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QUASI-ISOTHERMAL MEASUREMENT BY TMDSC IN ISOTACTIC POLYPROPYLENE

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We measure the frequency dependences of complex heat flows for isothermally crystallized isotactic polypropylene (iPP) by the quasi-isothermal TMDSC. Regarding the quasi-isothermal melting processes as a kind of the single relaxation process, we analyze them by the Debye model. The resultant heat capacity of iPP is larger (about 11%) than usual thermodynamic heat capacity. We also found that the excess of the heat capacity, C_p (excess), has non-monotonous temperature dependence. A simple model introducing some kinetic modes into amorphous producing after and during temperature modulation can reproduce the temperature dependence of C_p (excess) very well.

Keywords: *Debye process, excess heat capacity, isotactic polypropylene, quasi-isothermal TMDSC*

Introduction

In generally, a crystallization with a first order phase transition is not reversible process because super-cooling is always needed for its crystal growth. On the other hand, for polymer crystallites, this is not the case due to their meta-stability; i.e., they will melt below the equilibrium melting point while the crystal growth is still possible. This reversibility can be further studied by thermal analysis techniques employing a periodical modulation to the temperature, so-called temperature modulated differential scanning calorimetry (TMDSC) measurements [1–6]. In these measurements, observed heat flow can be divided into an underlying part and dynamic part expressed as a first-harmonic form of the temperature modulation which is called the 'reversing heat flow' of the sample.

By TMDSC, a reversing heat capacity corresponding to the reversing heat flow has been observed for various kinds of polymers and they are explained as an indication to the re-crystallization behavior in the melting processes [7–10]. In TMDSC measurement, the heat capacity contains two kinds of contributions: one is the thermodynamic heat capacity generated by local thermal vibration of the atoms, and the other is the excess heat capacity generated by some thermal processes. The excess reversing heat capacity from long-chain molecules were reported in heating processes in TMDSC [7]. These results indicate that there is an additional thermal behavior besides usual local thermal vibration of molecule. For polyethylene (PE) case, observed excess (about 20%) heat capacity can be explained by melting – re-crystallization behavior together with sliding diffusion of the chains in the crystals [7].

On the other hand, the structure formation during isothermal crystallization and melting processes of isotactic polypropylene (iPP) is observed by temperature dependent SAXS experiments [11]. It is found that the lamella thickness remains essentially constant during both the isothermal crystallization and the subsequent heating.

In this study, we have measured the excess heat capacity of iPP by the quasi-isothermal TMDSC after isothermal crystallization. We observed clear excess (about 11%) heat capacity around the melting region and found that there are slightly modulation frequency dependences in the excess heat capacity. From the SAXS experimental results that the lamella thickness of iPP keeps constant and has no sliding diffusion during heating [11]. Therefore, the excess of heat capacity may attribute to chain kinetics of iPP which is different from PE case. We also found the modulation time dependence for the additional heat capacity. These results suggest that there may be somewhat change in isothermal crystallization of iPP in the melting region. Based on these facts, the obtained excess heat capacity is analyzed by the Debye model [10] in this study and then we obtain a non-kinetic part of the heat capacity $C_p(\infty)$ and the thermal relaxation strength ΔC, respectively. For the resultant $C_p(\infty)$, we analyze them by a formula of a simple model which describe the excess heat capacity by crystallites and amorphous generated after temperature modulation (named 'new-born amorphous'). We found that the simple formula reproduce experimental data quite well.

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Experimental

Sample preparation

The sample iPP was synthesized in the Institute of Macromolecular Chemistry of Fakultät für Physik der Albert-Ludwigs-Universität. The isotacticity of iPP is over 0.98. The number-averaged molecular mass of iPP is M_n=32000 g mol^{-1} and the mass-averaged molecular mass of that is M_w=56000 mol^{-1}. Powdery sample was put in an aluminum pan and covered by an aluminum lid. Sample mass was 6.0 mg. Before quasi-isothermal measurement, the sample in the pan was crystallized in isothermal at 145°C for 1200 min after annealing at 250°C for 20 min. The heating rate to 250°C was 30 K min^{-1} and the cooling rate from 250 to 145°C was 30 K min^{-1}.

Instrumentation

The DSC and TMDSC measurement used in this work was Mettler Toledo DSC822^e module with high accuracy thermo-pile 'FRS5' sensor which has 56-fold thermocouples.

The quasi-isothermal measurements were carried out by TMDSC. The temperature was increased stepwise from 145 to 180°C by increment of 1 K for the 60 min (full modulation time t_d) at each step. Amplitude of the temperature modulation was 0.5 K.

The modulation period was fixed during one scan. The measured periods (t_p) were 90, 600, 900 and 1500 s.

Results and discussion

The heat capacity (C_p) of the sample

The heat capacity (C_p) of the sample for each period was obtained from the heat flow of the sample (H_{sample}) and aluminum lid (H_{calib}) measured by TMDSC. Those evaluations were used by following equation;

$$C_p(\text{sample}) = \frac{\dot{H}_{\text{sample}} - \dot{H}_{\text{calib}}}{m_{\text{sample}}\,\omega A_T} \qquad (1)$$

where m_{sample} is mass of the sample, ω is angular frequency (=2π/period) and A_T is an effective amplitude of the temperature modulation imposed to the sample. The value of A_T is determined to reproduce C_p at the high temperature (amorphous) region using ATHUS(amorphous) database, Fig. 1.

We found a peak of C_p (complex) around T=162–163°C for all different periods and a clear period dependence of C_p, i.e., bigger period gives larger C_p (complex). We will discuss more details later ('Excess heat capacity and a simple model').

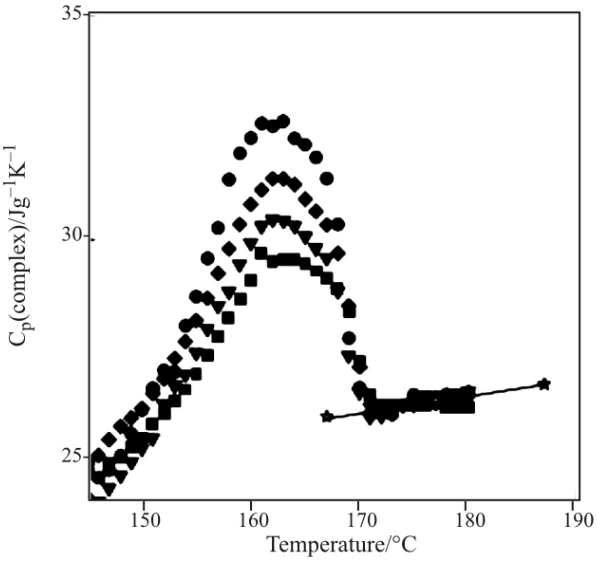

Fig. 1 Temperature dependence of C_p(complex) observed in quasi-isothermal TMDSC, 60 min modulation time; ■ – period P=90, ▼ – P=600, ◆ – P=900, ● – P=1500 s and ✱ – ATHUS

Analysis of $C_p(\infty)$ and ΔC

The measured C_p is analyzed by the following Debye model as a function of frequency [10],

$$C(\omega) = C_p(\infty) + \frac{\Delta C}{1 + i\omega\tau} \qquad (2)$$

where $C_p(\infty)$ is non-kinetic part of the heat capacity, ΔC is a relaxation strength, and τ is a relaxation time. To find $C_p(\infty)$ and ΔC, Eq. (2) is rewritten in the following form [10],

$$\left|C(\omega)\right|^2 = C_p(\infty)^2 + (2C_p(\infty) + \Delta C)\Delta C \cdot \frac{1}{1+\omega^2\tau^2} \qquad (3)$$

and τ is fixed some trial value (60, 120, 240 and 480 s) in our preliminary analysis for simplicity. The results of χ^2 (means that the squared deviation between measured point and calculated curve) fitting at several temperatures are shown in Fig. 2. In Figs 2a and b, $C_p(\omega)$ in Eq. (3) is extracted from the heat flow at (t_{mod}=) 30 and 60 min during the full quasi-isothermal modulation t_d.

Although there are ambiguities of errors, we found that 'global tendency' of τ *vs.* χ^2 values; i.e., there is a possibility of changing τ during quasi-isothermal modulation for different melting temperature region. It should be noted here that, at t_{mod}=30 min, it looks like that a small τ (less than 120 s) gives small χ^2. On the other hand, at t_{mod}=60 min, it is found more complicated τ dependence for each melting temperature region. These results may suggest that the relaxation processes occurred in the quasi-isothermal modulation is not single-relaxation processes expressed like Eq. (2).

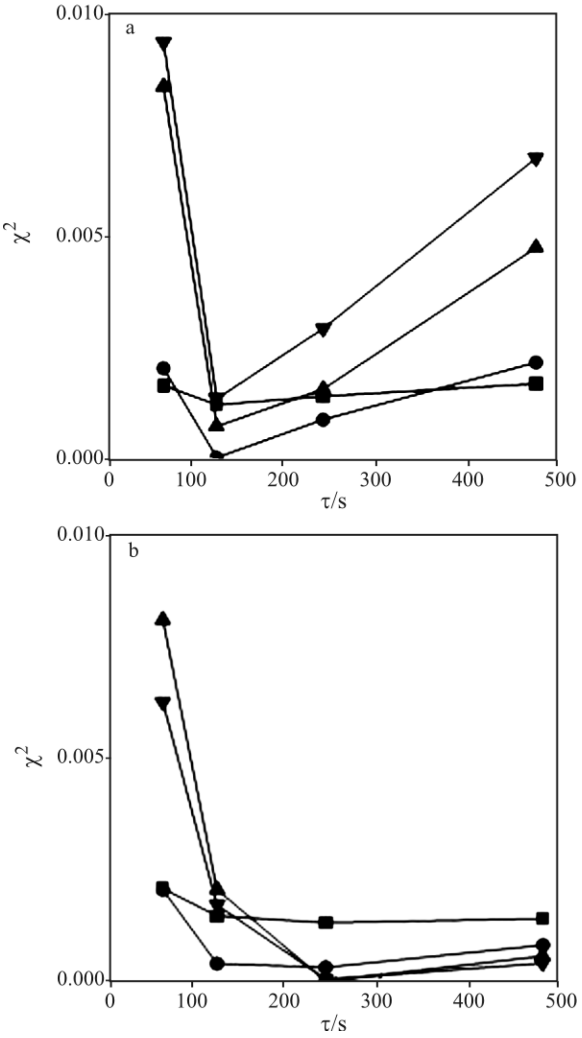

Fig. 2 The relaxation time τ – dependence of χ^2: a – τ=30 min, b – τ=60 min during quasi-isothermal measurement; ■ – temperature T=150, ● – T=155, ▲ – T=160 and ▼ – T=165°C

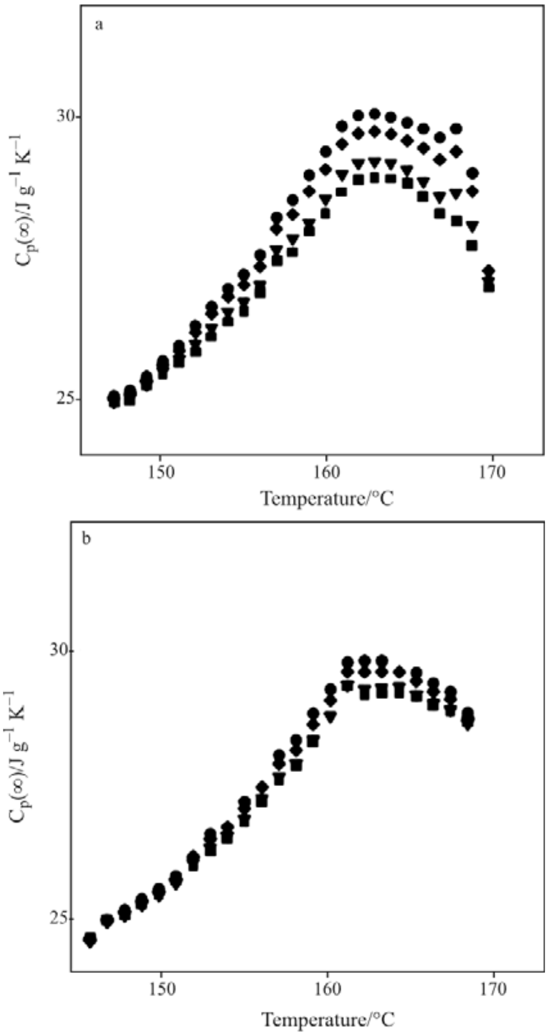

Fig. 3 Temperature dependence of $C_p(\infty)$: a – t_{mod}=30 min, b – t_{mod}=60 min during quasi-isothermal measurement; ■ – relaxation time τ=60, ▼ – τ=120, ◆ – τ=240 and ● – τ=480 s

Figures 3a and b show that the temperature dependence of non-kinetic part of heat capacity, $C_p(\infty)$, at t_{mod}=30 and 60 min, respectively. In t_{mod}=60 min case, it is found that there are no relaxation time τ dependence for $C_p(\infty)$ as seen in Fig. 3b. On the other hand, for t_{mod}=30 min case, we found the clear τ dependence in $C_p(\infty)$, Fig 3a. Since smaller τ gives smaller χ^2 as seen in Fig. 2a, we should read $C_p(\infty)$~2.9 J g^{-1} K^{-1} for t_{mod}=30 min case, while $C_p(\infty)$~3.0 J g^{-1} K^{-1} for 60 min case. It means that, during this 30 min iso-thermal modulation, about 3% enhancement of the non-kinetic part of heat capacity is observed due to some mechanisms.

Temperature dependence of the relaxation strength is also shown in Figs 4a and b. Although the relaxation strength ΔC is slightly different at t_{mod}=30 and 60 min case, we found similar temperature dependence.

Excess heat capacity and a simple model

The excess heat capacity of crystalline polymer is expressed the following equation using non-kinetic heat capacity, $C_p(\infty)$, and the thermodynamic heat capacity;

$$C_p\,(\text{excess})\equiv C_p\,(\infty)-C_p\,(\text{thermodynamic}) \qquad (4)$$

where C_p(thermodynamic) is given by superposition of heat capacity of crystalline and amorphous with mass of the crystallinity α,

$$\begin{aligned} &C_p\,(\text{thermodynamic})\equiv \\ &\alpha C_p\,(\text{crystalline})+(1+\alpha)C_p\,(\text{amorphous}) \end{aligned} \qquad (5)$$

The results of C_p(excess) are shown in Figs 5a and b.

We also show the results from simple model for excess heat capacity given by the following formula:

$$\text{excess heat capacity} \propto \alpha\cdot[\text{amount of amorphous}]^{\gamma} \qquad (6)$$

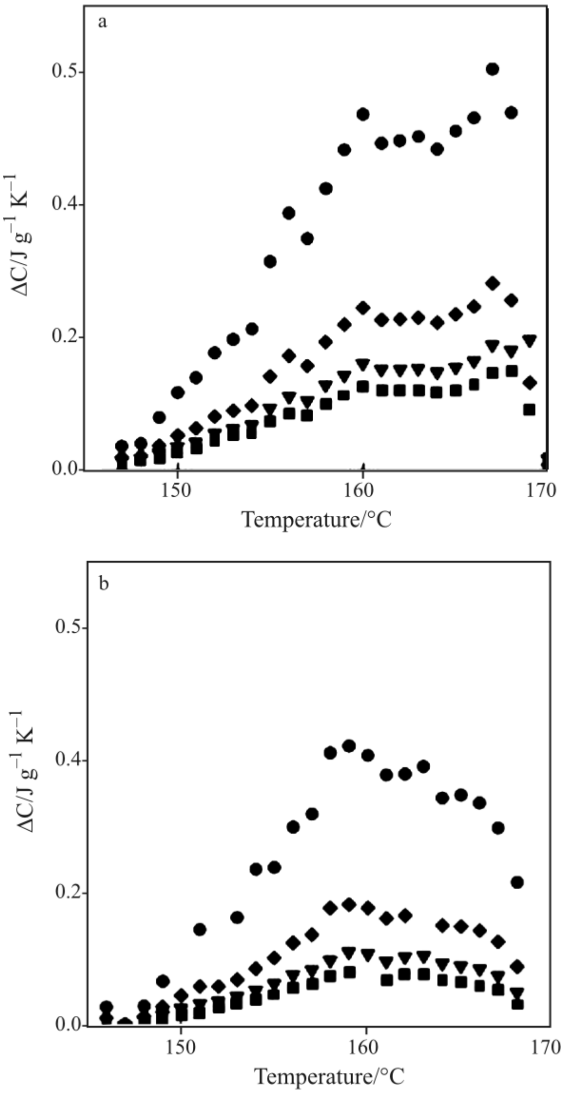

Fig. 4 Temperature dependence of ΔC : a – t_{mod}=30 min, b – t_{mod}=60 min during quasi-isothermal measurement; ■ – relaxation time τ=60, ▼ – τ=120, ◆ – τ=240 and ● – τ=480 s

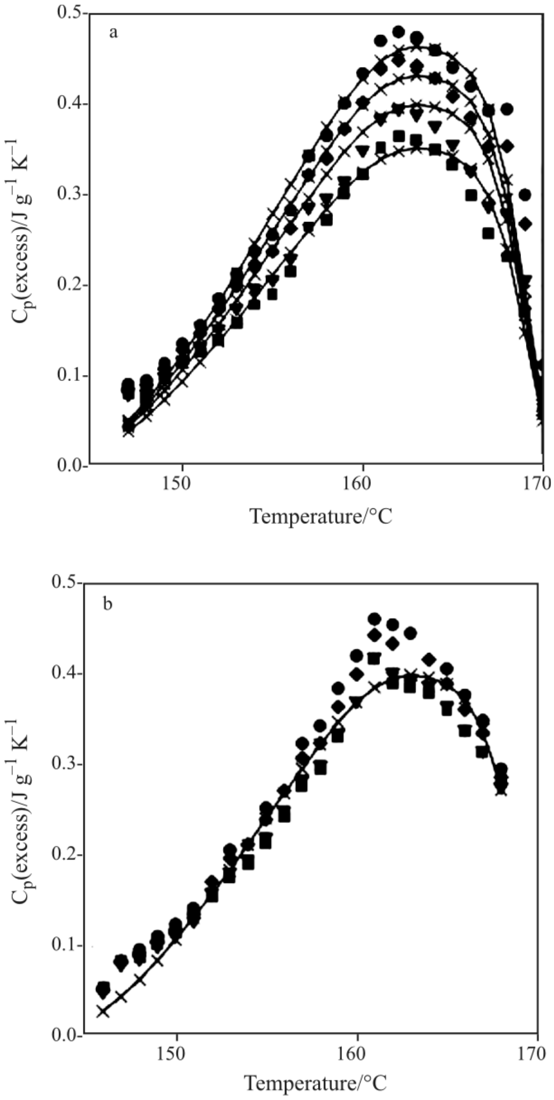

Fig. 5 Temperature dependence of C_p(excess): a – t_{mod}=30 min, b – t_{mod}=60 min during quasi-isothermal measurement; ■ – relaxation time τ=60, ▼ – τ=120, ◆ – τ=240, ● – τ=480 s and × – given by Eq. (6) (x=2/3)

One can regards this excess heat capacity as existence of some relation between crystallite and amorphous produced after quasi-isothermal temperature modulation. We here thought that such amorphous (i.e., an amorphous produced after quasi-isothermal temperature modulation) is different from usual amorphous in the thermodynamically sense. The parameter x seen in Eq. (6) means that the case of x=1 represents that the excess heat capacity is in proportion to the volume of amount of amorphous. Similarly, x=2/3 and 1/3 represents the surface and length of amorphous, respectively. As seen in Fig. 5, we found that x=2/3 reproduces the experimental data quite well. It means that the excess heat capacity, C_p(excess), can be explained by an existence of interface of new-born amorphous. It is also interestingly noted here that the $C_p(\infty)$ enhances during temperature modulation as seen in Figs 3a and b.

This new-born amorphous may be different in the mobility for a chain to normal one like well-known rigid amorphous appears interface between the lamella and the amorphous [12–18]. It does not seems that the excess heat capacity can be explained by the rigid amorphous with lower mobility for the chain. Also it may be possible that the new-born amorphous contains the reversible latent heat by some part of a polymer chain attached and detached on the surface of the crystal growth front during temperature modulation, i.e., it means well-known reversible melting [16–25]. Therefore the new-born amorphous would have excess heat capacity by the reversible melting. It will be desired that the new-born amorphous is related to either the rigid amorphous or the reversible melting.

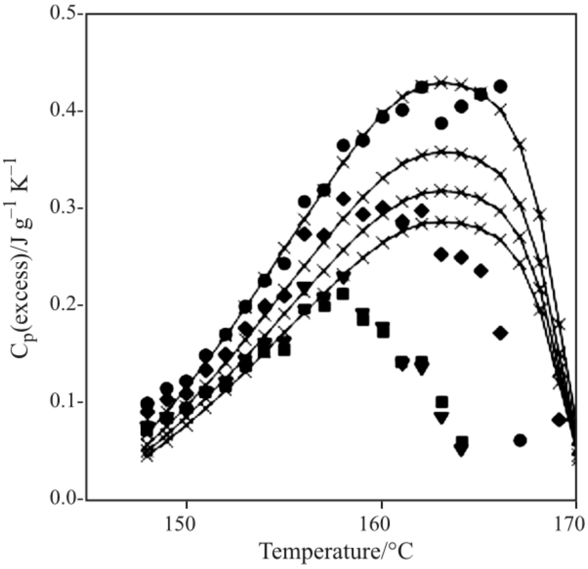

Fig. 6 Temperature dependence of C_p(excess) at t_{mod}=10 min; ■ – relaxation time τ=60, ▼ – τ=120, ◆ – τ=240, ● – τ=480 s and × – given by Eq. (6) (x=2/3)

Finally, a preliminary results of the C_p(excess) for 10 min modulation is shown in Fig. 6. Since it is found very strong τ dependence for the value C_p(excess) and peak temperature, we need determine precisely the relaxation time to investigate the mechanism of the excess heat capacity.

Conclusions

We observed the excess heat capacity C_p(excess) for iPP by TMDSC measurements. From the results, we found the frequency and modulation time dependence of C_p(excess). Although the behavior of the C_p(excess) is studied by the Debye model, the experimental results looks like suggest that the relaxation processes may not single- but multi-processes with several relaxation times. The physical origin of the excess heat capacity C_p(excess) is also discussed. We considered the excess heat capacity as consequence of existence of new-born amorphous produced after quasi-temperature modulation. As seen in Fig. 5, our simple model (Eq. (6)) with parameter x=2/3 can reproduce the experimental data quite well. These results may mean that the obtained excess heat capacity is to be related to 'surface' of amorphous in some way. It should be noted here that the Eq. (6) also proportional to the crystallinity α. These facts leads us to a possible origin of the excess heat capacity, that is there are some kinetic modes related to both amorphous and crystallinity. We may call named the amorphous which is generated after heating and during temperature modulation new-born amorphous. Since the new-born amorphous appears in relaxation processes for polymer melting, one can consider that it should be related to the non-equilibrium phenomena.

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