

DETECTION OF T_g BY MODULATED DIFFERENTIAL SCANNING CALORIMETRY*

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Abstract The glassy transition of the polyethylene terephthalate (PET) samples which have been subjected to solvent induced crystallization (SINC) was investigated by modulated differential scanning calorimetry (MDSC) and density measurement. The differential of heat capacity signal, dC_p/dT from MDSC, was used to monitor the SINC process. It reveals that the T_g temperature shifts to higher value with the advancement of SINC. When the toluene-immersing time was longer (168 h), the detection of T_g become more difficult, because some smaller peaks emerged at the lower temperatures and these are explained as the movement of small segments in the amorphous region. These observed results are due to the morphology and structure introduced by the SINC process.

Keywords Modulated DSC; Polyethylene terephthalate; SINC

INTRODUCTION

The glass transition temperature, T_g , is of particular importance to polymer science, many theoretical researches have been directed at this characteristic temperature, which gives us very useful information on molecular structures and transitions.

Except for some extreme conditions, polymeric materials usually exist in two-phase, i.e. crystalline and amorphous phases. According to this two-phase model^[1], crystalline region is dispersed in the bulk of amorphous region, a chain often traverses several crystalline region, so the restriction coming from this ordered region will make the detection of T_g s more difficult, especially when the degree of crystallization is rather high. In routine study, the detection of T_g s can be relied on many experimental methods and techniques, but it is more convenient to utilize the differential scanning calorimetry (DSC); whereas, in the conventional DSC test, for

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its inherent limitation such as the lack of sensitivity of the calorimeter, the increase of crystallinity will decrease the mobility of molecular segments in the crystalline regions as well as noncrystalline regions, this will subsequently make the detection of T_g more difficult and time-consuming.

Generally, the crystallization would display two opposite effects on the change of T_g for polymeric materials. Firstly, T_g will increase owing to the binding force derived from the crystalline domain and next, the uncrystallizable random chains and the impurities dispersed in the amorphous domain of the material, would result in the decrease of T_g . Commonly, the role of the former effect override that of the latter one.

In fact, the glass transition is not a true phase transition, the different segmental motions result in a glass transition spectrum. For polymers, the heat capacity does not change abruptly at the glass transition temperature. The differential of heat capacity signal can be used to define the process of glass transition^[2], and the peak position of the differential of heat capacity with respect to temperature corresponds to the point of inflection of the heat capacity curves for the glass and crystallized materials. At this point, the change rate of heat capacity is at its maximum. This point can be taken as the glass transition temperature of average-length segments. Thus, the differential signal of heat capacity is clearly sensitive to the glass transition process^[3,4]. Unfortunately, heat capacity (C_p) measurement by conventional DSC is a tedious task requiring multiple experiments and considerable operator's expertise to obtain results with reasonable accuracy and precision.

Modulated DSC (MDSC) has brought a new dimension to thermal analysis. Excellent review of this technique can be found in Ref.[5]. Among its unique benefits, the power of direct measurement of heat capacity and heat flow in a single experiment is very suitable for the detection of the variations of T_g for the duration of crystallization.

In this report, we used the MDSC technique to monitor the T_g 's change of PET samples, which have been immersed in toluene for variant length of time to acquire the crystallized specimens and this research may help us to have a better understanding of PET's crystallization.

EXPERIMENTAL

Material

The original PET films, which have a molecular weight $M_n = 19,000$ ($[\eta] = 0.92\text{dL/g}$, measured in a 60/40 phenol/tetrachloroethane solvent at 25°C), an av-

erage thickness of 0.160mm and $\rho = 1.3348\text{g/cm}^3$, were supplied by Chenguang Institute of Chemical Engineering, Chengdu, China. To obtain noncrystalline PET samples, PET films were first hermetically sealed in the DSC pan, then heated to 270°C for 8 min before rapidly quenched into liquid nitrogen. The partially crystallized PET samples were acquired by immersing the amorphous PET samples into A.R. toluene at room temperature, this treatment was normally called solvent induced crystallization (SINC). These crystallized samples were treated in vacuum oven at 40°C for at least 24 h to remove remnant solvent and moisture prior to DSC test.

MDSC measurement

Thermal analysis was performed using a Modulated DSC from TA Instruments (Model TA 2100). Both temperature and baseline were calibrated as in conventional DSC. In order to obtain the necessary accuracy, a calibration of heat capacity was carried out by running a standard sapphire sample. A scan rate of 5°C min^{-1} was used with a temperature modulation amplitude of 0.42°C and a temperature modulation period of 60s.

Density crystallinity

The densities of the samples were measured using a density gradient tube prepared from *n*-heptane and carbon tetrachthchloride. The mass crystalline fraction was estimated from the measured density (ρ) using the following expression:

$$\text{Mass crystallization fraction} = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right)$$

where ρ_c and ρ_a were the crystalline and amorphous densities, respectively; they were taken to be $\rho_c = 1.455\text{g/cm}^3$ and $\rho_a = 1.333\text{g/cm}^3$ [6].

RESULTS AND DISCUSSION

In the MDSC measurement, the T_g was indicated in the reversing heat flow signals. In the following investigations, T_g was defined as the inflection temperature (method I); meanwhile, owing to the greater sensitivity to the glass transition process, the peak position in the differential of heat capacity, which was correspond to the inflection temperature in the reversing heat flow signals, was also taken as the glassy transition temperature (method II). The variation of T_g was indicated in Table 1.

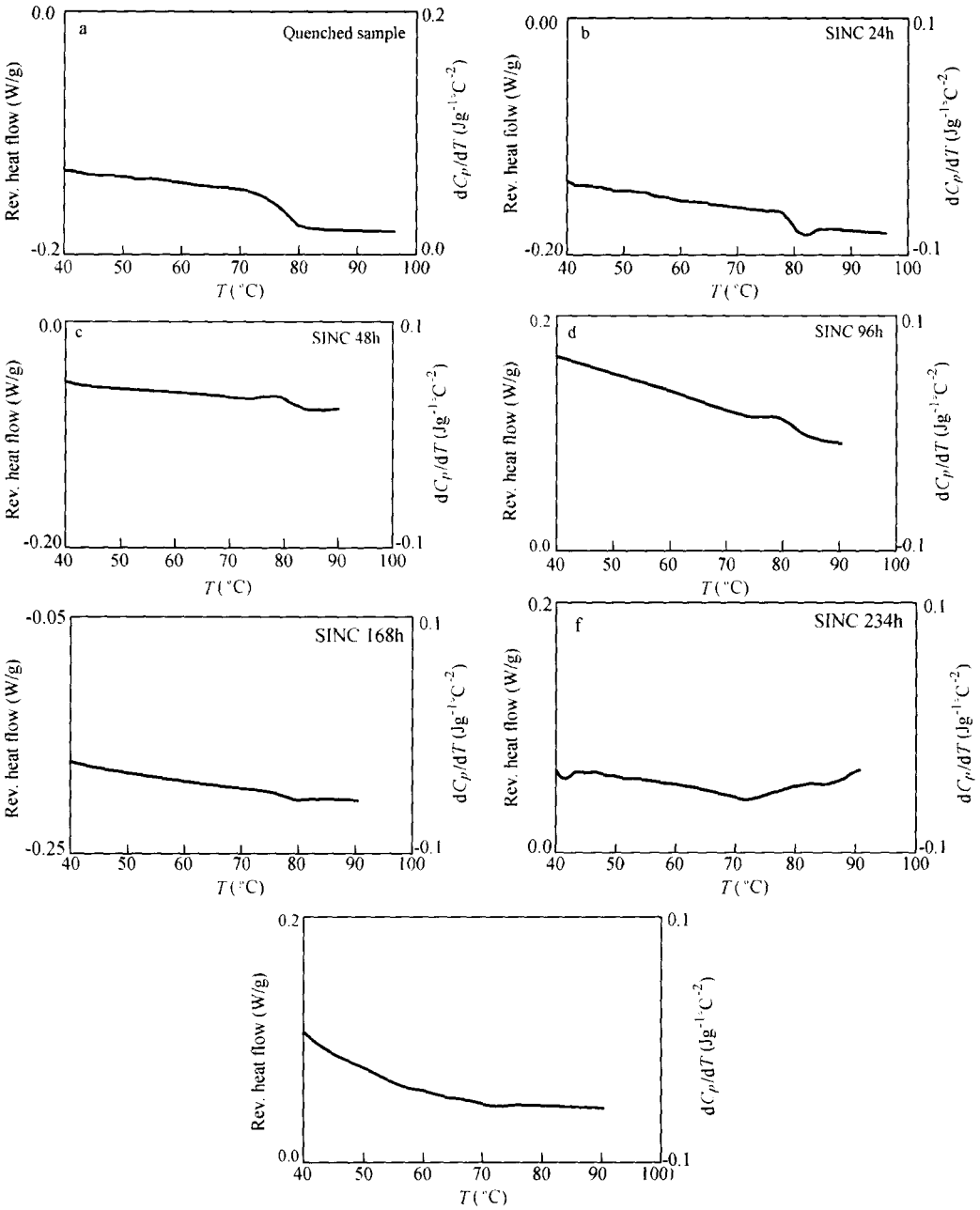


Fig. 1 Reversing heat flow curves *versus* temperature for PET samples underwent SINC for various length of time (a) quenched PET, (b) 24 h, (c) 48 h, (d) 96 h, (e) 168 h, (f) 234 h and (g) 402 h

The basic mechanism of SINC is very much the same as that of thermal induced crystallization from the glassy state, both involving, as a necessary step, the inducement of segmental mobility. The former achieves this goal by case of ‘chemical

energy' and the latter does so by use of thermal energy.

Table 1 Variation of T_g of PET samples which have been immersed in toluene for various length of time. T_g I and T_g II are the T_g s determined by the method I and method II, respectively

Sample (immersing time, h)	T_g I ($^{\circ}$ C)	T_g II ($^{\circ}$ C)
a (quenched)	77.1	77.2
b (24)	79.9	79.4
c (48)	81.3	81.7
d (96)	83.2	82.1
e (168)	77.3	77.1
f (234)	—	84.0
g (402)	—	—

Until now, much of the attention on the structural change invoked by SINC had been focused on the crystalline region. Desai, Wilkes^[7] and also Makarewicz and Wilkes^[8], using both light scattering and scanning electron microscopy, had showed definitively that a spherulitic structure was the characteristic morphology resulting from SINC. Prevorsek et al.^[9,10] from WAXD predicted the presence of crystalline, amorphous and intermediate mesomorphic phase. The proportions of the latter were determined from the intensities of diffraction peaks from the (110), (010) and (100) planes. Zachmann and coworkers^[11,12] studied the amorphous domain using NMR-spectra, their result implied the presence of swelling agents and suggesting that the polymer chains within the noncrystalline regions were under lower stress. More recently, Schick et al.^[13] observed that the glass transition in semicrystalline PET was influenced by the thickness of the amorphous layers between neighboring lamellae.

In the reversing heat flow curves of the PET samples that underwent various length of SINC time, we could find the inflection point which corresponding to glassy transition temperature become higher with the increase of immersing time. It is the general case we encountered as with the development of SINC. The molecules in the amorphous region are more difficult to move against the resistance coming from the crystalline domain. T_g , which is the initiative temperature at which the motion of free molecules change from glassy to rubbery state is initiated, usually moves to higher temperature position in the DSC scans. The increase of crystallinity, which can be verified by the development of densities (see Fig. 2), makes the transition points move to higher temperatures.

Fig. 3 displays the changes of the differential of heat capacity (dC_p/dT) with temperature at different crystallizing time in toluene. Comparing with the reversing heat flows, these signals enjoy a higher sensitivity, especially from the maximum peak positions, we can easily determine the T_g of the corresponding samples. Prior to 96 h, these transition temperatures increase with increasing of immersing time, but become obscure, gradually in that, some small transition-like peaks emerge at lower temperature position when the immersing time is longer than 168 h.

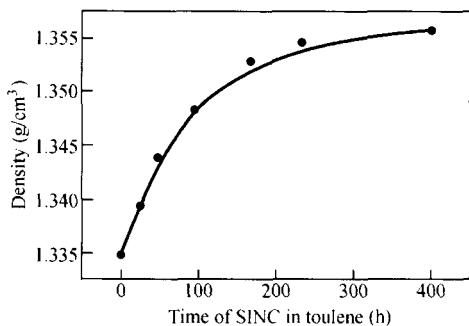


Fig. 2 The variation of density of PET samples *versus* SINC time

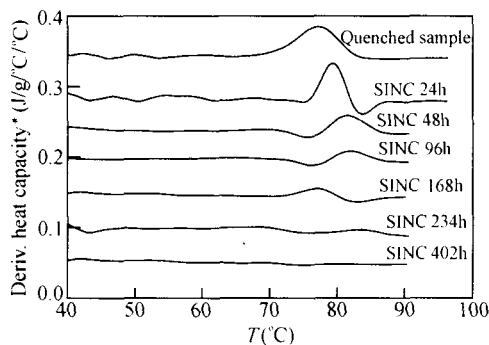


Fig. 3 dC_p/dT signals *versus* temperature for PET samples crystallized in toluene for time indicated on the curves

These variations may imply that some inner-structure changes have taken place during the SINC process. Comparing with other crystallization courses, such as thermal induced crystallization or strain induced crystallization of PET, SINC, owing to the exist of solvent, tends to form more imperfect, wide-distributed crystallites, i.e. with the development of SINC, it may be possible to introduce a wide-distributed noncrystalline domain. From the positions and magnitudes of the small peaks appeared in the scan curves in the vicinity of $40 \sim 70^\circ\text{C}$, it can be assured that they are not T_g transition and, it is too unreasonable to assign them to the second transitions of PET (the β transition in PET, ascribed to the motion of $-\text{COO}-$, usually appears at temperature near -70°C ^[14~16]); wherever, according to the widely accepted definition, the glassy transition temperature (T_g), corresponding to the temperature at which the motion of segment about $50 \sim 100$ C—C bonds chain length, starts to initiate when temperature is elevated from glassy state. In view of this fact, we presume that the humps in the dC_p/dT thermograms of SINC samples may be ascribed to movement of shorter chain length in dispersed amorphous region.

In order to further corroborate our speculation, a comparison is depicted in Fig. 4. Curve **a** and **b** denote the dC_p/dT signals of sample A (thermal induced crystallized) and sample B (solvent induced crystallized), respectively. The two samples have

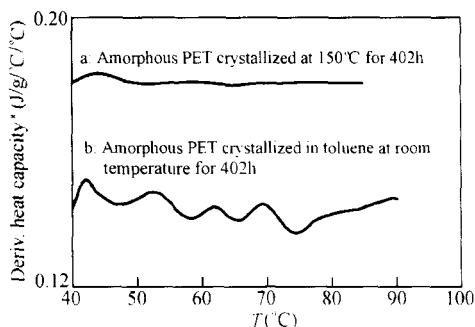


Fig. 4 Comparison of dC_p/dT signals of thermal crystallized PET a) and solvent-inducing crystallized PET b)

nearly same densities, $\sim 1.3576 \text{ g/cm}^3$, i.e. same degree of crystallization, $\sim 21.6\%$, derived by relative equation. In curve a, no remarkable undulation can be found but in curve b, at least 3 humps can be detected. This observation indicates that when crystallization is rather developed, the segment motion in thermal crystallized PET become impossible owing to the strong confinement coming from crystallized domains while the identical movement of segment in the scale of less C—C bond may take place in SINC circumstance.

However it should be make clear that the above mentioned observation and its interpretation are tentative at present, for DSC's limited sensitivity of detection of motions in polymeric materials, further work is needed to shed more light on this unusual phenomena in PET's SINC process.

REFERENCES

- [1] Bassett, S.C., "Principles of Polymer Morphology", Cambridge University Press, London, **1981**
- [2] Hourston, D.J., Song, M., Hammiche, A., *Polymer*, **1996**, 37, 243
- [3] Song, M., Hammiche, A., Pollock, H.M., *Polymer*, **1996**, 37, 5661
- [4] Hourston, D.J., Song, M., Hammiche, A., *Polymer*, **1997**, 38, 1
- [5] Reading, M., *Trends Polym. Sci.*, **1993**, 1, 248
- [6] Daubney, R.P., Bunn, C.W., Brown, C.J., *Proc. R. Soc., (A)*, **1954**, 226, 531
- [7] Desai, A.B., Wilkes, G.L., *J. Polym. Sci., Sympos.*, **1974**, 46, 291
- [8] Makarewicz, P.J., Wilkes, G.L., *J. Polym. Sci.*, **1978**, 16, 1529
- [9] Prevorsek, D.C., *J. Polym. Sci.*, **1971**, 32, 343
- [10] Prevorsek, D.C., Haque, P.J., *Macromol. Sci., Phys.*, **1973**, 138, 127
- [11] Eichhoff, J.V., Zachmann, H., *Makromol. Chem.*, **1971**, 147, 41
- [12] Zachmann, H., Schermann, W., *Kolloid Z. Z. Polym.*, **1970**, 241, 916
- [13] Schick, C., Wigger, J., Mischok, W., *Acta Polym.*, **1990**, 41, 137
- [14] Illers, K.H., Breuer, H., *J. Colloid. Sci.*, **1963**, 18, 1
- [15] Armeniades, C.D., Baer, E., *J. Polym. Sci.*, **1971**, A29, 1345
- [16] Ward, I.M., *Trans. Faraday Soc.*, **1960**, 56, 648