

APPLICATION OF THE LIGHT HEATING DYNAMIC DSC TO POLYMERIC MATERIALS

Y. Saruyama

Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Abstract

Light heating dynamic DSC was used to study the melting transition of polyethylene. The results show that melting and crystallization are different phenomena from each other in terms of the complex heat capacity. Frequency dependence of the complex heat capacity was examined from 0.01 Hz to 0.2 Hz. It is found that at the lowest frequency the phase of the complex heat capacity exceeds $\pi/2$ radians. Thermodynamic considerations were made for the large phase of the complex heat capacity.

Keywords: dynamic DSC, frequency dependence, light heating, melting, polyethylene

Introduction

Dynamic DSC (DDSC) is a combination of the ac calorimetry and DSC techniques. In the DDSC technique a modulated heat flow is applied to a sample and reference to generate cyclic temperature changes. We constructed a DDSC apparatus in which modulated light is used to generate the modulated heat flow [1, 2]. This is an alternative of the commercial DDSC apparatus in which a sinusoidal temperature profile is superimposed onto the steady heating/cooling of a conventional DSC [3, 4]. DDSC has been successfully applied to separation of heat absorption/emission accompanying irreversible process from the underlying heat capacity [3-5] and quantitative measurement of heat capacity with reduced time and improved accuracy [6, 7]. Application to the glass transitions and interpretation of their results are extensively studied. On the other hand the first order phase transitions have been studied by only a few authors [8-10]. In this paper we will report experimental results around the melting temperature of polyethylene crystals using the light heating DDSC. We will pay attention to frequency dependence of the results, because we will be able to obtain kinetic information of melting from the frequency dependence [11].

Experimental

Sample material was polyethylene (NIST SRM1475, $M_w = 5.2 \times 10^4$, $M_w/M_n = 2.9$). The measured sample was 0.1 mm thick and 1.5 mg of mass. Ordinary aluminum pan and lid were used. The upper surface of the lid was coated with carbon

black for light absorption. Light heating DDSC apparatus constructed in our laboratory was used [1, 2]. The modulated light was incident to both the sample and reference sides. Two types of measurement were made. Firstly, a wide temperature range from 312 to 440 K was studied with the modulation frequency of 0.1 Hz and the heating rate of the furnace of 1 K min^{-1} . Secondly, frequency dependence was studied at 0.01 Hz, 0.02 Hz, 0.05 Hz, 0.1 Hz and 0.2 Hz. At all these frequencies the heating rate was 0.1 K min^{-1} and the temperature range was from 394 to 413 K. Calibration method to obtain the complex heat capacity was reported elsewhere [2, 8].

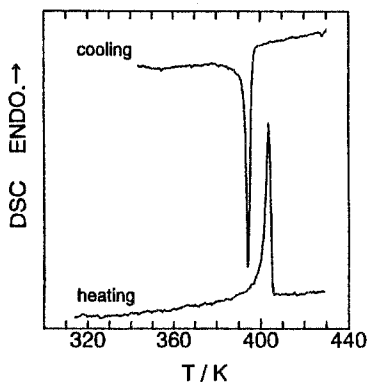


Fig. 1 Total heat flow of polyethylene. Heating rate: 1 K min^{-1}

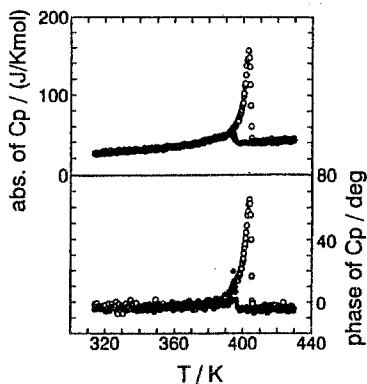


Fig. 2 Complex heat capacity of polyethylene. The upper and lower curves are the absolute value and the phase, respectively. The open and solid circles are the heating and cooling processes, respectively. Modulation frequency: 0.1 Hz. Heating rate: 1 K min^{-1}

Results and discussion

Figures 1 and 2 show the results of heating and cooling processes at 1 K min^{-1} . Figure 1 shows the total heat flow which is same with the results of the conventional DSC. Figure 2 shows the complex heat capacity; the upper and lower curves are the

absolute value and the phase, respectively. The open and solid circles are the heating and cooling processes, respectively. Melting and crystallization temperature ranges can be estimated from Fig. 1. It is apparent from Fig. 2 that the complex heat capacities on the heating and cooling processes exhibit distinctive behavior from each other. Small anomaly of the phase on the cooling process can be attributed to the irreversible nature of the crystallization from the supercooled liquid. From the phase shift on the cooling process we can obtain temperature dependence of the crystallization rate [9, 12]. Large peaks of both the absolute value and the phase on the heating process suggest notable coupling between the modulated heat flow and the phase transition. Frequency dependence was studied on the heating process.

Figure 3 shows frequency dependence of the complex heat capacity. The horizontal and vertical axes are the real and imaginary parts of the complex heat capacity, respectively. The modulation frequencies are given in the graph. At each frequency the observed point moves counterclockwise as temperature increases. At the lowest frequency, 0.01 Hz, the curve exhibits large shift to the negative direction of the real axis. At 0.02 Hz the top of the curve is shifted to the negative direction, too. These results suggest that there is notable tendency to shift to the negative direction as the frequency becomes lower. This frequency dependence is quite anomalous. In typical dispersion phenomenon, such as the mechanical or dielectric dispersion around the glass transition temperature, the real part of the elastic or dielectric constant becomes larger as the frequency becomes lower.

It should be remembered that melting of a polymeric material is a very complicated phenomenon. At a temperature in the melting temperature range of a polymeric material the system is far from the equilibrium state and various phenomena occur simultaneously. Small and defective crystals melt at lower temperatures, but the liquid state is not the most stable state because the temperature is lower than the equilibrium melting temperature. The liquid state has tendency to recrystallize, but the rate of the recrystallization is low because of the entanglement of the chain

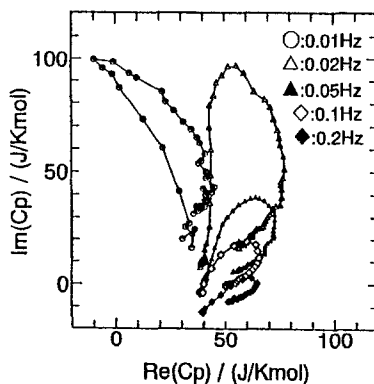


Fig. 3 Frequency dependence of the complex heat capacity. The horizontal and vertical axes show the real and imaginary parts, respectively. Measured temperature range is between 394 and 413 K. Observed point moves counterclockwise along each curve as temperature increases. Frequencies are given in the graph

molecules, fixed chain ends by the remaining crystals and narrow space surrounded by the remaining crystals. The remaining crystals have tendency to become thicker, but the thickening rate is also low because the long chain molecule can not move easily in the crystal. These transition phenomena are coupled with the modulated heat flow, that is, these transition phenomena contribute to the complex heat capacity and generate dispersion effect. There are two essential difference between dispersion phenomena of the complex heat capacity during the melting transition and the glass transition. Firstly, the melting transition contains the recrystallization which is irreversible process accompanying heat emission. Secondly, the recrystallization and the thickening of the crystal might have retardation time. The observed frequency dependence shown in Fig. 3 may be attributed to these characteristic features of the melting transition.

Conclusion

This is, as far as we know, the first report of frequency dependence of the complex heat capacity around melting transition temperature of a polymeric material over frequency range of one decade. The results were distinctive comparing with frequency dependence around the glass transition temperature [11]. Possible origins of the observed frequency dependence were considered.

References

- 1 M. Nishikawa and Y. Saruyama, *Thermochim. Acta*, 267 (1995) 75.
- 2 Y. Saruyama, *Thermochim. Acta*, 283 (1996) 157.
- 3 P. S. Gill, S. R. Sauerbrunn and M. Reading, *J. Thermal Anal.*, 40 (1993) 931.
- 4 M. Reading, D. Elliott and V. L. Hill, *J. Thermal Anal.*, 40 (1993) 949.
- 5 G. Van Assche, A. Van Hemelrijck, H. Rahier and B. Van Mele, *Thermochim. Acta*, 268 (1995) 121.
- 6 B. Wunderlich, Y. Jin and A. Boller, *Thermochim. Acta*, 238 (1994) 277.
- 7 A. Boller, Y. Jin and B. Wunderlich, *J. Thermal Anal.*, 42 (1994) 307.
- 8 Y. Saruyama, submitted to *Thermochim. Acta*.
- 9 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, *Polymer*, 38 (1997) 231.
- 10 M. Reading, A. Luget and R. Wilson, *Thermochim. Acta*, 238 (1994) 295.
- 11 N. O. Birge, *Phys. Rev.*, B34 (1986) 1631.
- 12 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, submitted to *Thermochim. Acta*.