EFFECT OF MOLECULAR WEIGHT OF POLYSTYRENE ON HEAT CAPACITY AND THERMAL TRANSITIONS*

B. V. KOKTA, J. L. VALADE, V. HORNOF AND K. N. LAW

Département d'Ingénierie, Université du Québec à Trois-Rivières, C.P. 500,
Trois-Rivières, P. Québec (Canada)

ABSTRACT

Differential scanning calorimetry was used to study the effect of the molecular weight of well-defined polystyrene samples, the effect of heating and cooling rates, sample weight on the specific heat under and above the glass transition temperature T_g. It has been found, that the C_p of polystyrene was indirectly proportional to molecular weight increased up to $\overline{M}_n = 100,000$.

The T_g was increasing with molecular weight up to $\overline{M}_n = 300,000$ and then levelled off which was in agreement with data obtained for activation energies and rates of polystyrene degradations.

Another weak transition, "third order" $T_{1.1}$ has been observed after the samples were quenches from 250°C to the temperature of ice water. The effect of $\overline{M}_n$ on $T_{1.1}$ was similar to the one on T_g. After levelling off ($\overline{M}_n = 300,000$) the $T_{1.1}$ was 178°C and $T_g = 108$°C.

INTRODUCTION

A knowledge of the specific heat, C_p and second-order transitions of high polymers is becoming increasingly important since the use of thermoplastic and thermosetting polymers is rapidly growing. An excellent review of the heat capacities of linear high polymers is given by Wunderlich and Baur[1] where a theoretical treatment is followed by an extensive collection of experimental data. The molecular weight dependence of heat capacity of PS was almost neglected in previous studies. Li[2] found, that for polystyrenes of molecular weights of 55,000; 125,000 and 425,000 the heat capacity decreased with increasing molecular weight by about 5% at temperatures between 340 and 390 K.

The molecular weights of samples measured by other authors were not known. Ueberreiter and Otto-Laupenmuhlen[3], who used a sample with $\overline{M}_n = 3,650$ have noted that below the glass transition temperature (T_g), the C_p is almost independent of the molecular weight.

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Ishihara et al.[13] have shown, that the thermal history did not have any effect on the C_p of PS before and after T_g, but a large effect was shown in the glass transition range[1].

As far as the second order transition is concerned, most authors have reported glass transition temperature T_g, which itself is strongly molecular weight dependent. Its value has been represented, i.e., by Fox and Loshack[1] as a function of molecular weight: $1/T_g = 1/373 + 0.864/M$.

Recently, Boyer[4] has pointed out that available data tend to indicate the existence of an amorphous transition in atactic polystyrene at $\sim 160°C$, which is designated $T_{l,l}$. Boyer has indicated *some* mol.-wt. dependence, i.e., from 137 to 192°C in the mol.-wt. range from 2,900 to 360,000. This transition seems to disappear at very slow heating rates. This weak transition, sometimes called the third order transition, is apparently difficult to observe experimentally, since it was not mentioned in the studies e.g. by: Ueberreiter and Kanig[5], Bianchi and Rossi[6], Illers[7], Heydemann and Guicking[8].

From a literature review it is clear that most of the studies on polystyrene deal with bulk samples of varying molecular weights (which are sometimes not mentioned at all). This may musk or distort some of the useful relationships between the structure and properties. In order to get a more complete picture of the thermal behavior of polystyrene, the authors of this article have used well-defined polystyrene samples for their measurement. In the first article, recently published[9], a dynamic TG method was used to study the effect of the molecular weight as well as the effect of heating rate and sample weight on the kinetic parameters of thermal decomposition.

In the present work, well-characterized polystyrene fractions are used to clarify the effect of molecular weight on the heat capacity below and above the glass transition T_g as well as to determine the correlation between the "tertiary" transition $T_{l,l}$ and molecular weight.

EXPERIMENTAL

Apparatus

The samples were studied by means of a Perkin-Elmer scanning calorimeter, Model DSC-1. Standard pans with cover were used and the scanning speed was usually 10 or 20°C min^{-1} with a sensitivity range 4-8 mcal sec^{-1} full scale for specific heat measurement or 1-2 mcal sec^{-1} for third order transition $T_{l,l}$ measurement. Sample weight used was between 0.5 and 1.5 mg. Dried oxygen-free ($O_2 < 0.1$ ppm) nitrogen gas was used as inert carrier at a flow-rate of 20 ml min^{-1}. The temperatures could be reproduced to within $\pm 0.1°C$. In case of specific heat measurements, the reproducibility was $3 \pm 1\%$ for the same sample (in the second and third run) and $\pm 7\%$ for consecutive identical samples.

Polymers

The PS was obtained from Pressure Chemical Co. The molecular weights and polydispersies of these samples are summarized in Table 1.

TABLE 1

MOLECULAR WEIGHT SPECIFICATIONS FOR POLYSTYRENE SAMPLES

$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Note
900	1.10	
1000	1.10	
4000	1.10	$\bar{M}_n$ averaged from V.P.O., cryoscopy and viscosity.
10000	1.06	
110000	1.06	
200000	1.06	
390000	1.06	
411000	1.06	
498000	1.20	$\bar{M}_n$ by membrane osmometry, $\bar{M}_w$ by light scattering.
670000	1.15	
1800000	1.20	
2000000	1.2	

RESULTS AND DISCUSSION

Specific heat

All measurements of specific heat have been made using sapphire as a standard. Typical DSC curves for specific heats as a function of temperature as plotted by computer are shown in the following Figs. 1-5. Each point represents an average value of at least five measurements. In the first run, samples were heated from the ambient temperature up to about 200°C and then cooled down usually with the same scanning speed. In the second run, the same sample was scanned again up to 200°C.

PS4000SS20FIRSTRUN

SP. HEAT VS. TEMPERATURE
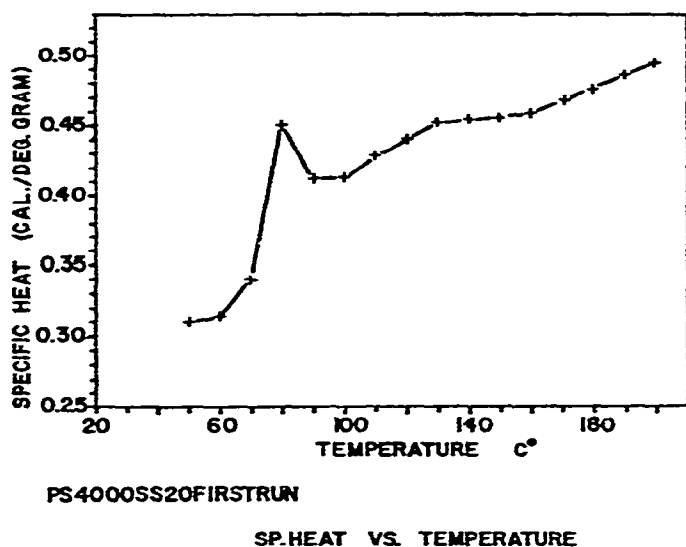
Fig. 1. Effect of temperature on specific heat. $\bar{M}_n = 4000$; scanning speed = 20 °C min^{-1}; first run.

The third run was obtained similarly by cooling and reheating again the same sample. Generally, the differences between the second and third run were negligible compared to differences between the first and second run, mainly in the T_g glass transition region. For this reason only the results of the first and second run are shown.
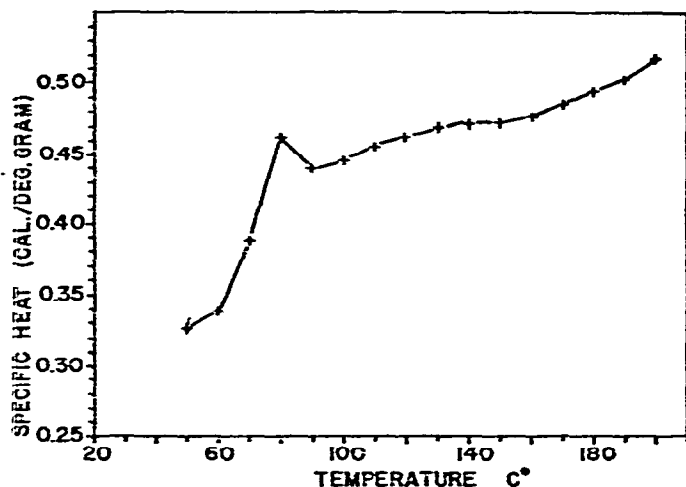
PS4000SS20CSSECONDRUN

SP. HEAT   VS.   TEMPERATURE

Fig. 2. Effect of temperature on specific heat. $\bar{M}_n = 4,000$; scanning speed $= 20\,^{\circ}C\ min^{-1}$; second run
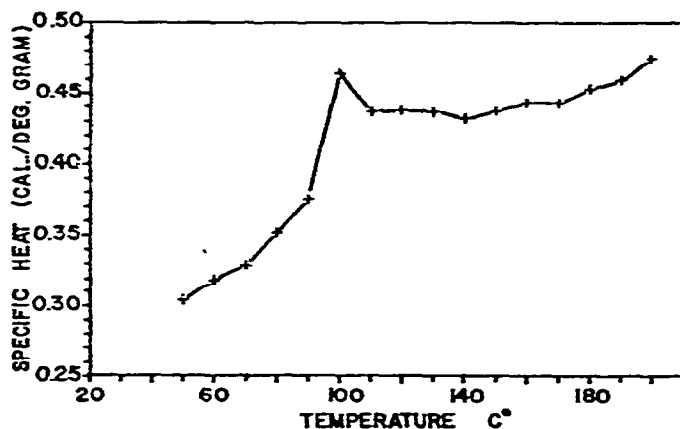
PSIOOOOSS20CS5SECONDRUN

SP. HEAT VS. TEMPERATURE

Fig. 3. Effect of temperature on specific heat. $\bar{M}_n = 10,000$; scanning speed $= 20\,^{\circ}C\ min^{-1}$; cooling speed $= 5\,^{\circ}C\ min^{-1}$; second run.

SP. HEAT VS. TEMPERATURE
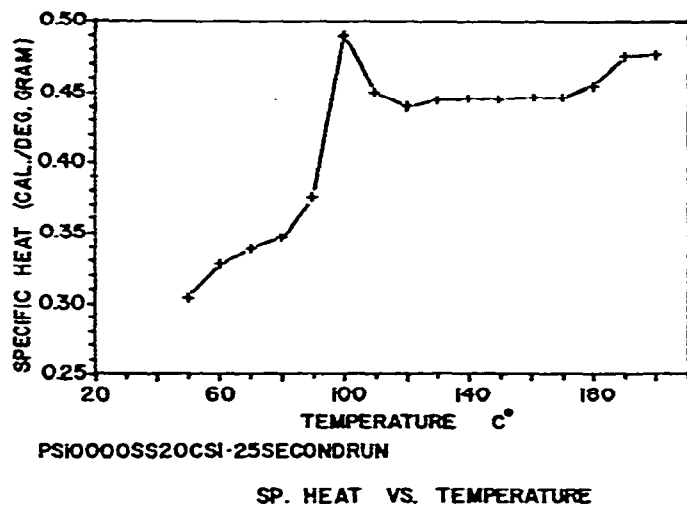
Fig. 4. Effect of temperature on specific heat. $\bar{M}_n = 10,000$; scanning speed $= 20\,^\circ C\,min^{-1}$; cooling speed $= 1.25\,^\circ C\,min^{-1}$; second run.

SP. HEAT VS. TEMPERATURE
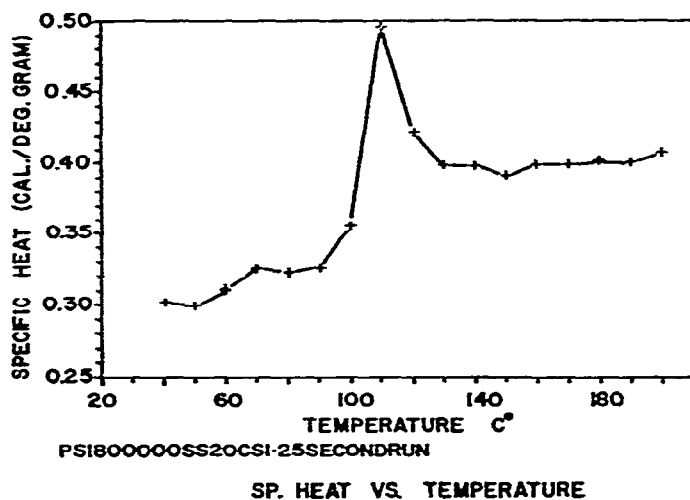
Fig. 5. Effect of temperature on specific heat. $\bar{M}_n = 1,800,000$; scanning speed $= 20\,^\circ C\,min^{-1}$; cooling speed $= 1.25\,^\circ C\,min^{-1}$; second run.

Effect of sample weight, and of cooling and heating rates

Experimental conditions as well as thermal history usually can influence the thermal behavior of polystyrene samples as was recently shown by Kokta et al.[9] in case of the kinetic parameters of thermal decomposition.

The effect of sample weight on specific heat is shown in Figs. 6–8 for temperatures below as well as above T_g. For sample weight below 10 mg the specific heat was not considerably influenced by the mass variation regardless of the molecular weight used.

76
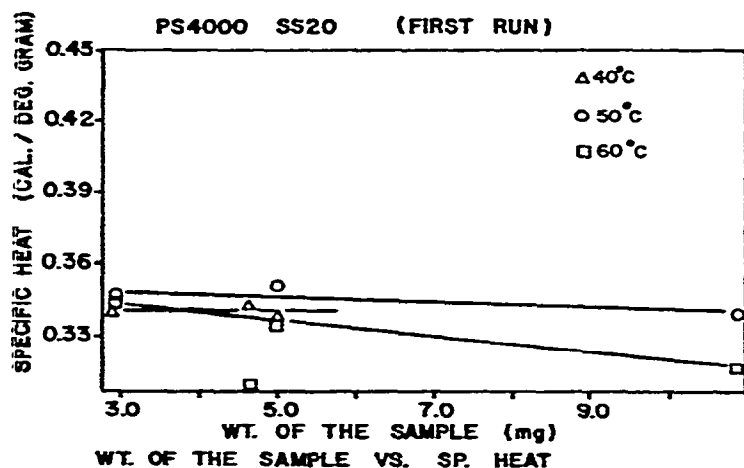
Fig. 6. Effect of sample weight on heat capacity. $\bar{M}_n = 4,000$; scanning speed = 20 °C min^{-1}; first run; temperatures below T_g.
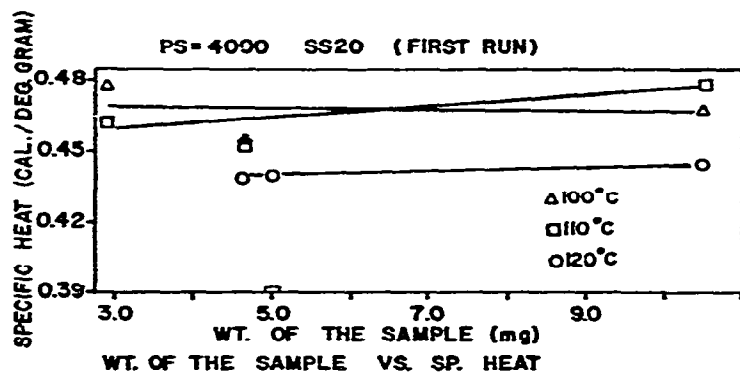

Fig. 7. Effect of sample weight on heat capacity. $\bar{M}_n = 4,000$; scanning speed = 20 °C min^{-1}; first run; temperatures above T_g.
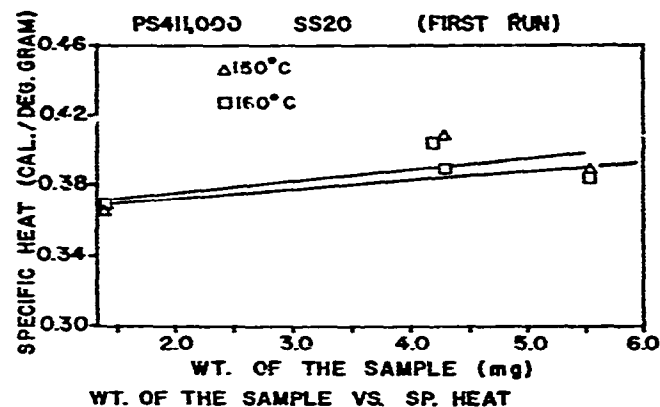

Fig. 8. Effect of sample weight on heat capacity. $\bar{M}_n = 411,000$; scanning speed = 20 °C min^{-1}; first run.

Similar results for the effect of scanning speed on C_p are shown in Figs. 9 and 10. No discernible pattern of the effect of heating speed on C_p has taken effect. A third parameter, which could have influenced the absolute values of C_p under or above T_g was the rate of cooling after the first run.
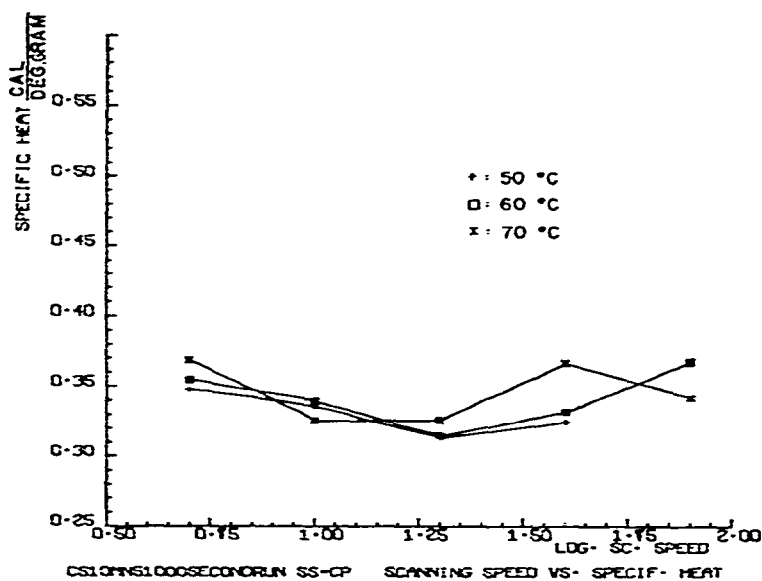

Fig. 9. Effect of scanning speed on heat capacity. $\overline{M}_n = 1000$; second run; temperature below T_g.
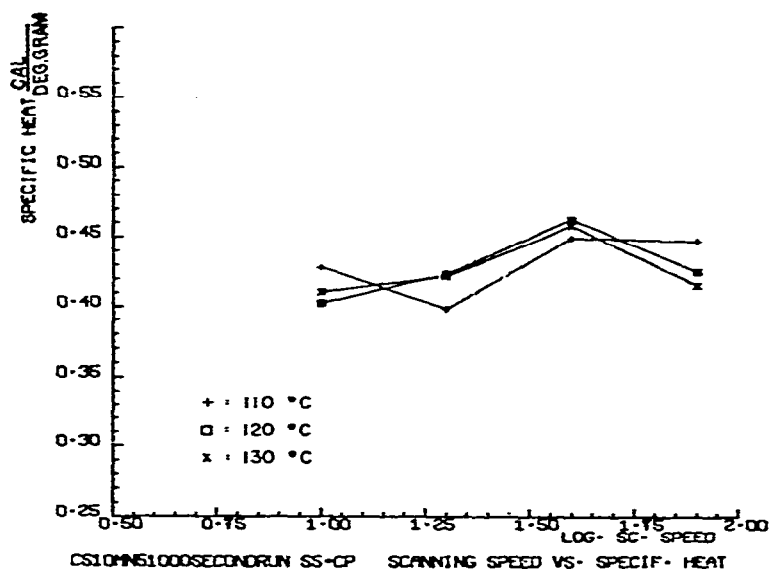

Fig. 10. Effect of scanning speed on heat capacity. $\overline{M}_n = 1000$; second run; temperature above T_g.

In order to clarify this question, different cooling rates were used for samples which have undergone the first run (up to 200°C with scanning speed 20°C min^{-1}). DSC curves obtained by scanning the samples after cooling are shown in Figs. 11 and 12.

As expected, this treatment affected C_p neither under nor above T_g. These results are in agreement with results published by Wunderlich[1].
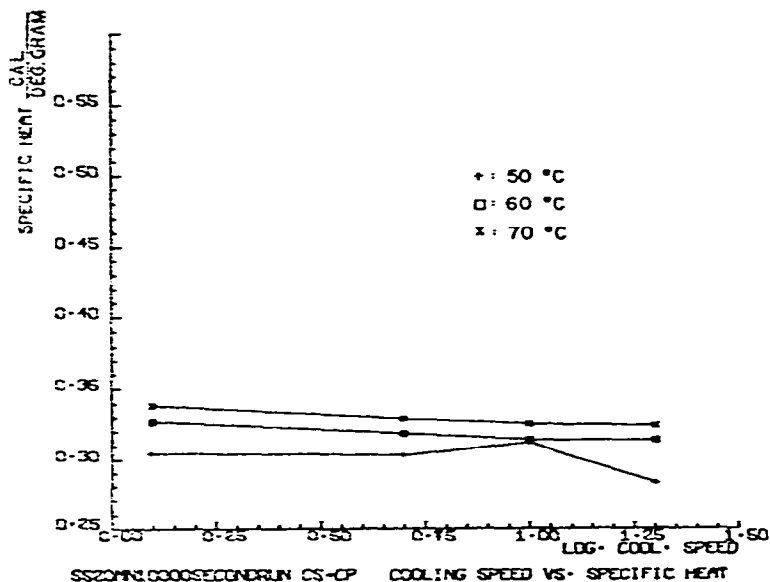

Fig. 11. Effect of cooling rate on heat capacity. $\bar{M}_a = 10,000$; second run, temperatures below T_g.
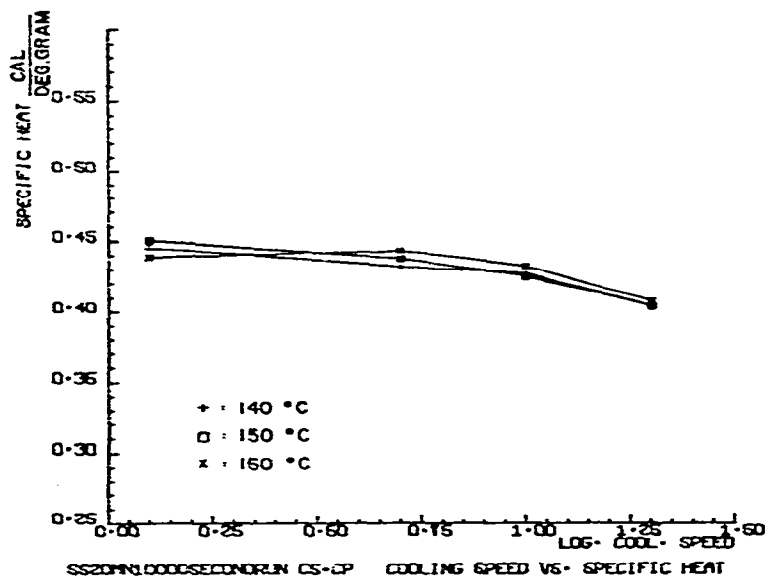

Fig. 12. Effect of cooling rate on heat capacity. $\bar{M}_a = 10,000$; temperature above T_g.

Effect of molecular weight

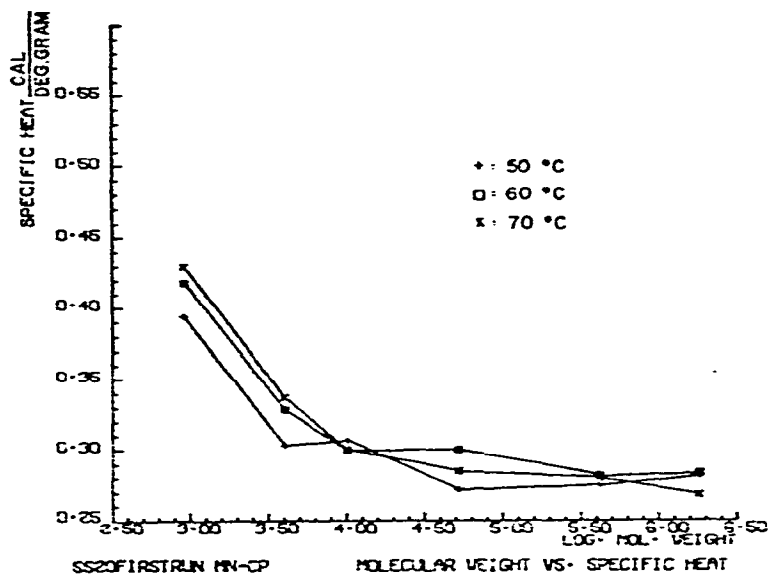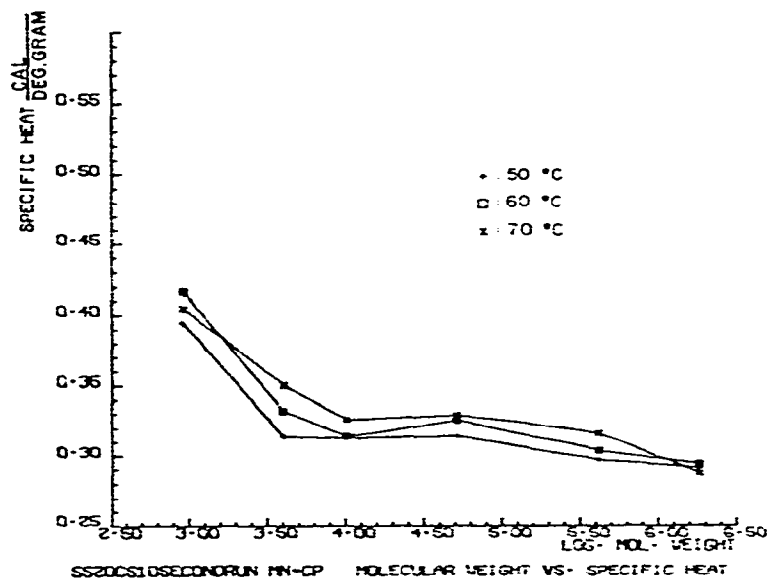The effect of molecular weight on the C_p for temperatures below as well as above the T_g is shown in Figs. 13–16.

Fig. 13. Effect of number-average molecular weight on heat capacity below the glass transition temperature T_g. Scanning speed = 20°C min^{-1}; first run.

Fig. 14. Effect of number-average molecular weight on heat capacity below the glass transition temperature T_g. Scanning speed = 20°C min^{-1}; cooling rate = 1C°C min^{-1}; second run.
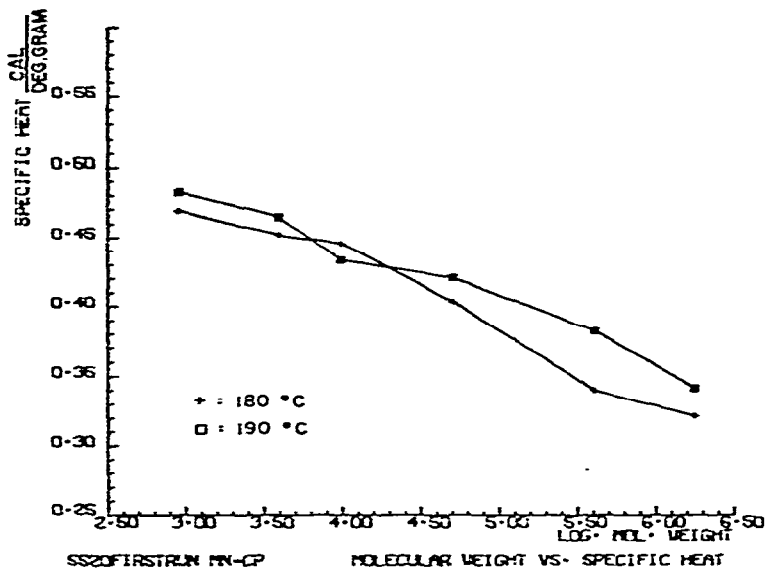
Fig. 15. Effect of number-average molecular weight on heat capacity above the glass transition temperature T_g. Scanning speed = 20 °C min^{-1}; first run.
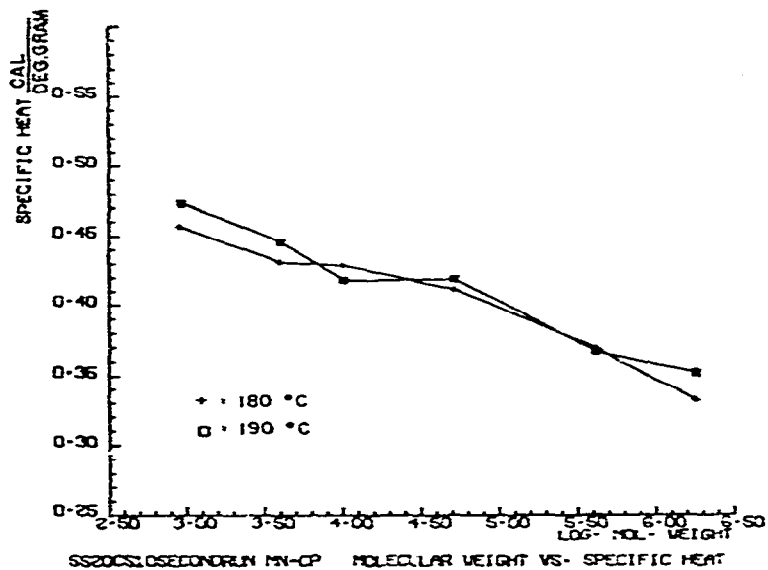

Fig. 16. Effect of number-average molecular weight on heat capacity above the glass transition temperature T_g. Scanning speed = 20 °C min^{-1}; cooling rate = 10 °C min^{-1}; second run.

It is obvious from Figs. 13–16 shown above that a definite dependence on the molecular weight occurs.

A decrease of C_p with increased molecular weight is clearly demonstrated. This pattern is in agreement with the results of Li[2] (see Fig. 17).
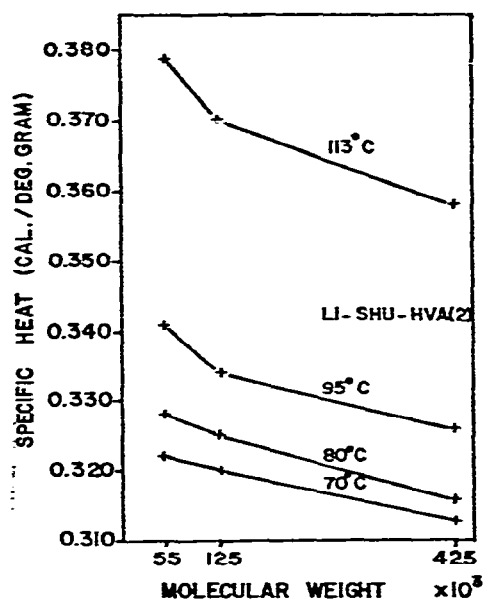
Fig. 17. Effect of molecular weight on heat capacities of polystyrene[2].

It is clear that the relationship between $\bar{M}_n$ and C_p is different for temperatures below and above T_g. These differences may be explained by the different character of vibrations, which contribute to C_p.

The change in C_p with $\bar{M}_n$ above the T_g can be rationalized in terms of the different torsional vibrations of end and middle repeating units of the polymeric chain[1] and below the glass transition temperature the C_p is a result of a transverse vibration[3].

In general, the decrease of specific heat with molecular weight may be explained as follows: (1) By the formation of large polymeric units, starting from styrene, the
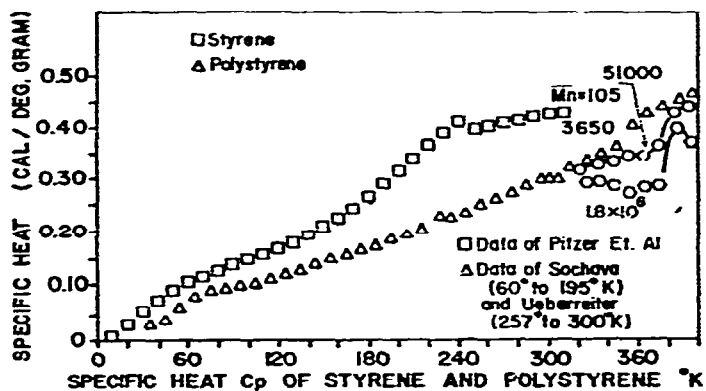

Fig. 18. Effect of temperature on specific heats of styrene and polystyrene.
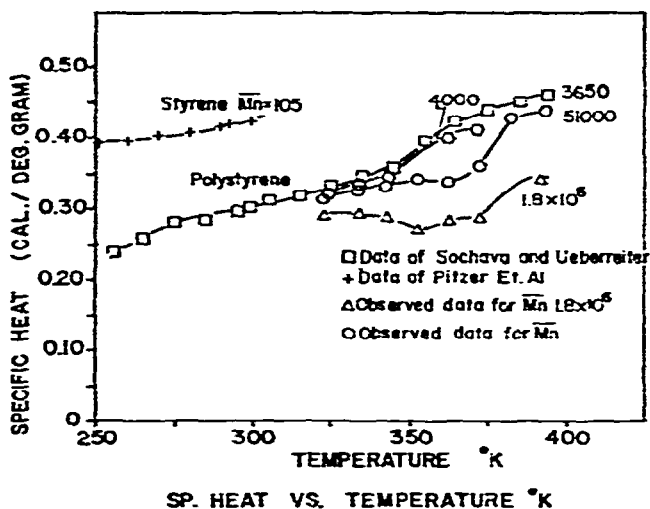
82

Fig. 19. Effect of temperature on specific heats of styrene and polystyrene.

specific heat will decrease by the limitation of some vibrations previously possible in styrene (optical vibrations). (2) By an increase of degree of polymerization (length of the chain), the relative contribution of chain end vibrations to C_p diminishes.

In Figs. 18 and 19 are compared C_p of styrene ($M_n = 104.15$) with polystyrene having $\overline{M}_n = 3,650; 4,000; 51,000$ and $1,800,000$. From Fig. 19 it is also clear that the results obtained by Sochava and Trapeznikova[10], Ueberreiter and Otto-Laupenmuhlen[3], and in our work can be related to different molecular weights of the samples used.
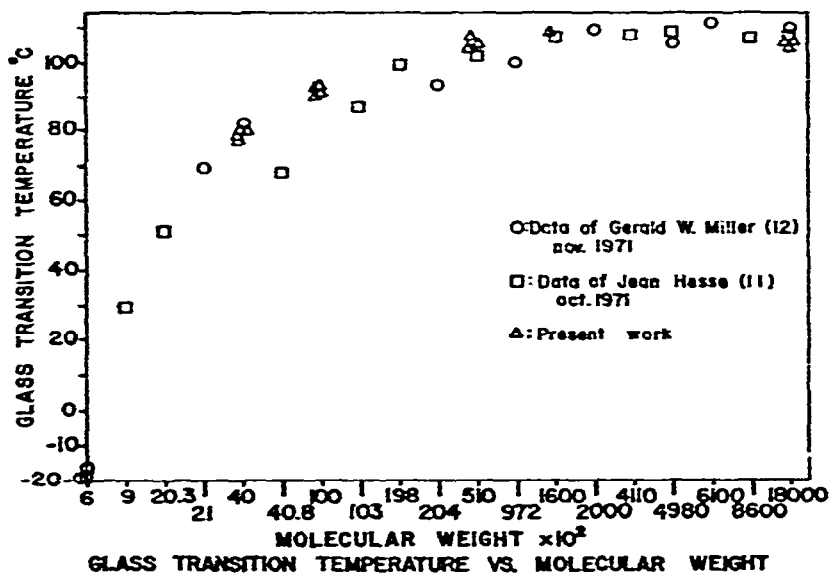

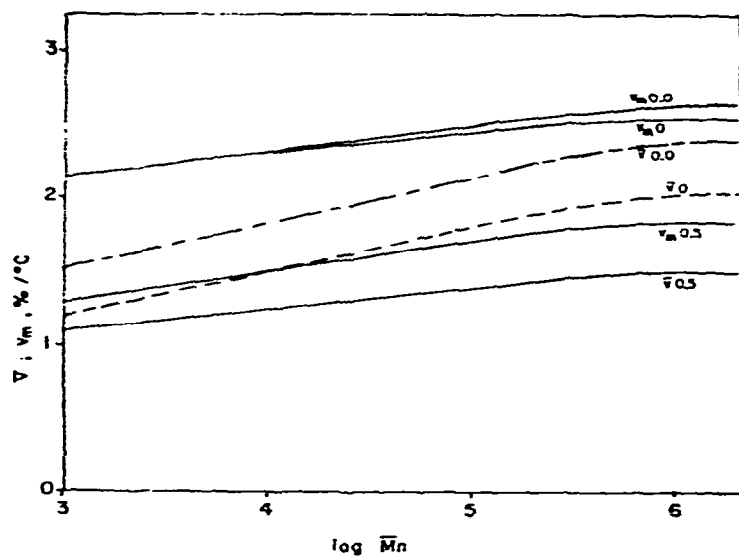Fig. 20. Effect of number-average molecular weight on the glass transition temperature T_g.

Fig. 21. Effect of number-average molecular weight on specific average rates $\bar{v}_{0.5}$, $\bar{v}_0$, and $\bar{v}_{0,0}$ and maximum rate of decomposition $r_{m0.5}$, r_{m0}, and $r_{m0,0}$ (ref. 9).
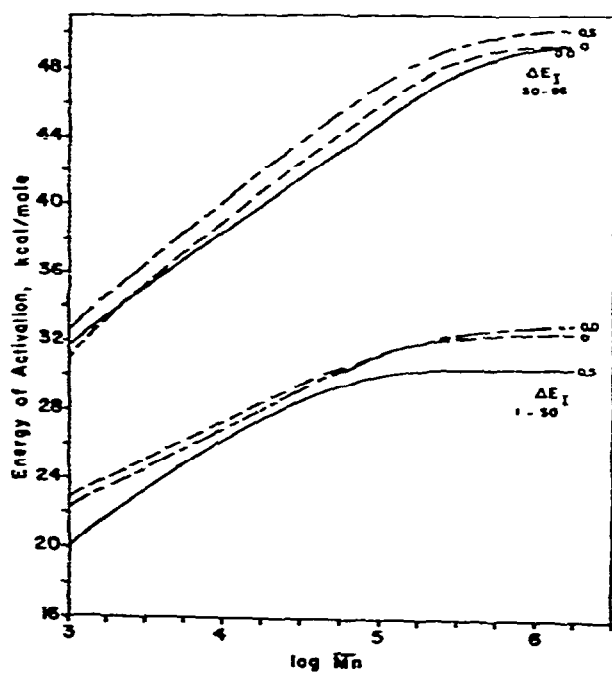

Fig. 22. Effect of number-average molecular weight on activation energies of the first ($\Delta E_{0.5(1-50)}$, $\Delta E_{0,0(1-50)}$, $\Delta E_{0(1-50)}$) and second half ($\Delta E_{0.5(50-95)}$, $\Delta E_{0(50-95)}$, $\Delta E_{c,0(50-95)}$) of decomposition[9].

More recently Sochava and Trapeznikova[10] have determined the C_p of monomeric methyl methacrylate and poly(methylmethacrylate) in the temperature range of 50–200 K. It was shown that the C_p decreases about 25% upon polymerization.

Second order transition

Effect of molecular weight on glass transition temperature T_g is shown in Fig. 20. An increase of T_g with molecular weight up to about $\overline{M}_n = 300,000$ and the subsequent levelling off is in agreement with the values of Hesse[11] recently reported. The similar character of correlation between the $\overline{M}_n$ of polystyrene and activation energies as well as the rate of degradation was reported recently by Kokta and Valade[9] (see Figs. 21 and 22).

Third order transition $T_{1,1}$

In the first part of our work using the polystyrene samples either non-treated or cooled as described above, no third order transition was observed. On the other hand, when the samples were heated up to 250°C with a scanning speed of 80°C min^{-1}, then quenched at 0°C and reheated at a low scanning rated (2.5 up to 10°C min^{-1}), the weak transition was observed. Typical DSC curves of the quenched samples are shown in Figs. 23 and 24.

An effect of molecular weight on $T_{1,1}$ is shown in Fig. 25. As can be seen, this effect is well discernible (contrary to the slight effect indicated by Boyer[4]) and resembles the effect of $\overline{M}_n$ on T_g.

An ad hoc mol. interpretation involving free volume and energy barriers to rotation about the chain axis is offered by Boyer[4]. The polystyrene $T_{1,1}$ transition results when the *entire* polymer can move *as a unit*.
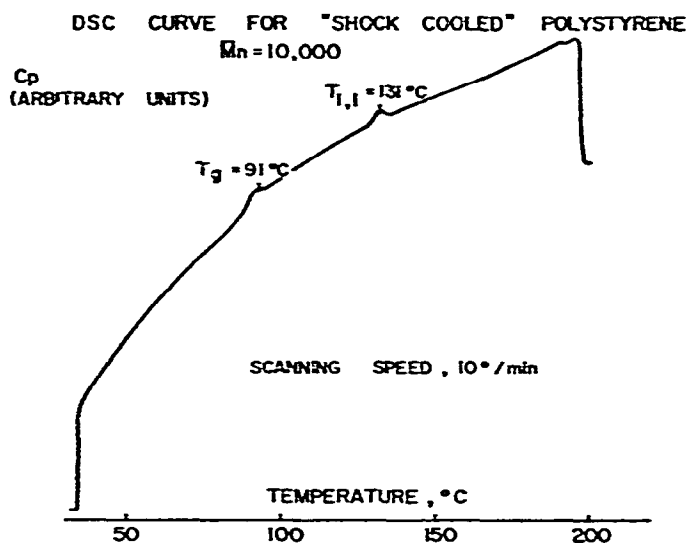

Fig. 23. Differential scanning calorimetry (DSC) curves for a quenched polystyrene. $\overline{M}_n$ 10,000; scanning speed = 10°C min^{-1}, range = 2 mcal full scale^{-1}.

DSC CURVE FOR "SHOCK COOLED" POLYSTYRENE

$\bar{M}_n = 20,400$

Cp
(ARBITRARY UNITS)

$T_g = 98\ ^\circ C$ $T_{l,l} = 141\ ^\circ C$

SCANNING SPEED , 10°/min

TEMPERATURE, °C
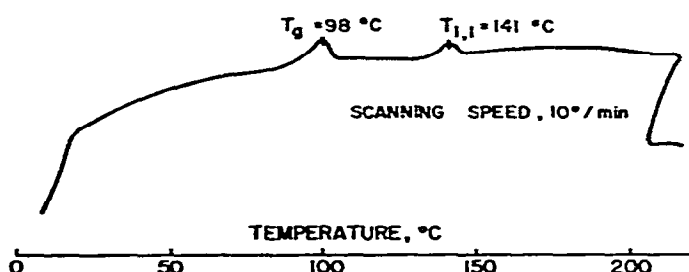
Fig. 24. Differential scanning calorimetry (DSC) curves for a quenched polystyrene. $\bar{M}_n = 20,400$; scanning speed = 10 °C min^{-1}; range = 1 mcal full scale^{-1}.

POLYSTYRENE
EFFECT OF MOLECULAR WEIGHT
ON GLASS TRANSITIONS

$T_{l,l}$

TEMPERATURE, °C

T_g

O — SECOND ORDER TRANSITION
X — THIRD ORDER TRANSITION
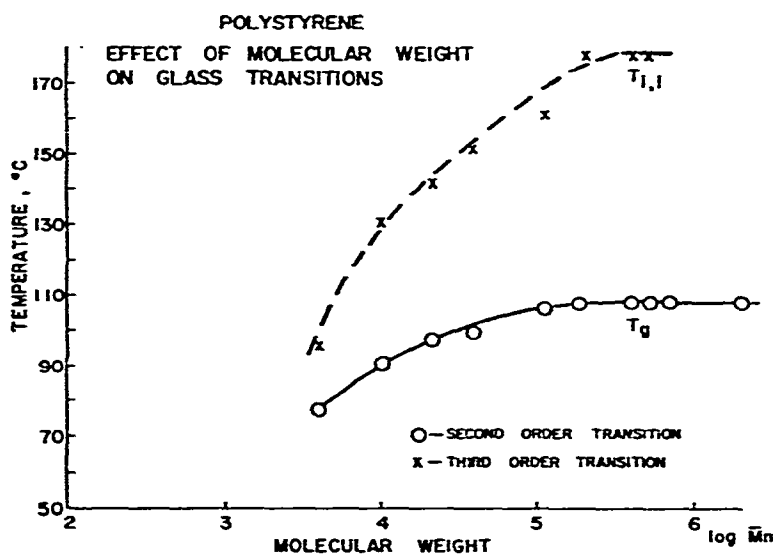
MOLECULAR WEIGHT   log $\bar{M}_n$

Fig. 25. Effect of number-average molecular weight on the second (T_g) and third order ($T_{l,l}$) transitions.

ACKNOWLEDGEMENTS

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