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Glass Transition of Polystyrene Versus Molecular Weight

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Summary

Glass transition temperature of polystyrene has been studied by D.S.C.. Glass transition, well known for macromolecules, has been observed up to the monomer. Measurements of the change in heat capacity ΔCp at Tg were carried out and a relationship between $\frac{\Delta Cp}{T}$ and $\overline{Dp}$ has been found. The results have been interpreted as a modification of interaction occuring at $\overline{Dp} \simeq 25$.

Introduction

It is now well known that the glass transition temperature (Tg) of polymers vary with the chain length

(1,2). In the case of polystyrene (3,4,5) the variation of Tg versus $\overline{Dp}$ seems to depend on three distinct relationships : region I where Tg is almost constant, region II where Tg depends on molecular weight (from $\overline{M}n$ = 21000 to $\overline{M}n$ = 1500 and region III where Tg vary very rapidly with chain length. Data in the literature are either dubious owing to the polydispersity of the sample, or simply lacking in low molecular weight and monomer. Recently, polystyrene model molecules have been studied to evaluate the influence of the configurational structure on Tg values (6).

Experimental

a. Products. Oligomer with $4 < \overline{Dp} < 7$ have been prepared by GPC using a Waters apparatus equipped with a refractometric detector R 401 and the following microstyragel columns : two 100 Å (Waters) one 500 Å (Waters), one 802 (Shodex) and one 803 (Shodex). Solvent flow (THF) was 1.5 $ml.mn^{-1}$. Starting material was an oligostyrene purchased from Waters. Bi and tristyrene have been prepared by fractionning pyrolysed polystyrene. IR and NMR analysis showed that PS_2 and PS_3 were diphenyl 2-4 butene 1 and 2-4-6 hexene 1 respectively. Commercially available polystyrene has been used for higher molecular weight.

b. D.S.C. measurements. A Mettler TA 2000 B heat flow D.S.C. apparatus has been used. Mass of sample ranged from 2 to 15 mg. Heating rate was 3.5 $K\ mn^{-1}$ giving a small hysteresis on warming or cooling. Tg was taken as the intersection of the base line with the tangent at the inflexion point of the curve due to the change in heat capacity. Gas flow in the apparatus was argon, chosen on the ground of its density and its low thermal conductivity.

Except in the case of styrene monomer, before any measurement was made, the product was subjected to several cycles of warming and cooling. Change in specific heat can be measured as described in several papers : Δ1 and Δ2 being the calorimetric signal before and after Tg

$$\Delta 1 - \Delta 2 = (Cp1 - Cp2)\ \frac{dT}{dt}$$

Cp1 and Cp2 refer to the specific heat of the sample pan and the sample. $\frac{dT}{dt}$ is the heating rate. Previous standardization gave the relation between Δ and the power developed in the DSC apparatus. Overall precision is thought to be ± 10 %.

c. Preparation of glassy styrene. Vapour of styren has been condensed under vacuum into the crucible maintened at liquid nitrogen temperature using the experimental setup described into the D.S.C. apparatus maintained at 100 K. The experiment was difficult since we found that the product must be kept below 140 K during preparation or manipulation.

Results

D.S.C. curve of glassy styrene is reported figure 1. Tg begins at 140 K and as soon as it has finished exothermal crystallizationoccurs and the melting of styrene is observed at 242.1 K. T = 150 K and Tm = 242.1 K then $\frac{Tg}{Tm} = 0.62$ as expected since generally $\frac{Tg}{Tm}$ lies between 0.5 and 0.66. Tg and cristallizationare not reversible and the sample is not totally glassy because heat of the recristallizationis lower than the heat of melting. Propene as observed by Haida (6) behaves in the same way : Tg at 55 K followed by recristallization then melting at 88 K.

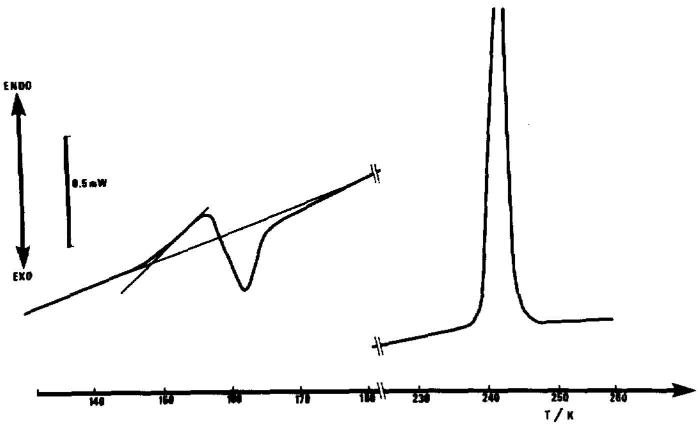

Fig. 1 - D.S.C. curve of styrene

Two different measurements have been carried out :
Tg as described before and change in specific heat.
Results are reported in table I.
Comparison of Tg values with previous results (8) shows great differences which are most probably related to the purity or the polydispersity of the sample.
For exemple we have found Tg = 206 K for diphenyl 2-4 hexane and 194.3 K for bistyrene.

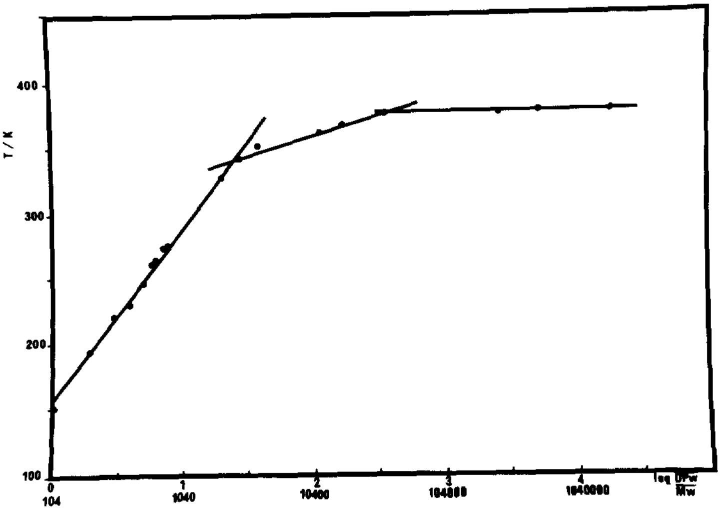

Fig. 2 : Tg versus log $\overline{Dp}$

Table 1

Name or Manufacturer	$\overline{Mw}$ g	$\overline{Mw}/\overline{Mn}$	Tg °K	ΔCp $J\ g^{-1} K^{-1}$	$\frac{\Delta Cp}{T} . 10^3$ $J\ g^{-1} K^{-2}$
Styrene*	104.1	1	150	x	x
diph *	208.2	1	194.3	0.091	0.456
tri *	312.3	1	221.3	0.084	0.378
PS4 *	416.4	1	231.5	0.072	0.310
PS5 *	520.5	1	247	0.077	0.317
PS6 *	624.6	1	262	0.074	0.281
PS7 *	728.7	1	265.5	0.075	0.274
a	650	1.2	265.5	x	x
b	800	1.2	279	0.076	0.275
c	2100	1.05	328	0.068	0.207
a	2850	1.10	343	0.073	0.214
c	4000	1.05	353.1	0.063	0.184
a	17500	1.06	369	0.068	0.185
b	37000	1.05	378	0.074	0.195
a	275000	1.05	379	0.076	0.200
b	600000	1.10	380.5	0.095	0.249
c	2.000000	1.15	381	0.090	0.237

* see experimental, a : Interchim, b : Pressure chem, c : Interchim

x : no measurement made

Figure 2 shows Tg versus log $\overline{Dp}$ and three regions can be seen :

i $1 < \overline{Dp} < 25$ where Tg = 135.7 log Pp + 155

ii $25 < \overline{Dp} < 450$ Tg has a much slower variation than in i

iii $\overline{Dp} > 450$ Tg approaches 383 K.

The plot of $\frac{\Delta Cp}{Tg} = f\ (\log \overline{D}p)$ clearly shows a change in slope for Dp = 25 but no sharp variation occurs at $\overline{Dp} \simeq 450$ (figure 3).

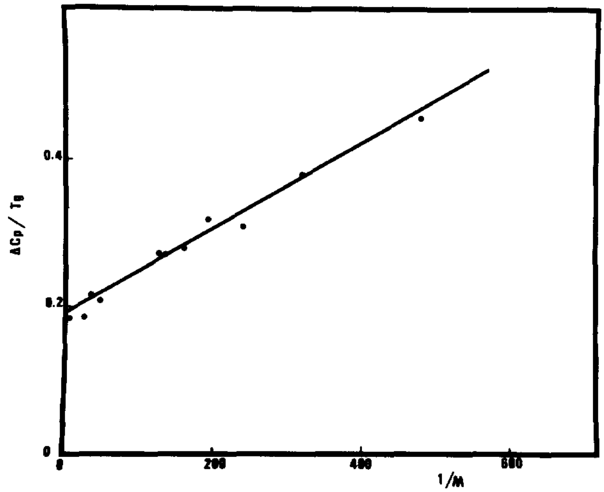

Fig. 3 : Plot of $\frac{\Delta Cp}{Tg} = f(\log \overline{Dp})$

Discussion

At Tg the following reaction is observed

Ag → Aℓ   Ag = compound A in glossy state
                 Aℓ = compound A in liquid state

Then the change in entropy is $\Delta S = S_{A\ell} - S_{Ag}$ and $\Delta S = f(T)$ can be expressed as :

$$\frac{d\Delta S}{dT} = \frac{Cp(A\ell)}{T} - \frac{Cp(Ag)}{T}$$

by extrapolation of Cp(Aℓ) and Cp(Ag) below and above Tg. At Tg : $\frac{d\Delta S}{dT} = \frac{\Delta Cp}{Tg}$ and with Cp expressed in $J\ g^{-1}\ K^{-1}$:

$$\frac{1}{M}\frac{d\Delta S}{dT} = \frac{\Delta Cp}{Tg}$$

This relation, interpreted in terms of order in solid and liquid phases, quantifies the change versus the temperature of the mobility of the molecules in solid and liquid phases. Or, in other words, the variation of interaction of molecules versus temperature in liquid and solid phases. Plot of $\frac{\Delta Cp}{Tg} = f(\frac{1}{M})$ shows a linear relationship in the range $200 < \overline{M}w < 2100$

(figure 4). Logarithmic variation of Tg = f($\overline{D}$p) suggests that the origine of the change in interaction is to be found in an additive property namely the chain length.

Comparison with other molecules such as n alkanes (9) shows a similar pattern of behavior for approximatly the same chain length : Tm increases slowly after $C_{40}H_{82}$. Furthermore solubility of polyvinyl chloride in vinyl chloride changes at $\overline{D}$p ≃ 20 (10). Thus the first linear part of figure 2 or figure 3 is the expression of simple interactions whose nature is essentially the same up to $\overline{D}$p = 25. It is possible that at Tg a second phenomenon occurs above $\overline{D}$p = 25 (for exemple rotation of a phenyl group) which was impossible at a lower temperature (or lower $\overline{D}$p).

Thus ΔS could possibly be the sum of two effects one of them being constant (expressed in J g^{-1} K^{-1}).

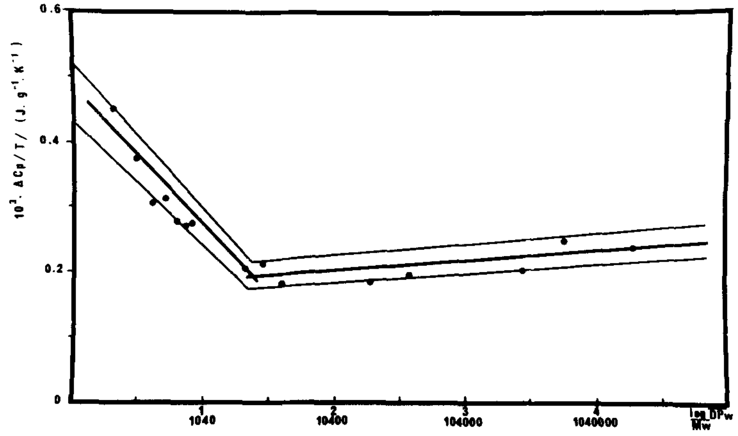

Fig. 4 : Plot of $\frac{\Delta Cp}{Tg}$ = f$(\frac{1}{M})$

A small thermal effect seen at Tg on warming and not on cooling is interpreted in terms of local variation of arrangement before and after Tg. It is interesting to note that a sharp exotherm is sometimes observed on cooling to temperature of up to 40 K below Tg. Some crystalline like arrangement is possible in liquid and solid phases. A calorimetric determination of the specific heat of polystyrene versus $\bar{D}p$ appears to be well suited to the study of the glass transition.

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