Application Brief

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DSC Measurements of Polystyrene

- The Effects of Molecular Weight on Glass Transition -

1. Introduction

Polystyrene (PS, Figure 1) is an all-purpose resin used in a variety of fields.

One structure factor that greatly influences the physical properties of PS is molecular weight. Increasing molecular weight produces rigid and strong material but it lowers workability so the appropriate molecular weight depends on how the material will be used. The weight-average molecular weight (Mw) of the commercially-available PS that is widely used as industrial material is generally 150,000 to 400,000.

On the other hand, the glass transition of polymers corresponds with the start of the translational motion of chain segments and the glass transition temperature (Tg) is essentially independent of molecular weight. However, it is known that in the molecular weight range where the degree of polymerization is low, the effects of chain ends lower Tg [1)].

In this brief, DSC is used to measure Tg of monodisperse PS with different molecular weights. The 8 monodisperse PS samples measured had comparatively low molecular weights, with weight-average molecular weights ranging from 1940 to 95,000.

2. Measurements

The measurement samples were standard monodisperse PS of 8 different molecular weights manufactured by American Polymer Standards. Table 1 shows the weight-average molecular weight (Mw), number-average molecular weight (Mn) and molecular weight distribution (Mw/Mn).

For the measurements, a DSC220 High-sensitivity Differential Scanning Calorimeter was connected to a SSC5200H Disk Station.

The sample weight was 10mg. The temperature was raised from room temperature to 160°C at 10°C/min during measurements.

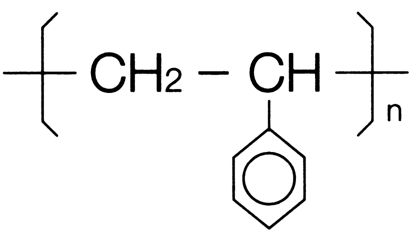

Figure 1 Chemical Structure of PS

Table 1 The Molecular Weights and Molecular Weight Distributions of the PS Samples

Sample	Mw	Mn	Mw/Mn
PS 1	1940	1690	1.15
PS 2	4380	3570	1.23
PS 3	5480	5200	1.04
PS 4	12600	12000	1.05
PS 5	35100	30500	1.15
PS 6	65000	63700	1.02
PS 7	275000	258000	1.07
PS 8	950000	925000	1.03

3. Results

Figure 2 and Table 2 show the DSC measurement results for the 8 PS samples. The results show that as the molecular weight of PS rose higher, the Tg shifted higher and the width of the shift became smaller.

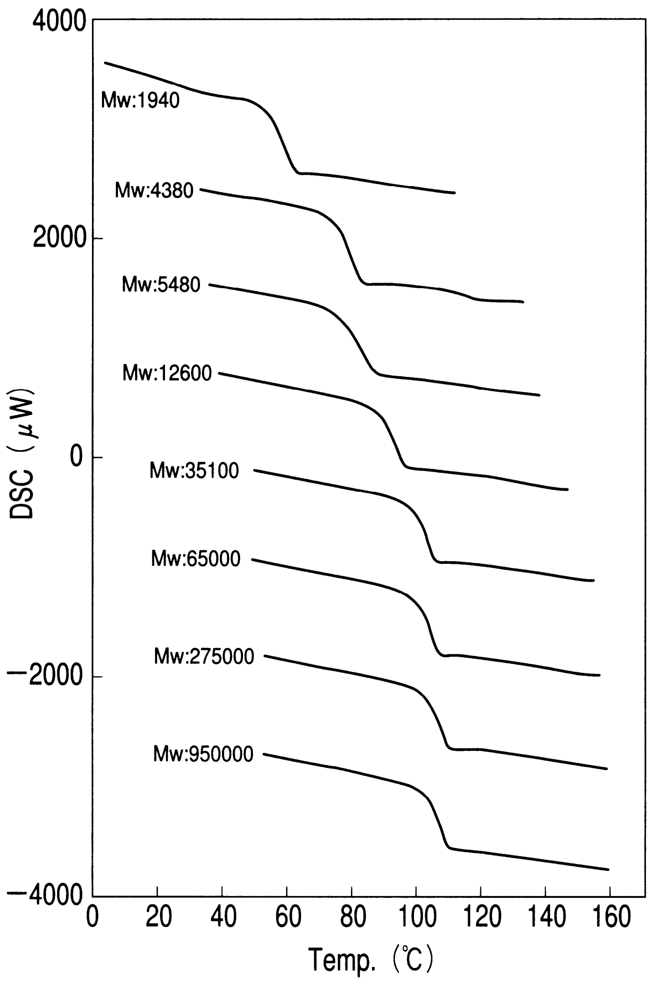

Figure 2 DSC Measurement Results for the PS Samples

Table 1 The Glass Transition Temperature (Tg) Measurement Results for the PS Samples

Sample	Mw	Tg (°C)		
		Tig*1	Tmg*2	Teg*3
PS 1	1940	56.8	60.4	64.2
PS 2	4380	76.2	79.9	83.7
PS 3	5480	77.0	82.4	87.8
PS 4	12600	89.6	93.4	96.7
PS 5	35100	100.2	103.1	105.9
PS 6	65000	100.6	104.0	107.3
PS 7	275000	103.5	106.4	109.4
PS 8	950000	103.9	106.7	109.7

∗1 Onset temperature of Tg
∗2 Mid-point temperature of Tg
∗3 End temperature of Tg

The research regarding the relationship between PS molecular weight and glass transition [2-7] has been widely reported in the past. P.Claudy, J.M.Letoffe, Y.Camberlain and J.P.Pascault [7] used DSC to investigate the relationship of the degree of polymerization of PS and glass transition.

T.G.Fox and P.J.Flory [2,4]

$$Tg = Tg^{\infty} - \frac{m}{n}\left(Tg^{\infty} - Tg^{m}\right)$$
$$= Tg^{\infty} - \frac{A}{M_n} \quad \cdots\cdots \text{①}$$

K.Ueberreiter and G.Kanig [3]

$$\frac{1}{Tg} = \frac{1}{Tg^{\infty}} + \frac{m}{n}\left(\frac{1}{Tg^{m}} - \frac{1}{Tg^{\infty}}\right) \quad \cdots\cdots \text{②}$$

P.R.Couchman [6]

$$\ell n\, Tg = \frac{n\Delta Cp^{\infty}\, \ell n\, Tg^{\infty} + m\left(\Delta Cp^{m}\, \ell n\, Tg^{m} - \Delta Cp^{\infty}\, \ell n\, Tg^{\infty}\right)}{n\Delta Cp^{\infty} + m\left(\Delta Cp^{m} - \Delta Cp^{\infty}\right)} \quad \cdots\cdots \text{③}$$

Figure 3 plots the relation of glass transition temperature (Tg) and the weight-average molecular weight (Mw) using the following results: the measurement results from this experiment (see Figure 2 and Table 2), the DSC measurement results of P. Claudy et al.[7], and, as an example, results calculated using theoretical formula of T.G. Fox et al.[2, 4] The results presented in this brief correlate well with the DSC results of P. Claudy et al.[7] Furthermore, P. Claudy et al.[7] reported that, at degrees of polymerization of 450 and higher (Mw: 46800), Tg is roughly constant and the same result was found in the experiment presented here.

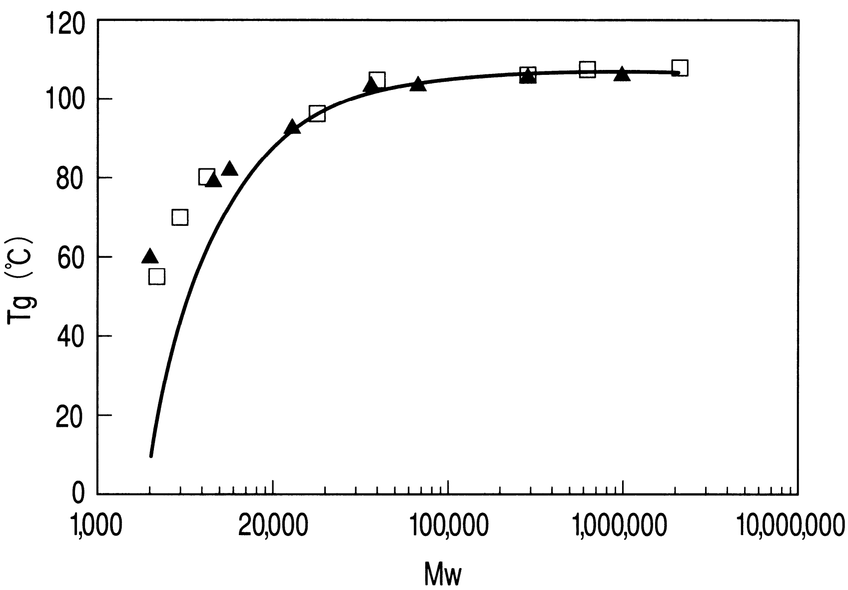

Figure 3 Dependence of Glass Transition Temperature on Molecular Weight

▲ Measurement results from this experiment (Figure 2 and Table 2)

□ Measurement results of P.Claudy et al.

— Results calculated from the theoretical formula of T.G.Fox et al.

4. Summary

In this brief, DSC was used to measure the glass transition temperature of polystyrene with different molecular weights.

The investigation of 8 monodisperse PS samples with weight-average molecular weight (Mw) ranging from 1940 to 95,000 showed that the higher the molecular weight, the higher the glass transition temperature. Furthermore, the measurement results presented here correlate well with the results of P. Claudy et al.[7)]

References

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