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Short Communication

Heating scans of stretched polystyrene films with stable baselines: Preparation method of samples for thermal analysis

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ABSTRACT

Differential scanning calorimetry (DSC) examinations were carried out for stretched polystyrene (PS) films. A specific sample preparation technique was developed to overcome the entropic shrinkage, which makes DSC baselines unstable and divergent with each other. As a result, the data were acquired for stretched PS film with stable baselines overlayable below and above glass transition temperature shoulder. This method enables us to observe shoulder shift and evaluate the area bounded by two heat flow curves with and without both thermal ageing and stretching.

1. Introduction

The structural relaxation behavior studies of polymers are currently increasing to seek for entirely appropriate descriptions of phenomenological models because of their flexible representations of basic relaxation features, such as hysteresis, non-linearity, non-exponentiality, and thermorheological simplicity/complexity. The structural relaxation study is concerned with the slow evolution of thermodynamic properties toward the equilibrium, where the effect of physical ageing is frequently observed using differential scanning calorimetry (DSC) technique with the measurement of enthalpy variation as an actual thermodynamic quantity. Polymers with confined or constrained situations have recently attracted considerable attention regarding the physical ageing; including, layered glassy films [1,2], composites with nanoparticle [3,4], and polymer networks with different degrees of cross-linking [5].

With this background, we investigated and reported the enthalpy recovery for a polystyrene (PS) film sample with a mild stretching ratio in comparison with a film without stretching [6]. In the experiment, it is necessary to conduct the heating measurement for a sample after the stretching. It is also required that DSC heating curves are overlayable in baselines before and after the glass transition temperature (T_g) shoulder for samples with and without stretching so that the recovered enthalpy can be calculated from the area bounded by the resulting two DSC curves.

In general, it is preferable to fill a DSC cup with powdered sample. Alternatively, DSC curves of the second run or even the third run are used for the analyses when sampling a bulk, resin, gel, or any other form of likely inhomogeneous polymers [7]. These methods may be assumed as semi-empirical to acquire DSC data with stable baselines. Whereas, DSC data are likely unstable and not overlayable in baseline through loading a solid film sample into DSC cup. Destabilization is mainly attributed to movements of the samples, namely shrinkage, inside the pans on DSC heating. The movements can cause frictional heat as well as volume change, which are included in DSC curve and thus even in the quantities determined from the curve. Moreover, the heat transfer coefficient between sample and pan surface is changed by the sample movements, which causes the shift of the baseline. In order to overcome the problem of baseline destabilization, we attempted data acquisition with looking for an appropriate condition in crimping DSC pan. In this paper, the repeat of the improvement for the loading of DSC cups is described to reach the suitable sampling method for PS film.

2. Experimental

2.1. Materials and examination methods

Polystyrene film was fabricated using hot press machine at pressure of approximately 20 MPa with thickness of 0.5–2 mm.

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Polystyrene pellet of G120K (Lot.1F1606) was kindly supplied by Nippon Polystyrene. The specimen with the size of 90 × 15 mm was cut out from the film and used for thermal ageing experiment with placing line markers for determining the stretch ratio ($d = L/L_0$), where L_0 and L are the distances between two markers before and after stretching. Polystyrene powder was prepared from G120K pellets via precipitation with methanol from solution in tetrahydrofuran.

Fig. 1(a) shows the experimental steps, including thermal ageing, stretching, and DSC examination. Film chucks and the chuck holder, on which the specimen lies, were used to stretch the specimen with a handle stretcher while performing the ageing process. The handle stretcher was placed in the oven at 84 °C of the ageing temperature (T_A). The specimen was heated to 200 °C before the thermal ageing, as shown in the period [I] in Fig. 1(a), to eliminate thermal history of the sample. Afterwards, it was moved from the oven of 200 °C and fixed to the stretcher while removing the chuck holder in the period [II], and then kept at T_A condition for the ageing process. We also checked the temperature variation of the chuck holder without removing it from the stretcher. The results are shown in Fig. 1(b). Consequently, it was verified that the temperature decreased at a constant rate to 84 °C. From this observation, the start of the thermal ageing (the start of ageing time (t_A)) was determined as 10 min after the specimen was taken out of the oven of 200 °C, shown as dashed line in Fig. 1(b). Subsequent to thermal ageing and stretching processes, the specimen was quenched and stored in a freezer at −28 °C.

Immediately before the measurement, the specimen was taken from the freezer, cut into pieces and was placed in a DSC cup to be used for DSC examination from the room temperature to 200 °C with a rate of 5 °C min^{-1}. The DSC examinations were conducted with Seiko DSC 200 instrument.

2.2. DSC sample preparation

In loading the DSC pan with the sample, sufficiently stable baselines were achieved through carrying on several improvements concerning the sample preparation, summarized in Table 1 as Methods 1–6. Two kinds of aluminum open sample pans of tall (5 mm in height) and short (2.5 mm in height) were used. An uncrimped reference pan was used when the sample pan was uncrimped and a crimped reference pan was used when the sample pan was crimped. Before conducting the DSC scan, the stored specimen was cut using a regular scissors or a paper cutter into small pieces, which shapes were also observed and roughly classified as hexagonal and rectangle. Rough sketches are also shown in Table 1 for loading the DSC pans.

3. Results and discussion

3.1. Sample storage

The specimens were stored in a freezer at −28 °C after thermal ageing. The effect of the storage period on the enthalpy relaxation was examined for the samples without ageing ($t_A = 0$) and without stretching. Fig. 2 shows DSC thermograms of the sample kept for various storage periods while the sample weight (w) was carefully controlled to be constant. The insignificant differences among the thermograms can indicate that the storage at −28 °C has no progress in enthalpy decrease even after 96 h in the freezer.

3.2. DSC observations

Samples with d ratios of 1.0, 2.0, and 2.1 were used in Method 1 with the uncrimped DSC tall pan, which was the first try to acquire the DSC thermograms for film samples. While the DSC thermogram for sample with d of 1.0 shows a stable baseline at

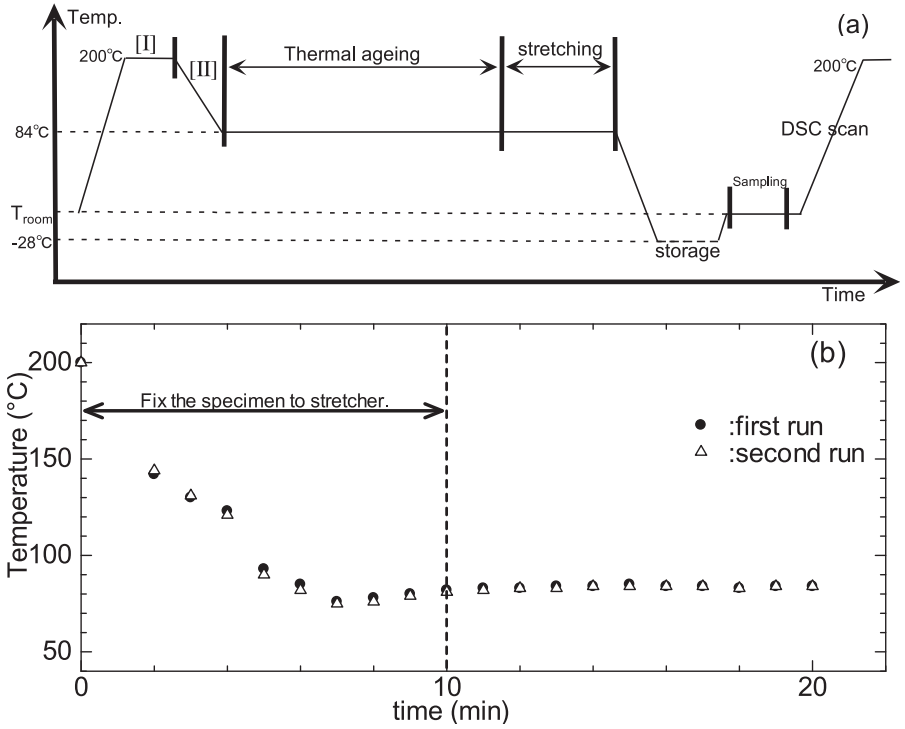

Fig. 1. (a) Schematic diagram for temperature program to acquire DSC data of stretched film samples. The thermal history in the sample was removed in the period [I]. While the temperature of the specimen decreased with a constant rate in the period [II], the specimen was fixed to the stretcher placed in an oven at T_A of 84 °C. (b) Temperature profiles of the chuck holder in the period [II]. The specimen was moved at t of 0 from an oven of 200 °C to another oven of 84 °C.

Table 1
Methods of preparation DSC samples.

Methods	DSC pan[a]	Crimpness	Bottom of pan	Stretching	Sample shape	Film thickness (mm)	number of film samples	Weight (mg)	Inside
Method 1	Tall	Uncrimped	Flat	Stretched	Random	1	~6	20–38	
Method 2	Tall	Uncrimped	Flat	Stretched	Random	1	~6	12–30	
Method 3	Short	Crimped	Uneven	Stretched	Random	1	~4	17–18	
Method 4	Short	Crimped	Flat	Un-stretched	Hexagon	1	~3	17–18	
Method 5-1	Short	Crimped	Flat	Un-stretched	Hexagon	2	1	16–18	
Method 5-2	Short	Crimped	Flat	Un-stretched	Fine pieces	1	~10	16–18	
Method 5-3	Short	Crimped	Flat	Stretched	Hexagon	1	2	16–18	
Method 6	Short	Crimped	Flat	Stretched	Rectangle	0.5	4 or 5	15–16	

[a] Tall: aluminum open sample pan of 5 mm in height; short: aluminum open sample pan of 2.5 mm in height and crimping cover, both supplied by Epolead Service Inc.

temperatures above the T_g shoulder, the thermograms for samples with d of 2.0 and 2.1 are unstable at temperatures above T_g, as shown in Fig. 3. The result can be attributed to the entropic shrinkage of the stretched samples [8]. In fact, the shapes of stretched samples were found changing inside DSC pans before and after the heating scans [9].

It was required to avoid the influence of sample shrinkage; therefore, we attempted to use the lids of DSC pan with and without crimping. Thermograms of samples with uncrimped and crimped pans are presented in Figs. 4 and 5, respectively. As shown in Fig. 4, the heating scans using uncrimped pans resulted in different baseline slopes between unstretched and stretched films at temperatures above T_g, whereas the difference in the baseline slopes became less significant between these films when the crimped pans were used (Fig. 5). Thermograms in Fig. 4 also display a conventional result that the overshoots at T_g become more pronounced when t_A was increased.

The observations presented in Fig. 5 indicate that the crimping is effective to some extent to avoid the influence of shrinkage of the stretched samples [10]. Nevertheless, the baselines at T above T_g diverge as the temperature increases, revealing a divergence of 107 μW at 140 °C, indicated by arrows, which is unsuitable to calculate the peak area for the amount of enthalpy relaxation. The divergence was considered because of the uneven bottom surface of pan made by tightly crimping. In fact, the bottom surfaces of pans were visually observed to be uneven.

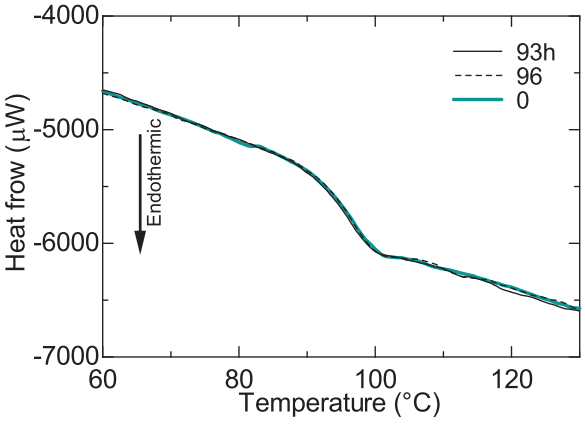

Fig. 2. Effects of the storage period shown in Fig. 1 on the DSC thermograms of PS film without ageing and stretching. The storage periods for three samples are shown in the figure. The sample weight was kept constant of 26.40 mg.

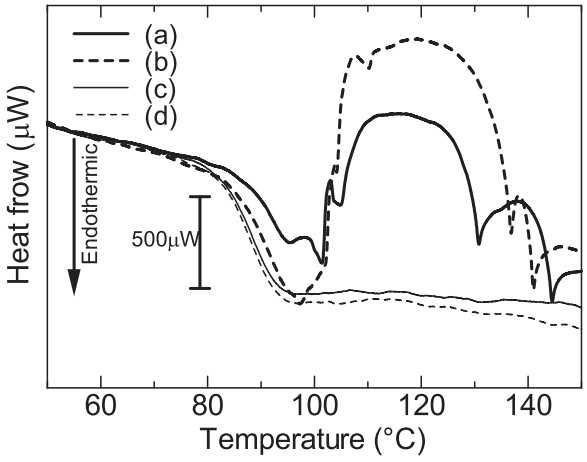

Fig. 3. Heating DSC thermograms of PS films with various stretch ratio (d) values and ageing time (t_A) acquired through following Method 1. (a) t_A = 60 min, d = 2.1, w = 27.00 mg; (b) t_A = 300 min, d = 2.0, w = 37.40 mg; (c) t_A = 0 min, d = 1.0, w = 35.38 mg and (d) t_A = 0 min, d = 1.0, w = 34.38 mg.

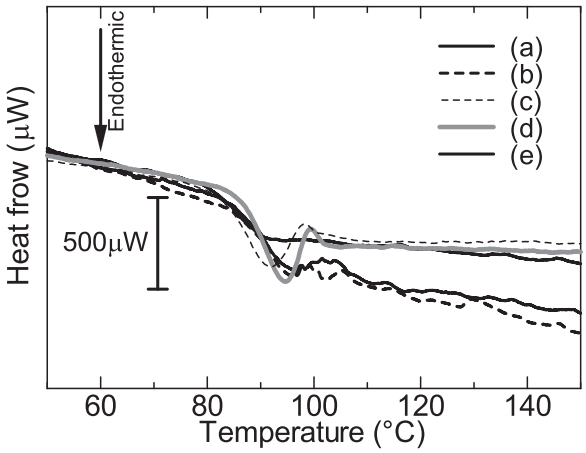

Fig. 4. Heating DSC thermograms of PS films acquired through following Method 2. (a) t_A = 120 min, d = 1.9, w = 13.80 mg; (b) t_A = 540 min, d = 2.1, w = 13.86 mg; (c) t_A = 120 min, d = 1.0, w = 18.39 mg; (d) t_A = 540, d = 1.0, w = 18.39 mg and (e) t_A = 0 min, d = 1.0, w = 13.02 mg.

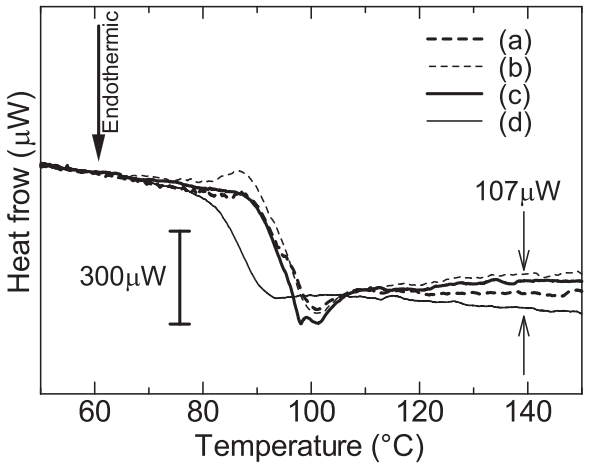

Fig. 5. Heating DSC thermograms of PS films acquired through following Method 3. (a) t_A = 120 min, d = 3.1, w = 17.11 mg; (b) t_A = 120 min, d = 3.1, w = 17.61 mg; (c) t_A = 120 min, d = 3.1, w = 17.55 mg and (d) t_A = 0, d = 1.0, w = 18.01 mg.

After carefully studying the thermograms of Fig. 5, the following three points were taken into consideration to obtain DSC curves that enable us to calculate the peak area with the thermal ageing and stretching:

(i) the flat bottom surface of the pan,
(ii) the shape of the sample as hexagonal or rectangle,
(iii) the number of film samples.

Furthermore, in our experimental plan, the stable baselines of the unstretched sample were initially ensured and then the examinations were proceeded to the stretched samples. A flat bottom surface pan of (i) can be obtained through controlling the lever handle of the crimping tool. No direct relations between the sample shape of (ii) and the acquisition of stable and overlayable baselines were observed. However, the samples cut in rectangles could be laid denser inside the pan than those cut in hexagonal form, in particular when laying one over another, which is supposed to be influential to the stability. The number of film samples of (iii) revealed close relations to the sample weight. Because the scans were performed under almost constant weight, the film thickness would be altered according to the number of film samples. Fig. 6 shows the shapes of sample pieces and their loadings into the pan. The heating scans with stable baselines were attempted using Methods 4–6 with considerations of these points.

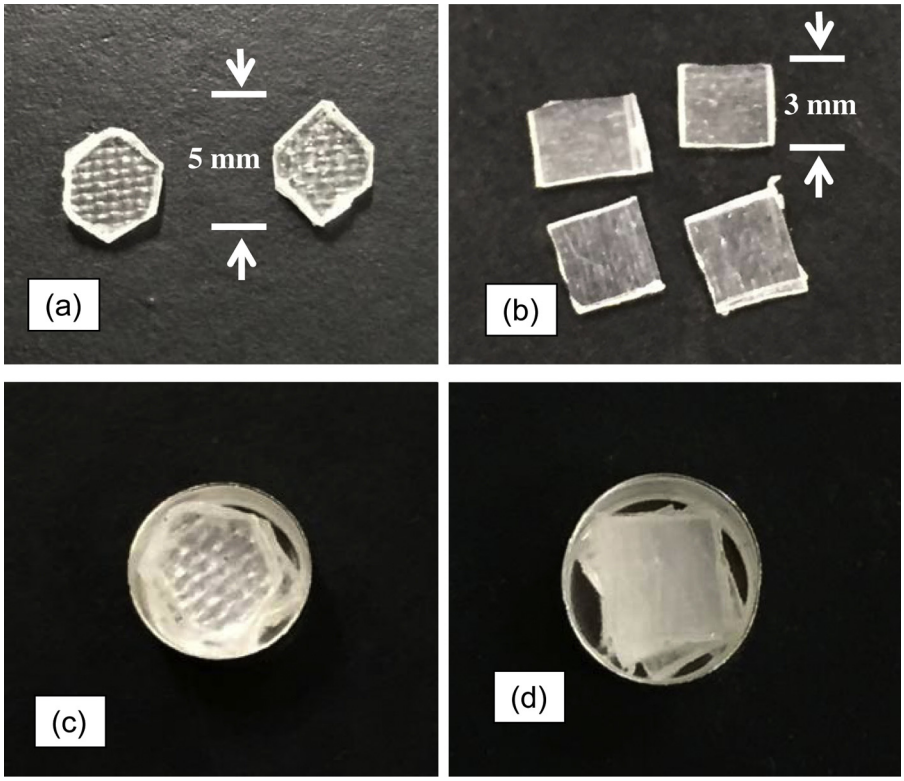

Fig. 6. Views of sample pieces and their loadings into the DSC pan. (a) Hexagonal sample pieces used in Method 5; (b) rectangle sample pieces used in Method 6; (c) DSC pan containing hexagonal pieces and (d) DSC pan containing rectangle pieces.

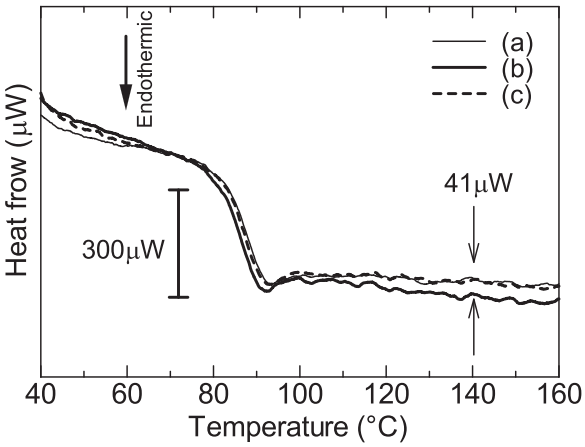

Fig. 7. Heating DSC thermograms of PS films without ageing and stretching acquired through following Method 4. (a) w = 18.18 mg; (b) w = 18.37 mg and (c) w = 18.42 mg.

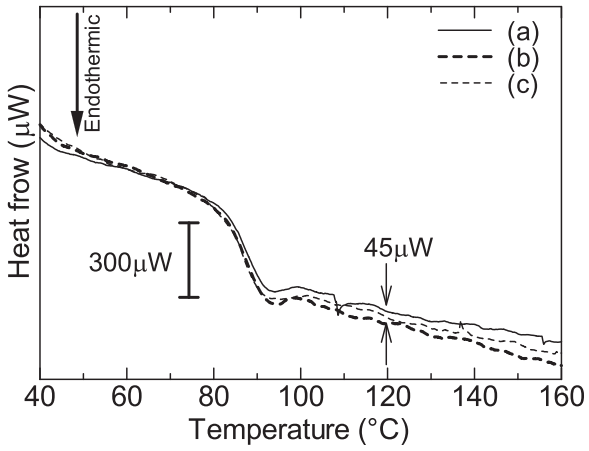

Fig. 9. Heating DSC thermograms of PS films without ageing and stretching acquired through following Method 5-2. (a) w = 18.70 mg; (b) w = 18.82 mg and (c) w = 18.79 mg.

Fig. 7 reveals DSC thermograms of samples obtained using flat surface pans of Method 4. Well overlayable baselines are clearly observed in comparison with the thermograms presented in Fig. 5.

Fig. 8 shows the result of scans for the film of 2 mm thickness. Very stable DSC curves with less diverged baselines could be observed, which can be attributed to one piece lying inside DSC pan, whereas the film of 2 mm thickness provided some disadvantages. This film appears inappropriate for the stretching with the stretcher used in this work. In fact, it was more likely to break the film during stretching, especially when d is greater than 2.5 and t_A is longer than 600 min. In addition, the sample cut out with scissors from the specimen tended to be cracked, which seems to be influential to the heat flow during the scan.

The experiment was also conducted with a sample of fine grains cut out from a specimen of a 1 mm film (Fig. 9). The divergence of the baseline was rather larger, as shown by the arrows in the plot. Moreover, the baseline slope became steep. In consequence, it was found that the films thinner than 1 mm are more suitable for the stretching process and placing samples neatly in the DSC pan results in a stable baseline.

The scans for stretched film samples were performed using those of hexagonal and rectangle cuts, resulting in DSC thermograms as shown in Figs. 10 and 11, respectively. Films of 0.5 mm thickness were used in Method 6, which were easier to make rectangle cut from the specimen. In the scans of hexagonal cut, some baselines were observed inconsistent with each other at T above T_g. For example, see curves (b) and (d) in Fig. 10, but not others. In the scans of rectangle cut samples, the baselines were found overlayable enough to calculate the peak area.

Lastly, the effect of stretching on T_g shoulder of DSC thermograms was investigated. Although the shoulder of DSC curve shifted in response to stretching in this work (see Figs. 10 and 11), this observation cannot be generally acceptable. Rault reported the enthalpy relaxation data concerning oriented polymer glasses using uniaxially and biaxially stretched films of polycarbonate and PS, whereas any obvious shoulder shift at T_g by virtue of stretching has not been reported [8]. No shoulder shift has been observed for DSC data of stretched sheet polymer of crosslinked poly(isobutyl methacrylate) [10]. On the contrary, the shoulder shifts were observed for the stretched sheets of polylactide and poly(ethylene terephthalate) [9,11,12]. The relation between the film stretching and the shift at T_g is currently an unsolved matter. The experimental method of this work helps to collect the data of stretched film sample and is practically usable to clarify the relationship.

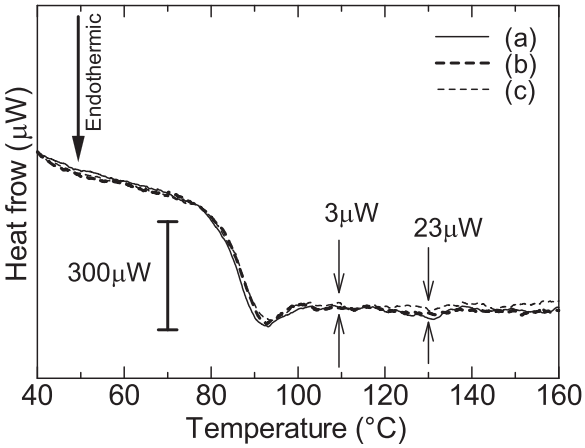

Fig. 8. Heating DSC thermograms of PS films without ageing and stretching acquired through following Method 5-1. (a) w = 18.66 mg; (b) w = 18.67 mg and (c) w = 18.68 mg.

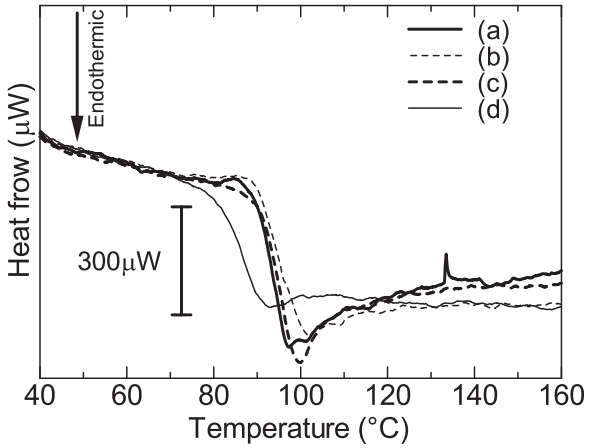

Fig. 10. Heating DSC thermograms acquired through following Method 5-3. (a) t_A = 15 min, d = 3.0, w = 18.41 mg; (b) t_A = 15 min, d = 3.0, w = 18.18 mg; (c) t_A = 15, d = 3.0, w = 18.12 mg and (d) t_A = 0 min, d = 1.0, w = 18.27 mg.

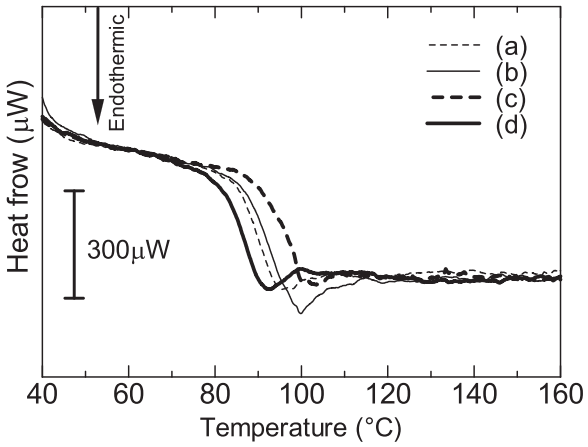

Fig. 11. Heating DSC thermograms acquired through following Method 6. (a) t_A = 90 min, d = 1.5, w = 16.75 mg; (b) t_A = 90 min, d = 3.5, w = 16.71 mg; (c) t_A = 90 min, d = 4.0, w = 16.02 mg and (d) t_A = 0 min, d = 1.0, w = 16.70 mg.

4. Conclusions

Data acquisition in DSC scans was presented for stretched PS film with stable baselines overlayable below and above T_g shoulder. It enables us to observe the shift of T_g shoulder and calculate the area bounded by two heat flow curves with and without both thermal ageing and stretching. It is required for the data acquisition to keep samples weights almost constant and to place samples neatly inside the DSC pan. The appropriate clamping in DSC pan is effective for preventing entropic shrinkage which is influential to the heat flow curve.

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