molar mass of less than 3000, which is used for producing polyurethane elastomers [8]. The DSC curve of poly(oxytetramethylene) glycol (POTMG) exhibits double endothermic peaks that depend on the molar mass of POTMG. This phenomenon is observed when the molar mass of POTMG is significantly less than

1400. The occurrence of the double endothermic peaks was attributed to the melting of metastable crystals and pure large crystals.

In order to obtain more information about the relationship between the multiple endothermic phenomena and the critical molar mass, we have compared the apparent relaxation times in the melting temperature region for samples with different molar masses.

Experimental

Materials

POTMG samples with molar masses of 650 (600–700), 1000 (950–1050), 1400 (1350–1450) and 2000 (1900–2120) were purchased from Wako Pure Chemical Industries, Ltd., and one having a molar mass of 2900 was purchased from Sigma Aldrich Co. These materials were used without further purification. These oligomers were named as POTMG650, POTMG1000, POTMG1400, POTMG2000 and POTMG2900, corresponding to molar masses of 650, 1000, 1400, 2000 and 2900, respectively.

Methods

DSC experiments

The DSC experimental methods were the same as those reported elsewhere [8, 9]. A PerkinElmer DSC 7 equipped with a DDSC kit was used for the experiments. Approximately 10 mg of the sample was

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placed in an aluminium pan that was then covered with an aluminium lid. All samples were preheated at 50°C (above the melting temperature of POTMGs) and subsequently cooled to -50°C at a cooling rate of 50 K min⁻¹ in the DSC. In the TMDSC experiments, the temperature was controlled by saw-tooth modulation without cooling. The average heating rate was 1.0 K min⁻¹ and the amplitude of modulation was 0.2 K. By using our equipment, the modulation periods, which are a combination of the programming heating rate and the amplitude, were selected as 24, 48, 60 and 96 s. Baseline files for the modulations were obtained using an empty pan. The total C_p curve, which can be obtained from the standard DSC, was obtained from the TMDSC data.

Data analysis

From tanδ-T curves of the different modulation frequencies, the phase angle spectra within the melting temperature region were obtained by plotting the tanδ value vs. the modulation frequency ω. The spectra were analysed by the following equation:

$$\tan\delta = \frac{C''(\omega)}{C'(\omega)} = \frac{\alpha_1 \omega \tau_1^2 (1 + \omega^2 \tau_2^2) + \alpha_2 \omega \tau_2^2 (1 + \omega^2 \tau_1^2)}{\alpha_1 \tau_1 (1 + \omega^2 \tau_2^2) + \alpha_2 \tau_2 (1 + \omega^2 \tau_1^2)} \quad (1)$$

where τ, α, C'(ω) and C''(ω) denote the relaxation time, fraction of a component, real part and imaginary part of the complex heat capacity, respectively [8]. The relaxation times τ₁ and τ₂ and their respective fractions α₁ and α₂ were estimated by non-linear fitting (Marquardt method).

Results and discussion

Data analysis

The modulation-frequency dependence of the phase below the melting temperature region was analyzed by Eq. (1). Figure 1 shows the phase angle spectra of POTMG1400. The calculated curves approximately fit the experimental data. In any case, the relaxation time of the faster component, τ₂, was approximately 0.1 s, which is nearly equal to the relaxation time of the melting temperature region of POTMG. Moreover, the fraction ratio α₂ was larger than the longer relaxation-time component α₁. Therefore, the faster relaxation process can be assumed to be independent of the melting of POTMGs.

Figure 2 shows plots of C_p vs. α₁ for POTMGs. The data of POTMG2900 and POTMG2000 fit on almost identical lines. Although POTMG650 exhibits

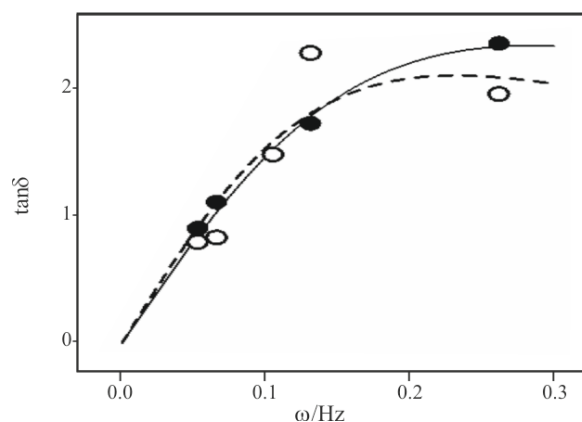


Fig. 1 Phase angle spectra of POTMG1400: ● - 20; ○ - 25°C

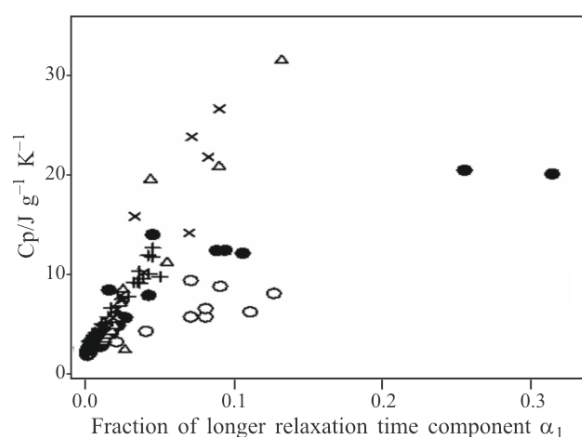


Fig. 2 Plots of the longer relaxation time τ₁ vs. fraction of the component α₁: + - POTMG650, ○ - POTMG1000, ● - POTMG1400, □ - POTMG2000 and × - POTMG2900

a double endothermic phenomenon in the same manner as POTMG1000 or POTMG1400 on the DSC curve, the data fit on the same line. However, the difference from the line appears to increase with the order of the molar mass of these POTMGs. Therefore, the C_p-α₁ plot may suggest the cause of this phenomenon.

Temperature dependence of relaxation time

Relaxation time is the time required for a certain change of population in a state. An Arrhenius plot of the relaxation time shows the ease of movement of the macromolecular segment in the temperature region. Figure 3 shows the Arrhenius plot of the relaxation time τ₁ for POTMG1000 and POTMG1400. Each plot may be divided into four regions based on the behaviour of the relaxation time increasing with temperature: relaxation time increases below the melting region (I), the change in the relaxation times is small (II), relaxation time increases (III) and relaxation time decreases above the melting peak temperature (IV).

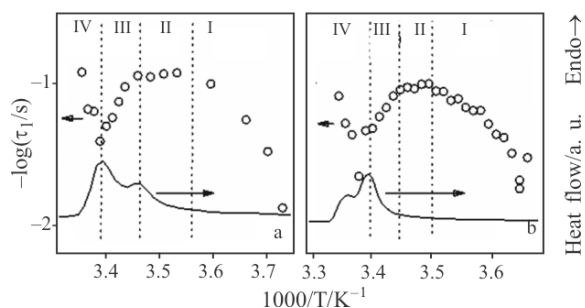


Fig. 3 Arrhenius plots of the relaxation time τ_1 for POTMGs. Solid curve is the standard DSC curve as a function of the reciprocal of the temperature. a – POTMG1000 and b – POTMG1400

Within temperature region I, the system is in the solid state. Therefore, the relaxation time observed in this region is considered to reflect the relaxation of the structure of the solid or the diffusion of small molecules or segments. In region II, the temperature dependence of the relaxation time is small, and the relaxation time is as short as 10 s. Therefore, the melting of small crystals having low crystallinity and the recrystallization of the melt, which is expected in this region, may be responsible for the small temperature dependency. In the case of POTMG1000, an endothermic peak was observed in this region. Pak *et al.* reported that the melting peak was dependent on the thermal history [pak03]. This was also observed in the case of POTMG650. These results suggest that the melting of crystals having low crystallinity causes the endothermic peak at low temperature in the double endothermic peaks. In region III, both the heat flow by the melting of the crystal and the relaxation time increased with temperature, although the increasing temperature increased the speed of movements. The opposite dependence in this region may be explained by the change in size responsible for the relaxation motion. In region IV, the behaviour is almost the same as that in region I, although the system is not in the solid state. The system can be considered to be in a transient state between a crystalline structure and a melted structure. Therefore, the decrease in the relaxation time with the increase in temperature can correlate to the diffusion of the molecule or their segment.

Apparent activation energies

The relaxation time can be correlated to the relaxation of the structure of the solid or diffusion of the small molecule or segments in region I, and to the diffusion of the polymer chain from crystal-like arrangements in region IV. The apparent activation energy for these temperature regions has been estimated, and the results of samples with different molar masses are compared in Fig. 4. A critical molar mass for the apparent

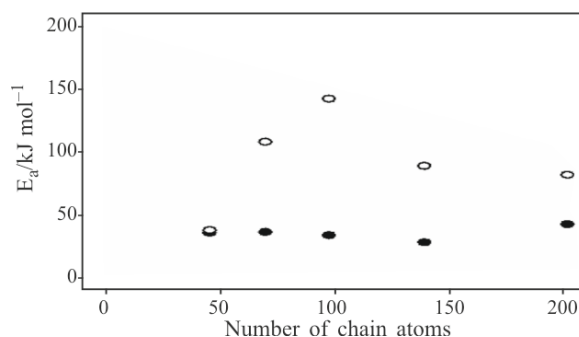


Fig. 4 Plots of apparent activation energy vs. the number of chain atoms in the backbone of the POTMG. Filled and unfilled circles denote below the melting temperature region and above the melting peak temperature region, respectively

activation energy is observed in region IV, whereas little dependence of the activation energy on the molar mass was observed in region I. The activation energy increased with the molar mass in the range of 650 to 1400; however, little change was observed above a molar mass of 2000. Although the molar mass dependence of the activation energy in the former case may be attributable to the high mobility of small molecules, the larger activation energy of POTMG1400 than POTMG2000 or POTMG2900 suggests other causes. In the case of a molar mass of 1400, the relaxation times within the lower endothermic temperature region changed with the heat flow. This is the same tendency as that of POTMGs with molar masses of 2000 and 2900. The activation energy of POTMG1400 after the melting process was larger than that of the molar masses of POTMG2000 and POTMG2900. Since a crystal of POTMG1400 melting at the second melting temperature is expected to have higher crystallinity, this large activation energy may be attributed to the crystallinity.

Conclusions

A multiple endothermic phenomenon of poly(oxy-tetramethylene)glycol oligomers was studied by comparing the DSC curve and the Arrhenius plot of the apparent relaxation time. The cause of the double endothermic phenomenon of POTMG1400 has been distinguished from that of the lower-mass oligomers: the melting of loose crystals and metastable crystals may be the cause of the double endothermic phenomena of POTMG with molar masses of 650 and 1000, whereas the melting of metastable crystals and more stable crystals produced by cold crystallization from the melt of the metastable crystal may be the cause of the phenomenon of POTMG1400. The critical molar mass or number of backbone atoms of a double endothermic phenomenon can be considered as the results of the

ease of crystallization with a high crystallinity and the ease of the diffusion of the molecule from the molten state: the longer the polymer, the higher the possibility of producing a high crystallinity crystal; however, this will lead to a slower reorganization process.

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