Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. V. Polystyrene

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The heat capacity of polystyrene from 0 K to 600 K is reviewed on the basis of measurements on 29 samples reported in the literature. A set of recommended data for amorphous polystyrene is derived. The effect of tacticity on the heat capacity is also evaluated. Entropy and enthalpy functions are calculated. This paper is the fifth in a series of publications which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: atactic; crystal; crystallinity; density; enthalpy; fusion; glass transition; heat capacity; isotactic; linear macromolecule; melt; polystyrene.

Contents

1. Introduction

This paper is the fifth paper in a series of discussions of heat capacities of linear macromolecules. In the preceding papers [1,2,3,4][1], the heat capacities of selenium, polyethylene polypropylene and a series of polyoxides were analyzed. In this paper the heat capacity of polystyrene, the simplest organic linear macromolecule with a large (aromatic) side group has been critically analyzed. In subsequent publications the analysis of heat capacities of groups of more complicated linear macromolecules will be reported.

2. Heat Capacity of Polystyrene

2.1. Introduction

Polystyrene derives from polyethylene by substitution of phenyl groups on every second carbon atom. The repeating unit of polystyrene is CH_2–CHC_6H_5–(formula weight 104.15). The chemical structure is complicated by the possibility of stereoisomers of which the simplest are atactic, isotactic and syndiotactic. Atactic polystyrene, which has random placement of the phenyl groups on either of the two isomeric positions, has no crystallinity. Isotactic polystyrene, which has sterically identical placement of the phenyl groups over long sequences can be crystalline (typical crystallinities range up to 0.5). Finally, syn-

[1]Figures in brackets refer to the literature references in section 5.

[2]See AIP document no. PAPS JPCRD-11-0313-9 for 9 pages of data tables. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N.Y. 10017. The price is $1.50 for a microfiche or $5.00 for photocopies. Airmail is additional. This material also appears in *Current Physics Microform*, the monthly microfilm edition of the complete set of journals published by AIP, on the frames following this journal article.

diotactic polystyrene is known which has sterically an alternating placement of phenyl groups. Heat capacities have been measured only for isotactic and atactic polystyrene.

The crystal structure of isotactic polystyrene is trigonal (space group $R\bar{3}c$). The molecular chains form a 2*3/1 helix along the crystallographic c-axis. The unit cell parameters have been determined by Natta et al. [5]

$$a = 2.19 \text{ nm}, b = 2.19 \text{ nm}, c = 0.665 \text{ nm}.$$

The crystalline density is 1.127 Mg m^{-3} at 298 K which corresponds to a packing fraction of 0.67 [6].

The density of amorphous, isotactic polystyrene at room temperature is 1.054 Mg m^{-3} [6]. This corresponds to a packing fraction of 0.63. For atactic polystyrene values of 1.04 to 1.065 Mg m^{-3} have been reported for the density [7]. In this work, the above densities of amorphous and crystalline isotactic polystyrene were used to calculate crystallinities.

Equilibrium melting parameters for isotactic polystyrene ($T_m^0 = 516$ K and $\Delta H_f = 10.0$ kJ mol^{-1}) have been evaluated by Wunderlich [8].

The glass transition for polystyrene as a function of molecular weight can be presented by the following equation [7,9].

$$1/T_g = (1/373) + (0.864/M). \quad (1)$$

2.2. Literature Data on the Heat Capacity of Polystyrene

Forty-four investigations of the heat capacity of isotactic and atactic polystyrene have been reported in the literature. Heat capacity of sixty samples of various crystallinities and molecular weights have been measured over a wide range of temperature.

All investigations were critically evaluated in terms of sample characterization, experimental technique, error limit and accuracy of representation of the data. It was found that only nineteen of the forty-four investigations met our standards of acceptable data (discussed in ref. [1]). These investigations are listed in table 1. They contain heat capacity data on twenty-nine samples of isotactic and atactic polystyrenes. The samples cover a range of crystallinity from 0 to 0.43, most of the investigated samples being completely amorphous. The twenty-five investigations which did not contain acceptable data were not included in further analysis. These are listed in table 2, along with brief comments of the reasons for exclusion from this study.

Table 1 lists chronologically all investigations from which data were retrieved. Each sample has been given a number which is in accordance with the file number of our data bank. The temperature region over which the determination of heat capacity was carried out is given in kelvins. The experimental technique used by the investigators and their claimed experimental uncertainties are listed. A review of various experimental techniques used for measuring heat capacities of linear macromolecules is given in reference [1]. Sources of data (tables, graphs, or curve fitted functions) are also listed. If the data were presented in tabular form, but not in temperature intervals desired by us (0.1 K below 1 K to 10 K at higher temperatures), the data were interpolated.

Characterization of the samples is also given in table 1. Commercial names and origin of the samples are given. Molecular weight and a brief thermal history of the sample, if reported by the investigators, are also listed. The key characterization parameter useful for our analysis is the crystallinity of the samples. If the density at 298 K was reported, the weight fraction crystallinity was recalculated as

$$w^c = \left(\frac{\rho_c}{\rho}\right)\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \quad (2)$$

where ρ, ρ_c and ρ_a are densities of the semicrystalline, completely crystalline and completely amorphous states, respectively ($\rho_c = 1.127$ M gm^{-3}; $\rho_a = 1.054$ Mg m^{-3}).

For a number of samples the crystallinity is not reported. Most of these are atactic commercial samples with little or no crystallinity. Thus, we assumed that these samples are completely amorphous.

The heat capacity data on various polystyrene samples retrieved from the literature are given in tables A1 to A6. These tables have been deposited with Physics Auxiliary Publication Service of the American Institute of Physics. The low temperature data (below 5 K) are given in table A1. Tables A2 and A3 contain the data on atactic and isotactic polystyrene below the glass transition temperature. The data between the glass transition and melting temperatures for semicrystalline isotactic polystyrene samples are given in table A4. Finally, tables A5 and A6 contain data on molten atactic and isotactic polystyrene, respectively.

Table 1. Heat capacity measurements of polystyrene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data [d]
Brickwedde (1952) [12][b]	1. Atactic $w^c = 0$[a]	20-400	Adiabatic (unreported)	Table[b]
Sochava and Trapeznikova (1958, 1961) [13, 14]	2. Atactic $w^c = 0$[a]	50-160	Adiabatic (unreported)	Table
Noer, Dempsey and Gordon (1959) [15]	3. Atactic $w^c = 0$[a]	1.4-4.2	Heat Pulse (5%)	Equation 1
Koplin (1962) [16]	4. Atactic $w^c = 0$[a]	300-410	Adiabatic (1.5%)	Table
Dainton, Evans, Hoare and Melia (1962) [17]	5. Isotactic[e] $w^c = 0.43$ (X-ray)	22-310	Adiabatic (1%)	Table
Hellwege, Knappe and Wetzel (1962) [18]	6. Atactic Polystyrol III (BASF) $w^c = 0$[a]	290-450	Adiabatic (1%)	Graph
Abu-Isu and Dole (1965) [19]	7. Atactic; Styron 690 (Dow Chemical) $\bar{M}_v = 240,000$ $\rho = 1.051$ Mg m^{-3} $w^c = 0$	220-590	Adiabatic (0.5%)	220-340 K Eq. 2 370-590 K Eq. 3
	8. Isotactic; EP 1340 (Dow Chemical) Quenched $\bar{M}_v = 900,000$ $\rho = 1.056$ Mg m^{-3} $w^c = 0.03$	220-340[h]	Adiabatic (0.5%)	Equation 4
	9. Isotactic; EP 1340 (Dow Chemical) $M_v = 9000,000$ $\rho = 1.073$ Mg m^{-3} $w^c = 0.27$	230-350	Adiabatic (0.5%)	Equation 5
	10. Isotactic; EP 1340 (Dow Chemical) Annealed $\bar{M}_v = 900,000$ $\rho = 1.077$ MgM^{-3} $w^c = 0.33$	290-560	Adiabatic (0.5%)	290-350 K; Eq. 6 390-450 K; Eq. 7 510-560 K; Eq. 8
Karasz, Bair and O'Reilly (1965) [20] O'Reilly and Karasz (1966) [21]	11. Atactic; NBS 706 $\bar{M}_n = 136,000$ $\bar{M}_w = 258,000$ $\rho = 1.047$ Mg m^{-3} $w^c = 0$ (X-Rays)	20-470[g]	Adiabatic (0.4%)	Table[f]

Table 1. Heat capacity measurements of polystyrene--Continued

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data [d]
	12. Isotactic; 6811 (Monsanto Co.) Quenched $\bar{M}_v$ = 320,000 ρ = 1.053 Mg m^{-3} w^c = 0 (X-ray)	310-350[h]	Adiabatic (0.4%)	Table[f]
	13. Isotactic; 6811 (Monsanto Co.) $\bar{M}_v$ = 320,000 ρ = 1.080 Mg m^{-3} w^c = 0.37	310-520	Adiabatic (0.4%)	Table[f]
Reese (1966) [22]	14. Atactic w^c = 0[a]	1.0-4.5	Transient method	Equation 9
Chang and Bestul (1968) [23]	30. Atactic; NBS 705 $\bar{M}_n$ = 180,000 $\bar{M}_w$ = 193,000 (Narrow MW distribution) w^c = 0[a]	10-350	Adiabatic (0.1%)	Table
Currie and Dole (1969) [24][c]	15. Atactic; Styron 690 (Dow Chemical) $\bar{M}_v$ = 240,000 ρ = 1.051 Mg m^{-3} w^c = 0	390-480	DSC (10%)	Graph
	16. Atactic; Styron 690 (Dow Chemical) Annealed at 473 K for 14 h. $\bar{M}_v$ = 240,000	390-510	DSC (1%)	Graph
	17. Atactic; NBS 706 Annealed at 473 K for 14 h. $\bar{M}_n$ = 136,000 $\bar{M}_w$ = 258,000	390-420	DSC (1%)	Graph
	18. Atactic; NBS 706 Molded and quenched $\bar{M}_n$ = 136,000 $\bar{M}_w$ = 258,000	390-420	DSC (1%)	Graph
	19. Isotactic; EP 1340 (Dow Chemical) Annealed $\bar{M}_v$ = 900,000 ρ = 1.077 w^c = 0.33	380-530	DSC (1%)	Graph

Table 1. Heat capacity measurements of polystyrene--Continued

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[d]
	20. Isotactic; EP 1340 (Dow Chemical) Quenched $\bar{M}_v$ = 900,000 ρ = 1.056 Mg m^{-3} w^c = 0.03	380-530	DSC (1%)	Graph
	21. Isotactic; 6811 (Monsanto) Quenched $\bar{M}_v$ = 320,000	370-520	DSC (1%)	Graph
Choy et al. (1970) [25], Stephens et al. (1972) [26].	22. Atactic $\bar{M}_n$ = 179,000 ρ = 1.04 Mg m^{-3} w^c = 0[a]	0.1-4.0	Heat pulse (1%)	0.1-0.5 K Eq. 10 0.8-4.0 K Eq. 15
Bares and Wunderlich (1973)	23. Atactic; PS-37 (Dow Chemical) $\bar{M}_n$ = 198,000 $\bar{M}_w$ = 357,000 melt	400-590	DSC (1%)	Table
Zoller, Fehl and Dillinger (1973) [28]	24. Atactic (Dow Chemical) $\bar{M}_v$ = 365,000 w^c = 0[a]	1.6-4.0	Heat pulse (2%)	Eq. 11
	25. Atactic; Lustrex HF77 (Monsanto) $\bar{M}_v$ = 349,000 w^c = 0[a]	1.6-4.0	Heat pulse (2%)	Eq. 12
	26. Atactic; (Dow Chemical) $\bar{M}_v$ = 34,600 w^c = 0[a]	1.6-4.0	Heat pulse (2%)	Eq. 13
	27. Atactic; (Borden) $\bar{M}_v$ = 33,600 w^c = 0[a]	1.6-4.0	Heat pulse (2%)	Eq. 14
Gilmore and Hay (1976) [29] Gilmore et al. (1978) [30]	28. Average data for five samples $\bar{M}_w$ = 930-19,800	300-450	DSC (2%)	300-370 K (Glassy): Eq. 16 300-450 K (melt): Eq. 17

[a] Estimated value of crystallinity (see text).

[b] Data retrieved from Boundy and Boyer [12].

[c] Heat capacity data also reported over a limited temperature range (20-40 K) below the glass transition for samples 15 to 21.

[d] Equations cited as source of data are listed separately in table 1a.

[e] Atactic content less than 5% and probably near 1%.

[f] Data were interpolated using the spline function technique to give heat capacities at ten kelvin intervals.

[g] The sample was cooled from 470 K to 300 K at 10 K h^{-1} and the heat capacity was found to be reproducible from 300 to 350 K.

[h] The sample crystallized above the glass transition.

Table 1a. Sources of data[a]

Equation 1	$C_p = 1.5 \cdot 10^{-5} T^3$ cal g^{-1} K^{-1} [b]
Equation 2	$C_p = 0.2595 + 1.024 \cdot 10^{-3}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 3	$C_p = 0.3705 + 0.607 \cdot 10^{-2}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 4	$C_p = 0.2599 + 1.022 \cdot 10^{-3}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 5	$C_p = 0.2654 + 1.045 \cdot 10^{-3}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 6	$C_p = 0.257 + 1.082 \cdot 10^{-3}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 7	$C_p = 0.2771 + 1.160 \cdot 10^{-2}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 8	$C_p = 0.3506 + 6.51 \times 10^{-3}(T-273.15)$ cal g^{-1} K^{-1} [b]
Equation 9	$C_p = 735\ T^3$ erg cm^{-3} K^{-4} [b]
Equation 10	$C_p = 5.2 \cdot 10^{-6} T + 4.6 \cdot 10^{-5}\ T^3$ J g^{-1} K^{-2} [b]
Equation 11	$C_p = 5.07 \cdot 10^{-2} T^3 + 2.09(16.6/T)^2 \exp(16.6/T) / [\exp(16.6/T)-1]^2$ mJ g^{-1} K^{-1} [b]
Equation 12	$C_p = 5.22 \cdot 10^{-2} T^3 + 1.47(15.6/T)^2 \exp(15.6/T) / [\exp(15.6/T)-1]^2$ mJ g^{-1} [b]
Equation 13	$C_p = 4.83 \cdot 10^{-2} T^3 + 2.42(17.2/T)^2 \exp(17.2/T) / [\exp(17.2/T)-1]^2$ mJ g^{-1} K^{-1} [b]
Equation 14	$C_p = 4.79 \cdot 10^{-2} T^3 + 1.91(16.7/T)^2 \exp(16.7/T) / [\exp(16.7/T)-1]^2$ mJ g^{-1} K^{-1} [b]
Equation 15	$C_p = \exp[-0.324444(\ln T)^3 + 0.545113(\ln T)^2 + 3.03949(\ln T) - 5.37229]$ J mol^{-1} K^{-1} (RMS dev. = 1.8%) [c]
Equation 16	$C_p = 0.50968T - 26.12$ J mol^{-1} K^{-1} (RMS dev. = 1.4%) [c]
Equation 17	$C_p = 0.3907T + 49.95$ J mol^{-1} K^{-1} (RMS dev. = 0.9%) [c]

[a] Equation numbers correspond to the equations in table 1.

[b] Equation reported by the authors.

[c] Authors' tabulated data, fitted with the given equation.

Table 2. Investigations not included in this study

Reference	Reason(s) for exclusion
Stull (1944) [31]	Heat capacity measurements reported on a commercial sample (Styraloy 22) from 270 to 350 K. The data are associated with large error limits.
Li (1951) [32]	Data reported for three samples M_w = 55,000; 125;000; 425,000 over a limited temperature range (350-380 K). Heat capacity decreases with increasing molecular weight by about 5%.
Ueberreiter, et al. (1951, 1953) [33, 34]	Heat capacity measurements reported for oligomers (DP = 9-35).
Hellwege, Knappe and Semjonow (1959) [35]	Sample characterization not reported. Data superceeded by later publication [18].
Warfield, Petree and Donovan (1959) [36]	Data could not be read accurately from too small graphs.
Tautz, Glück, Hartmann and Leuteritz (1963, 1964) [37, 38].	Sample characterization not reported. Data could not be read accurately from too small graphs.
Martin and Müller (1964) [39]	Data could not be read accurately from too small graphs; large error limits (5%).
Chernobyl'skii and Tertyshnik (1966) [40]	Sample characterization not reported; large error limits.
Mishchenko, Samoilov, and Buchatskii (1966) [41]	Heat capacity measurements reported for impure sample (3% volatiles). Data could not be read accurately from too small graphs.
Zoller, Fehl, and Dillinger (1970) [42]	Heat capacity measurements reported on polystyrene crosslinked with 1, 5, 20, and 40% divinylbenzene from 1.6 to 4.0 K. Heat capacity decreases with increasing number of crosslinks by 30%.
Aleman (1971) [43]	Data associated with large error limits (1-10%).
Ichihara, et al. (1971) [44, 45]	Data could not be read accurately from too small groups.
Savina, Briskman and Bondarev (1972) [46].	Effect of γ-radiation (0-5000 Mrad) on heat capacity of polystyrene was studied. Only the melting range was investigated.

Table 2. Investigations not included in this study--Continued

Reference	Reason(s) for exclusion
Anderson and Sundquist (1975) [47]	The pressure dependence of heat capacity of polystyrene was determined from simultaneous measurements of thermal conductivity and diffusivity at 300 K in the pressure range 0-25 kbar. The heat capacity decreases with increasing pressure, and its value at 25 kbar is 0.93 times than at atmospheric pressure.
Bashinov, et al. (1975, 1976) [48, 49]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Richardson and Savill (1975) [50]	Effect of thermal history on the heat capacity change at the glass transition temperature was investigated.
Brown et al. (1978) [51]	
Kokta, et al. (1976) [52]	Heat capacity measured as a function of molecular weight 4,000-411,000. Data are associated with large error limits (7%).
Belostotskii, et al. (1977) [53]	Heat capacity reported at 303 and 333 K as a function of pressure (0-5 kbar).
Lai (1976) [54]	Heat capacity data reported over a limited temperature range (40 K below and above the glass transition). The data above the glass transition are in good agreement, however, the data below the glass transition are somewhat lower than here recommended.
Dushchenko, et al. (1977, 1978) [55, 56]	Heat capacity in the glass transition region reported as a function of thermal history. The effects of isothermal annealing and heating rate have been evaluated.

2.3. Recommended Data on Heat Capacity of Amorphous and Molten Polystyrene

In the preliminary analysis, all heat capacity data on atactic polystyrene below the glass transition from 10 to 360 K (table A2) were plotted on a composite plot. It was found that all data were in quite good agreement with one another with the exception of six data points. Furthermore, all heat capacity data on isotactic polystyrene below the glass transition were also plotted on the same graph and it was found that above 70 K, the heat capacity of all isotactic samples ($w^c = 0$ to 0.43) were in good agreement ($\pm 1.5\%$) with the heat capacities of the atactic samples. The heat capacity of semicrystalline isotactic polystyrene (sample 5) below 70 K is somewhat lower than the heat capacity of the atactic samples. This situation seems to indicate that the heat capacity of polystyrene from 70 K to temperatures close to the glass transition has very limited dependence on crystallinity (and tacticity). Since most of the heat capacity measurements on polystyrene below 70 K are either on completely amorphous samples or on samples of low crystallinity, the extrapolation of the heat capacity vs the crystallinity using the two phase model equation below 70 K would not be very accurate. Thus, no estimate has been made for the heat capacity of fully crystalline polystyrene below 70 K.

Above the glass transition temperature, heat capacity measurements for only three semicrystalline isotactic polystyrene samples (10, 13, 19; table A4) have been reported. They vary in crystallinity from 0.33 to 0.37. One would expect the heat capacities of these three samples to be closely similar. However, the data on these three samples differ by about 10%. Thus, the data or sample characterization are questionable. The heat capacity values could possibly be associated with premelting (the average heat capacity value of all the three samples at 450 K (216.9 J mol^{-1} K^{-1}) is higher than the heat capacity of the melt (214.5 J mol^{-1} K^{-1}) at that temperature). Thus, the crystallinity extrapolation of the heat capacity data above the glass transition to estimate the heat capacity of crystalline polystyrene is also not possible at present.

Heat capacity measurements on seven amorphous samples have been reported below 5 K. All the data (table A1) on these samples (3, 14, 22, 24, 25, 26, and 27) were compared on a logarithmic plot. The data are in fair agreement with one another with the exception of Reese's data on sample 14. Reese's data are consistently higher than the data on all other samples by 25-40%. Measurements on sample 14 were made using the transient technique in which the heat capacity is measured indirectly from thermal conductivity. The data on all other samples were obtained using the heat pulse method. Since the heat pulse method is considered more reliable than the transient technique, the data of Reese on sample 14 were discarded. To determine recommended values of the heat capacity of amorphous polystyrene below 5 K, the data on samples 3, 22, 24, 25, 26, and 27 were fitted with the equation

$$C_p = \exp[-0.0738699(\ln T)^3 + 0.25189(\ln T)^2 + 2.90478(\ln T) - 5.21616]\ \mathrm{J\ mol^{-1}\ K^{-1}}. \quad (3)$$

The RMS deviation was 8.6%.

To determine the recommended data on the heat capacity of amorphous polystyrene below the glass transition temperature, the data on all samples were averaged at each temperature. Since the heat capacity is dependent on crystallinity below 70 K, the data on isotactic semicrystalline samples from 30 to 60 K were not used. From 140 to 160 K, the heat capacity values of sample 2 were not included in averaging. The data on sample 2 from 140 to 160 K are 1.3 to 4.2% higher than the average values of other samples. The reason for this deviation is not apparent. At 220 K, the data on samples 7 and 8 were also excluded. These data points are 3% lower, possibly because they are the first data points of the heat capacity determination. For the same reason, the data points on sample 6 at 290 and 300 K were also excluded. These data points are 4–8% higher than the averaged values. A total of 214 data points were used for averaging. The maximum standard deviation was 1.5%. In most cases the standard deviation was better than 1%.

The heat capacity of amorphous polystyrene obtained by averaging the data on various samples below the glass transition temperature were further smoothed as follows: Average heat capacity values from 10 to 240 K were fitted with the equation

$$C_p = \exp[-0.098338(\ln T)^3 - 1.30958(\ln T)^2 + 6.5499(\ln T) - 8.13656]\ \mathrm{J\ mol^{-1}\ K^{-1}}. \quad (4)$$

The RMS deviation was 0.5%. The data from 200 to 360 K were fitted with the equation

$$C_p = 7.7551 \cdot 10^5 T^{-2} + 0.53447\ T - 41.58\ \mathrm{J\ mol^{-1}\ K^{-1}}. \quad (5)$$

The RMS deviation was 0.5%. The smoothed values from 0.1 to 5 K, obtained from eq. (3), from 10 to 220 K, obtained from eq. (4) and from 230 K to the glass transition temperature (373 K), obtained from eq. (5) are given in table 9. The smoothed values are also plotted in figure 1.

To determine the recommended heat capacity data for molten polystyrene, the data of all molten samples (tables A5 and A6) were plotted. Agreement between atactic and isotactic samples from various laboratories was good. The heat capacity data on all the samples were fitted with the equation.

$$C_p = 0.2653T + 95.12\ \mathrm{J\ mol^{-1}\ K^{-1}}. \quad (6)$$

The RMS deviation was 2.5%. Equation (6) was used to calculate the heat capacity of molten polystyrene from 373 to 600 K. These values are listed in table 3. A plot of the best values of molten polystyrene is shown in figure 1.

The difference in the heat capacity between the glassy and molten polystyrene at the glass transition temperature is 30.7 J mol^{-1} K^{-1}. This corresponds to 15.4 J mol^{-1} K^{-1} $bead^{-1}$, where a bead is defined as a smallest section of the molecule that can move independently as a unit in internal rotation. This is not in agreement with Wunderlich's rule of constant heat capacity change at the glass transition (ΔC_p/mole of bead = 11.3 J g^{-1} K^{-1}) [11]. Similar deviations have been observed for aromatic polyoxides [3] and ladder type polymers which contain large number of benzene rings [10]. The discrepancy can be removed by assigning a ΔC_p value of 21.6 J mol^{-1} K^{-1} to phenyl or phenylene containing beads [57].

Table 3. Recommended thermodynamic data for amorphous polystyrene[a]

T(K)	C_p^a	$H_T^a - H_o^a$	$S_T^a - S_o^a$
	(J mol^{-1}K^{-1})	(J mol^{-1})	(J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
0.1	0.0000633	0.0000030	0.0000410
0.2	0.000132	0.0000122	0.000102
0.3	0.000269	0.0000317	0.000179
0.4	0.000496	0.0000691	0.000285
0.5	0.000838	0.000135	0.000430
0.6	0.00133	0.000242	0.000624
0.7	0.00200	0.000406	0.000876
0.8	0.00288	0.000648	0.00120
0.9	0.00401	0.000990	0.00160
1.0	0.00543	0.00146	0.00209
1.2	0.00929	0.00291	0.00340
1.4	0.01480	0.00529	0.00522
1.6	0.02231	0.00896	0.00767
1.8	0.03217	0.01436	0.01084
2.0	0.04477	0.02201	0.01485
3.0	0.1622	0.1170	0.05179
4.0	0.4058	0.3885	0.1282
5.0	0.8215	0.9860	0.2598
10.0	3.33	9.995	1.399
15.0	7.03	35.76	3.438
20.0	10.77	80.31	5.975
25.0	14.26	143.0	8.758
30.0	17.47	222.5	11.65
40.0	23.13	426.2	17.47
50.0	28.01	682.4	23.17
60.0	32.37	984.7	28.67
70.0	36.38	1328.	33.96
80.0	40.17	1712.	39.07
90.0	43.81	2132.	44.01
100.0	47.37	2588.	48.81
110.0	50.88	3079.	53.49
120.0	54.38	3605.	58.07
130.0	57.89	4166.	62.56
140.0	61.43	4763.	66.98
150.0	65.01	5395.	71.34
160.0	68.65	6063.	75.65
170.0	72.36	6768.	79.92
180.0	76.14	7511.	84.16
190.0	80.01	8291.	88.38
200.0	83.97	9111.	92.59
210.0	88.03	9971.	96.78
220.0	92.19	10872.	101.0
230.0	96.01	11812.	105.2
240.0	100.2	12792.	109.3
250.0	104.4	13815.	113.5

Table 3. Recommended thermodynamic data for amorphous polystyrene[a]--Continued

T(K)	C_p^a (J mol^{-1}K^{-1})	$H_T^a - H_o^a$ (J mol^{-1})	$S_T^a - S_o^a$ (J mol^{-1}K^{-1})
260.0	108.9	14882.	117.7
270.0	113.4	15993.	121.9
273.15	114.8	16352.	123.2
280.0	118.0	17149.	126.1
290.0	122.6	18352.	130.3
298.15	126.5	19367.	133.7
300.0	127.4	19602.	134.5
310.0	132.2	20900.	138.8
320.0	137.0	22246.	143.1
330.0	141.9	23641.	147.4
340.0	146.8	25084.	151.7
350.0	151.8	26578.	156.0
360.0	156.8	28121.	160.3
370.0	161.8	29714.	164.7
373.0 (T_g)	163.4	30202.	166.0
373.0	194.1	30202.	166.0
380.0	195.9	31567	169.6
390.0	198.6	33539.	174.8
400.0	201.2	35538.	179.8
410.0	203.9	37564.	184.8
420.0	206.5	39616.	189.8
430.0	209.2	41695.	194.7
440.0	211.9	43800.	199.5
450.0	214.5	45932.	204.3
460.0	217.2	48090.	209.0
470.0	219.8	50275.	213.7
480.0	222.5	52486.	218.4
490.0	225.1	54724.	223.0
500.0	227.8	56989.	227.6
510.0	230.4	59280.	232.1
520.0	233.1	61597.	236.6
530.0	235.7	63941.	241.1
540.0	238.4	66312.	245.5
550.0	241.0	68709.	249.9
560.0	243.7	71132.	254.3
570.0	246.3	73582.	258.6
580.0	249.0	76059.	262.9
590.0	251.6	78562.	267.2
600.0	254.3	81092.	271.5

[a] The tables may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

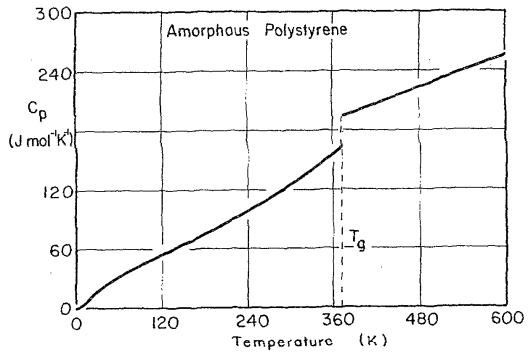

FIGURE 1. Recommended data on the heat capacity of amorphous polystyrene.

3. Thermodynamic Functions

Thermodynamic functions for amorphous polystyrene have been derived from the heat capacities. These are also listed in table 3. H^a_0 and S^a_0 refer to zero point enthalpy and residual entropy of the amorphous polymer. Details of the integrations have been reported earlier in reference [1].

4. Conclusions

The heat capacity of polystyrene from 0 to 600 K has been reviewed on the basis of twenty-nine measurements reported in the literature. A set of recommended heat capacity, enthalpy, and entropy data for amorphous polystyrene have been derived. In addition we have arrived at the following conclusions.

1. The heat capacity of amorphous polystyrene is a smooth function of temperature from 0 to 310 K. The heat capacity of molten polystyrene is also a linear function of temperature from the glass transition to 600 K.

2. The heat capacity of polystyrene from 70 K to temperatures close to the glass transition is practically independent of crystallinity and tacticity.

3. The change in heat capacity at the glass transition temperature does not fit the rule of constant $\Delta C_p(T_g)$. Similar deviations have been observed for other polymers containing phenyl structural units.

4. The heat capacity of crystalline polystyrene is not well enough known to establish thermodynamic data for completely crystalline polystyrene and to establish absolute values for the entropy and Gibbs energy of amorphous polystyrene.

5. References

[1] Gaur, U., Shu, H.-C., Mehta, A., and Wunderlich, B., Heat capacity and other thermodynamic properties of linear macromolecules I. Selenium, J. Phys. Chem. Ref. Data **10** 89 (1981).

[2] Gaur, U., and Wunderlich, B., Heat capacity and other thermodynamic properties of linear macromolecules II. Polyethylene, J. Phys. Chem. Ref. Data **10**, 119 (1981).

[3] Gaur, U., and Wunderlich, B., Heat capacity and other thermodynamic properties of linear macromolecules III. Polyoxides, J. Phys. Chem. Ref. Data **10**, 1001 (1981).

[4] Gaur, U., and Wunderlich, B., Heat capacity and other thermodynamic properties of linear macromolecules IV. Polypropylene, J. Phys. Chem. Ref. Data **10**, 1051 (1981).

[5] Natta, G., Corradini, P., and Bassi, I. W., Crystal structure of isotactic polystyrene, Nuovo Cimento Suppl. **15**, 68 (1960).

[6] Wunderlich, B., Macromolecular Physics, Vol. 1, Crystal Structure, Morphology, Defects; Vol. 2, Crystal Nucleation, Growth, Annealing; Vol. 3, Crystal Melting, Academic Press, New York, N.Y., 1973, 1976, 1980.

[7] Brandrup, J., and Immergut, E. H., Polymer Handbook, 2nd Ed. John Wiley, New York 1975.

[8] Wunderlich, B., Equilibrium melting of flexible linear macromolecules. Polym. Eng. Sci. **18**, 431 (1978).

[9] Fox, T. G. and Loschaek, S., Influence of molecular weight and degree of crosslinking on the specific volume and glass temperature of polymers. J. Polymer Sci. **15**, 371 (1955).

[10] Wrasidlo, W., Transitions and relaxations in aromatic polymers. J. Polymer Sci. **9**, 1603 (1971).

[11] Wunderlich, B., Study of the change in specific heat of monomeric and polymeric glasses during the glass transition. J. Phys. Chem. **64**, 1052 (1960).

[12] Brickwedde, F. G., Data published in Boundy, R. H., Boyer, R. F. (Ed.), Styrene, New York, Reinhold Publ. Corp. 1952.

[13] Sochava, I. V., and Trapeznikova, O. N., Internal rotation and heat capacity of a few polymers at low temperatures. Vestn. Leningr. Univ. **13**, Ser. Fiz. i. Khim. **2**, 65 (1958).

[14] Sochava, I. V., Specific heat of polymethylmethacrylate and polystyrene at low temperatures. Vestn. Leningr. Univ. **16**, Ser. Fiz. i. Khim. **2**, 70 (1964).

[15] Noer, R. J., Dempsey, C. W., and Gordon, J. E., Low temperature specific heats of three plastics. Bull. Am. Phys. Soc. **4**, 108 (1959).

[16] Koplin, H., Spezifische Wärme von reinem und weichgemachtem Polystyrol. Dissert. Techn. Hochschule Aachen 1962.

[17] Dainton, F. S., Evans, D. M., Hoare, F. E., and Melia, T. P., Thermodynamic functions of linear high polymers. Polymer **3**, 286 (1962).

[18] Hellwege, K. H., Knappe, W., Wetzel, W., Spezifische Wärme von Polyolefinen und anderen Hochpolymeren im Temperaturbereich von 30-180 °C. Kolloid-Z. **180**, 126 (1962).

[19] Abu-Isa, I., and Dole, M., Specific heat of synthetic high polymers. XII. Atactic and isotactic polystyrene. J. Phys. Chem. **69**, 2668 (1965).

[20] Karasz, F. E., Bair, H. E., and O'Reilly, J. M., Thermal properties of atactic and isotactic polystyrene. J. Phys. Chem. **69**, 2657 (1965).

[21] O'Reilly, J. M., and Karasz, F. E., Specific heat studies of transition and relaxation in polymers. J. Polymer Sci. **C14**, 49 (1966).

[22] Reese, W., Low temperature thermal conductivity of amorphous polymers: polystyrene and polymethylmethacrylate, J. Appl. Phys. **37**, 864 (1966).

[23] Chang, S. S., Bestul, A. B., Heat capacities for atactic polystyrene of narrow molecular weight distribution to 360 °K. J. Polymer. Sci. Part A2 **6**, 849 (1968).

[24] Currie, J. A., and Dole, M., Specific heat of synthetic high polymers. XIII Amorphous polystyrene, J. Phys. Chem. **73**, 3384 (1969).

[25] Choy, C. L., Hunt, R. G., and Salinger, G. L., Specific heat of amorphous polymethyl methacrylate and polystyrene below 4. deg. K. J. Chem. Phys. **52**, 3629 (1970).

[26] Stephens, R. B., Cieloszyk, G. S., and Salinger, G. L., Thermal conductivity and specific heat of monocrystalline solids. Polystyrene and poly(methyl methacrylate) Phys. Lett. A **38**, 215 (1972).

[27] Bares, V., and Wunderlich, B., Heat capacity of molten polymers. J. Polym. Sci., Polym. Phys. Ed. **11**, 861 (1973).

[28] Zoller, P., Fehl, D. L., and Dillinger, J. R., Low-temperature specific heat of polystyrene and related polymers (1.6 — 4. deg. K). J. Polym. Sci., Polym Phys. Ed. **11**., 1441 (1973).

[29] Gilmour, I. W., and Hay, J. N., Determination of the specific heat of polystyrene by DSC. Polymer **18**, 281 (1977).

[30] Gilmour, I. W., Trainor, A., and Haward, R. N., The thermoelastic effect in glassy polymers. J. Polym. Sci., Polym. Phys. Ed. **16**, 1277 (1978).

[31] Stull, D. R., unpublished, but quoted by Boyer, R. F., and Spencer, R. S., Thermal expansion and second-order transition effects in high polymers. J. Appl. Phys. **15**, 398 (1944).

[32] Li, S.-H., Physique moléculaire. Cohésion et degré de polymérisation des grosses molécule de polystyrolène d'après leurs chaleurs spécifiques. Compt. Rend. Acad. Sci., Paris **232**, 821 (1951).

[33] Ueberreiter, K., and Nens, S., Spezifische Wärme, spezifisches Volumen, Temperatur- und Wärmeleitfähigkeit von Hochpolymeren. Teil I: Distyrol und ein hochpolymeres Styrol. Kolloid-Z. **123**, 92 (1951).

[34] Ueberreiter, K., and Otto-Laupenmuhlen, E., Spezifische Wärme, spezifisches Volumen, Temperatur- und Wärmeleitfähigkeit von Hochpolymeren-Teil II. Kettenlangenabhängigkeit bei fraktionierten Polystyrolen. Z. Naturforsch. **8a**, 664 (1953).

[35] Hellwege, K. H., Knappe, W. and Somjonow, V., Quasistationäre Messung der spezifischen Wärme und Wärmeleitfähigkeit an Kunststoffen. Z. Angew. Phys. **11**, 285 (1959).

[36] Warfield, R. W., Petree, M. C., and Donovan, P., The specific heat of high

polymers. SPE Journal **15**, 1055 (1959).
[37] Tautz, H., Glück, M., Hartmann, G., and Leuteritz, R., Die spezifische Wärme von Hochpolymeren im Temperaturbereich von − 150 bis + 180 °C. Plaste Kautschuk **10**, 648 (1963).
[38] Tautz, H., Glück, M., Hartmann, G., and Leuteritz, R., Die spezifische Wärme von Hochopolymeren in Abhängigkeit von der Vorgeschichte des Materials. Plaste Kautschuk **11**, 657 (1964).
[39] Martin, H., and Müller, F. H., Spezifische Wärmen und Einfrierwärmen eines Polystyrols mits verschiedener Temperaturbehandlung. Makromol. Chem. **75**, 75 (1964).
[40] Chernobyl'skii, I. I., and Tertyshnik, K. G., Thermophysical properties of some thermoplastic polymers. Khim. Prom, Ukr. **1966**, 24.
[41] Mischenko, M. I., Sarnoilov, A. V., Buchatskii, V. A., Thermal properties of polymers over a wide range of temperatures. Plasticheskie Massy, **1966** 59.
[42] Zoller, P., Fehl, D. L., and Dillinger, J. R., Effect of cross-linking on the specific heat of polystyrene between 1.6 and 4. deg. K. Phys. Lett. A **32**, 228 (1970).
[43] Aleman, J. V., Thermodynamic properties of epoxy reaction systems. J. Polym. Sci., Part A-1 **9**, 3501 (1971).
[44] Ichihara, S., Komatsu, A., Tsujita, Y., Nose, T., and Hata, T., Thermodynamic studies on the glass transition and the glassy state of polymers. I. Pressure dependence of the glass transition temperature and its relation of other thermodynamic properties of polystyrene. Polym. J. **2**, 530 (1971).
[45] Ichihara, S., Komatsu, A., and Hata, T., Thermodynamic studies on the glass transition and the glassy state of polymers. II. Enthalpies and specific heats of polystyrene glasses of different thermal histories. Polym. J. **2**, 644 (1971).
[46] Savina, V. F., Briskman, B. A., and Bondarev, V. D., Effect of radiation on the specific heat of polyethylene and polystyrene. Vysokomol. Soedin., Ser. A **14**, 1180 (1972).
[47] Anderson, P., and Sundquist, B., Pressure dependence of the thermal conductivity, thermal diffusivity and specific heat of some polymers. J. Polymer Sci. Polym. Phys. Ed. **13**, 243 (1975).
[48] Bashinov, A. B., and Manukyan, A. N., Heat capacity of polymers. Mekh. Polim. **1975**, 555 (1975).
[49] Bashinov, A. B., Akhundov, K., and Selenev, Yu. V., Investigation of the specific heats of polymers, Plaste Kautschuk **23**, 31 (1976).
[50] Richardson, M. J., and Savill, N. G., Derivation of accurate glass transition temperatures by differential scanning calorimetry. Polymer **16**, 753 (1975).
[51] Brown, I. G., Wetton, R. E., Richardson, M. J., and Savill, N. G., Glass transition and thermodynamic state of densified polymeric glasses. Polymer **19**, 659 (1978).
[52] Kokta, B. V., Valade, J. L., Hornot, V., and Law, K. N., Effect of molecular weight of polystyrene on heat capacity and thermal transitions. Thermochim. Acta **14**, 71 (1976).
[53] Belostotskii, M. V., Arvtyunov, B. A., Bil, V. S., and Stephanov, R. D., Effect of hydrostatic pressure on the thermophysical properties of some amorphous polymers. Mekh. Polim. **1977**, 163 (1977).
[54] Lai, J. H., Heat capacity of random copolymers of styrene and methacrylates. J. Appl. Polym. Sci. **20**, 1059 (1976).
[55] Dushchenko, V. P., Gannichenko, Y. I., Tytyuchenko, V. S., Zemlyana, G. Y., and Smola, V. N., Effect of the heating rate on the specific heat capacity of some amorphous linear polymers. Teplofiz. Teplotekh. **32**, 62 (1977).
[56] Duschensko, V. P., Ganninchenko, Y. I., Tytyuchenko, V. S., Menyailov, N. E., and Shut, N. I., Effect of heat treatment on the thermal properties of some amorphous linear polymers. Teplofiz. Teplotekh. **34**, 33 (1978).
[57] Gaur, U. and Wunderlich, B., Additivity of the heat capacity of linear macromolecules in the molten state. ACS Polymer Preprints **20**, 429 (1979).