Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules

X. Update of the ATHAS 1980 Data Bank

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The prior published ATHAS 1980 Data Bank of experimental heat capacities of linear macromolecules that included critically reviewed material on almost 100 polymers is updated. In addition, the data bank has been computerized so that future updates can be made continuously, and new print-outs or computer files will be available from the authors from 1990 on.

Key words: data bank, enthalpy, entropy, Gibbs function, glass transition, heat capacity, linear macromolecule, polymer.

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[a] See AIP document no. PAPS JPCRD-20 No. 2, 349, 1991 for 27 pages comprising Tables A1–A57. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.

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1. Introduction

In an effort to correlate the macroscopically observed heat capacity of linear macromolecules with the microscopic structure, a compilation and critical analysis of all available literature on experimental heat capacities was completed in 1980. In a series of nine publications heat capacities were recommended for selenium,[1] polyethylene,[2] various types of polyoxides,[3] polypropylene,[4] polystyrene,[5] acrylic polymers,[6] other carbon backbone polymers,[7] polyesters and polyamides,[8] and various aromatic and inorganic polymers.[9] The data bank of heat capacities was incorporated in ATHAS (Advanced THermal AnalysiS). Excerpts and reviews based on this data bank were contributed to the Polymer Handbook[10] and the Encyclopedia of Polymer Science and Technology.[11] Since then new heat capacity measurements in our laboratory were concentrated in the areas where prior efforts to establish the data bank revealed shortcomings. In addition, a computer search from 1981 to the end of 1989 accumulated all new heat capacities measured in other laboratories. The ATHAS data bank of recommended experimental heat capacity data has thus been updated to the level of 1990 and contains now data on nearly 150 macromolecules. The data bank has been transferred to an IBM-compatible PC to be updated continually. This paper is the final publication in the printed literature displaying a review of experimental heat capacities of linear macromolecules. The data bank will in the future be updated every six months and is then available on software based on Lotus 1-2-3. In addition to the critically reviewed experimental data, descriptive text on individual polymers as presented here, and data tables on thermodynamic functions [enthalpy, entropy and free enthalpy (Gibbs function)] derived with the help of theory-based computed heat capacities from 0 to 1000 K, fitted to the here discussed experimental data over the range of measurement will also be available on request from the authors.

A wide variety of polymers are reviewed in this paper using the methods outlined before.[1,2] These include carbon-backbone polymers and polymers with hetero-atoms and aromatic groups in the main- and side-chains. In addition, polymers with long pendant side groups have been covered. In all, new recommended heat capacities are presented for 42 new polymers and four polymers on which recommendations had not been made before. The ATHAS Table of Thermal Properties given in the Appendix shows a summary of all updatings performed since 1980. A complete table containing data on nearly 150 macromolecules is available in the ATHAS data bank and is updated every six months.

2. Update on Polymers Already Present in ATHAS Data Bank 1980

Based on the standards of acceptability laid down in 1980,[1] all the available literature heat capacities were critically reviewed for quality and reliability. For this purpose sample characterization, experimental technique used, error limits and accuracy of representation of data are considered. In case recommended heat capacities had already been included in the ATHAS data bank (1980), the new data were compared with it and if deviations were less than ±1%, the new data were incorporated in the data bank without altering the recommended data. All acceptable data (smoothed, in case unsmoothed data are reported) are stored in the standard temperature intervals of the data bank. All the available and acceptable data are given in Tables A1–A57 which have been deposited with the Physics Auxillary Publication Service of the American Institute of Physics. The tables 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.

Additional heat capacities were found in the literature from 1980 onwards on polyethylene, polypropylene, *poly*(1-butenylene) (*cis* and *trans*), *poly*(vinyl fluoride), *poly*(vinylidene fluoride), polytrifluoroethylene, polytetrafluoroethylene, polystyrene, polyoxymethylene, polyoxyethylene, *poly*(ethylene terephthalate), polycarbonate, *poly*(oxy-2,6-dimethyl-1,4-phenylene), *poly*(diethyl siloxane) and Nylon 6.12. The recommended data (1990) of polyethylene are only insignificantly changed from those of 1980. This includes the change of glass transition temperature (temperature of half devitrification) from 252 K[1] to a value of 237 K which is based on more extensive experiments done in our laboratory. The five investigations[12-16] published after 1980 that did not meet our standards and have, therefore, not been included in the update are listed in Table 1. Heat capacities of polypropylene are altered slightly in the glass transition region to include the glass transition temperature as 270 K (instead of the previous value at 260 K) as reported by Bair and Schilling[17] on atatic polypropylene made by hydrogenation of *poly*(1,3-dimethyl-1-butylene). The change in heat capacity at T_g (ΔC_p) thus obtained is 22.93 J/(K mol) and close to the previous recommended value of 23.54 J/(K mol). Three additional investigations[18-20] did not meet our data standards as measurements were made on uncharacterized commercial samples over limited temperature ranges and have, therefore, not been included in the update (see Table 1).

Four additional investigations[15,18,21,22] have been reported for polystyrene for which the recommended heat capacity had earlier been arrived-at based on nineteen out of the forty-five investigations reported in the literature.[5] Among these new publications the data reported by Chang *et al.*[22] and Richardson *et al.*[21] agreed to better than ±1% over the range of measurement, so that it was not considered necessary to alter the ATHAS recommended data 1980. The details of the measurements are given in Table 2 and the new acceptable data are given in Tables A1–A4. Two investigations which did not meet our standards of acceptability are listed in Table 1 together with the reasons for their exclusion.

On the basis of measurements on well characterized, semicrystalline *poly*(vinyl fluoride), *poly*(vinylidene fluoride) and *poly*(trifluoroethylene);[23] polyoxymethylene and polyoxyethylene;[24] it was possible to arrive at a preliminary, recommended set of heat capacities for the melt. In addition Feklina *et al.*[25] and Rekhleta *et al.*[26] have reported heat capacity of *poly*(vinylidene fluoride) (PVF2) and *poly*(trichlorofluoroethylene) (PCTFE), respectively. These measurements have been excluded as for PVF2 the data are on uncharacterized, semicrystalline polymers above the glass transition temperatures and for PCTFE data are presented over a narrow temperature range in the form of two small graphs and the main topic of this investigation was the effect of pressure on heat capacity.

The recommended heat capacities of fluorinated polymers above and below the melting temperature, but above glass transition temperature are given in Table 3 and can be described by two linear equations. The data for the melt between T_g and T_m were obtained by the authors by subtracting the fractional contribution of solid heat capacity (calculated from the vibrational spectrum)[23] from the semicrystalline data. The liquid heat capacities thus obtained were found to be non-linear. The liquid heat capacities of all polyfluoroethylenes could be established as folows.[23]

above 480 K: C_p =

$$N_F\,(104.749 + 0.0568\,T) + (1-N_F)\,(36.840 + 0.0854\,T) \quad (1)$$

and below 480 K as: C_p =

$$N_F\,(54.976 + 0.162\,T) + (1-N_F)\,(37.754 + 0.0829\,T) \quad (2)$$

Where N_F is the mole fraction of fluorine atoms. In case of PVF2 and P3FE agreement between data calculated using these equations and the experiment was better than ± 1%. The agreement was less good for PVF, but still less than 5%. This disagreement could, in addition, have been caused by the beginning of decomposition in PVF. The recommended melt data for these polymers was, therefore, obtained with these equations and is given in Table 3.

The recommended heat capacities for molten polyoxymethylene and polyoxyethylene extrapolated down to T_g (190 K for POM, and a new recommended value of 206 K for POE) are given in Table 4. They are based on the data listed in Table 2 and a critical review of all data on aliphatic polyoxides.[24]

Additional data for *poly*(4,4′-isopropylidene diphenylene carbonate)[27] and *poly*(oxy-2,6-dimethyl-1,4-phenylene)[27–30] are given in Tables A10–A12. The details of the measurements are given in Table 2. Recommended heat capacities (1990) of polycarbonate are only insignificantly changed in the glass transition region, from those of 1980. Based on an extensive investigation carried out in our laboratory, T_g is changed from 418 K to 424 K. The ΔC_p remains almost unchanged at about ~ 49 J/(K mol). Melt heat capacities (1980) were retrieved from graphs and were, therefore, not so accurate. These have also been replaced by the more reliable new data[27] which is slightly different from the previous recommended heat capacities.

In case of *poly*(oxy-2,6-dimethyl-1,4-phenylene) the previously recommended data (1980),[3] were based on only one investigation. This has been updated to include Jauhianen's[28] and Cheng's[30] data. Later is based on a more extensive work carried out in our laboratory and agrees with Karasz's[3] and Jauhianen's data in the region of overlap to a precision of better than 1%.

No recommendations were made earlier for heat capacities of polytetrafluoroethylene, *poly*(1-butenylene) (*cis* and *trans*), *poly*(ethylene sebacate) and *poly*(diethyl siloxane) as the reported data were found to show large uncertainties. In addition, heat capacity data for Nylon 6.12 were based on only one investigation. Since then, new measurements have been carried out on these polymers and a recommended set of data will be discussed in this paper together with the polymers that were not discussed before.

TABLE 1. Investigations not included

Polymer	Reference	Reasons for exclusion
Polyethylene	1. Mathot and Pÿpers (1983) [12].	Data could not be read accurately from to small graphs.
	2. Fritzsch (1983) [13].	Heat capacity of crosslinked thin layer samples of unknown degree of crystallinity.
	3. Finlayson and Mason (1985) [14].	Sample characterization not reported. Heat capacity data below 2 K reported for semicrystalline samples.
	4. O'Reilly and Connelly (1985) [15].	Semicrystalline data reported from 325 to 440 K are within the melting range and data could not be read accurately from the small graphs.
	5. Shut, Musaelyan, Besklubenko, Karpovich and Kasperskii (1986) [16].	Heat capacity on low density polyethylene before and after γ-irradiation are reported. Data could not be read accurately from too small graphs.
Polypropylene	1. Zhongde, Xuexin (1983) [17]	Data retrieved from the graph was $\sim 3\%$ lower below T_g and $\sim 3\%$ higher above T_g than the recommended data.
	2. Vargha-Butler and Neumann (1982) [18].	Commercial sample, characterization not reported. Deviations of nearly 5% from the recommended data.
	3. Mostafa and Gaber (1986) [19].	Commercial sample, characterization not reported. Decrease in heat capacity at 350 K has been reported.
	4. Cometto and Giulianelli (1986) [20].	Commercial samples, characterization not reported. Data could not be read accurately from too small graphs.
Polystyrene	1. Vargha-Butler and Neumann (1982) [18].	Sample characterization not reported. Large deviations from the recommended data.
	2. O'Reilly and Connelly (1985)	Small graphs and very few data points.

Table 2. Heat capacity measurements of various linear macromolecules

Polymer	Investigator	Sample number, characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Polystyrene	Richardson *et al.* (1979) [21]	1. Quenched $M_w = 36{,}000$	250–320	DSC (1%)	Graph
	Chang *et al.* (1984) [22]	2. Amorphous[a] $M_n = 35{,}800$ $M_w/M_n = 1.045$	5–360	Adiabatic (Above 50 K it is 0.02%)	Table
		3. Quenched	80–360	Adiabatic (Above 50 K it is 0.02%)	Table
		4. Annealed	40–360	Adiabatic (Above 50 K it is 0.02%)	Table
poly(Vinylfluoride)	Loufakis (1986) [23]	1. Melt[b] $M_w = 126{,}000$	480–530	DSC-2 (0.1%)	480–530 K: Equation[c]
poly(Vinylidene fluoride)	Loufakis (1986) [23]	1. Semicrystalline[b] $M_w = 120{,}000$	260–580	DSC-2 (0.1%)	260–310 K: Equation[d] 450–580 K: Equation[e]
poly(Trifluoroethylene)	Loufakis (1986) [23]	1. Semicrystalline[f]	330–600	DSC-2 (0.1%)	330–410 K: Equation[g] 480–600 K: Equation[h]
Polyoxymethylene	Wunderlich *et al.* (1985) [24]	1. Melt[i] $M_n = 38{,}000$ $M_w = 76{,}000$	430–540	DSC-2 (0.1%)	430–540 K: Equation[j]
Polyoxyethylene	Wunderlich *et al.* (1985) [24]	1. Melt and Semicrystalline[k] $M_w = 15{,}000 - 20{,}000$	330–430	DSC-2 (0.1%)	330–430 K: Equation[l]
poly(4,4'-Isopropylidenediphenylene carbonate)	Wunderlich *et al.* (1986) [27]	1. Quenched[m] $M_w = 40{,}250$ $M_n = 14{,}400$	440–610	DSC-2 (0.1%)	440–610 K: Equation[n]
poly(Oxy-2,6-dimethyl-1,4-phenylene)	Jauhiainen (1982) [28]	1. Semicrystalline	160–280	Adiabatic	Table
	Dopp *et al.* (1982) [29]	2. Amorphous[o] $M_n = 16{,}800$ $M_w = 57{,}400$	310–600	DSC (1%)	Table
	Wunderlich *et al.* (1987) [30]	3. Amorphous and Semicrystalline $M_w = 44{,}000$ $M_n = 19{,}000$	220–460	DSC-2 (0.1%)	220–460 K: Equation[p]
		4. Melt	480–580	DSC-2 (0.1%)	480–580 K: Equation[q]
poly(2-Methyl-1,3-pentadiene)	Zhongde *et al.* (1985) [17]	1. Quenched $M_n = 11.7 \times 10^4$ $M_w = 12.5 \times 10^4$	230–320	DSC-2 (1%)	Graph

Table 2. Heat capacity measurements of various linear macromolecules — Continued

Polymer	Investigator	Sample number, characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
poly(1-Butenylene)	Dainton *et al.* (1962) [7]	1. *trans poly*(1-butenylene) 96.2% pure 3.8% 1,2 addition	22–340	Adiabatic (1%)	Table
		2. *cis poly*(1-butenylene) 94% pure 3% *trans* isomer 3% 1,2 addition	22–310	Adiabatic (1%)	Table
	Wunderlich *et al.*(1986) [31]	3. 100% *poly*(1-butenylene)^{r} $\bar{M}_w = 2.3 \times 10^5$	220–450	DSC-2 (0.1%)	260–450 K: Equation^{s}
		4. 100% *trans* *poly*(1-butenylene)^{t}	220–450	DSC-2 (0.1%)	220–270 K: Graph 410–450 K: Equation^{s}
poly(1-Butenylene)	Wunderlich *et al.* (1986) [31]	5. 89% -*trans* 9% *cis*, 2% vinyl *poly*(1-butenylene)^{u} $\bar{M}_w = 3.67 \times 10^5$	220–450	DSC-2 (0.1%)	360–450 K: Equation^{s}
		6. 83%-*trans*, 12.4 *cis*, 4.6%-1,2-*trans* *poly*(1-butenylene)^{v}	220–450	DSC-2 (0.1%)	310–450 K: Equation^{s}
Polytetrafluoroethylene	Furukawa *et al.* (1952) [7]	1. Teflon^{w} Powder $\Delta H_f = 1.90$ kJ·mol^{-1}	5–365	Adiabatic	Table
		2. Teflon^{w} Average data for molded and quenched samples Molded: $\Delta H_f = 1.744$ kJ·mol^{-1} Quenched: $\Delta H_f = 1.82$ kJ·mol^{-1}	5–365	Adiabatic	Table
		3. Teflon^{w} Annealed	5–365	Adiabatic	Table
	Noer *et al.* (1959) [7]	4. Teflon^{w}	1.4–4.2	Heat pulse (5%)	Equation^{x}
	Reese and Tucker (1965) [7]	5. Teflon^{w} $\rho = 2.160$ Mg m^{-3}	1.0–4.5	Transient (10%)	Equation^{y}
	Douglas and Harman (1965) [7]	6. Teflon^{w} Powder $w^c = 0.95$	340–560	Drop calorimeter (5%)	Equation^{z}
		7. Teflon^{w} Quenched	330–720 (5%)	Drop calorimeter	330–560 K: Equation$^{a\,a}$ 660–720 K: Equation$^{a\,b}$
Polytetrafluoroethylene	Choy *et al.* (1979) [7]	8. Teflon^{w} $w^c = 0.9$	5–100	Adiabatic (2%)	Table

Table 2. Heat capacity measurements of various linear macromolecules – Continued

Polymer	Investigator	Sample number, characterization		Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
	Salinger and Cieloszyk (unpublished) [7]	9.	Teflon^{w}	0.3–4.4	Heat pulse (2%)	Equation$^{a\ c}$
	S. F. Lau, B. Wunderlich, *et al.* (1984) [32]	10.	Semicrystalline$^{a\ d}$ ΔH_f = 1.36 kJ/mol w^c = 0.332	200–700	DSC-2 (0.5%)	Table
		11.	Semicrystalline$^{a\ d}$ $\bar{M}$w = ~10^6 ΔH_f = 1.76 kJ/mol w^c = 0.43	390–480	DSC-2 (0.5%)	Table
		12.	Semicrystalline^{a,d} $\bar{M}_w$ = 5 × 10^5 ΔH_f = 2.72 kJ/mol w^c = 0.662	390–480	DSC-2 (0.5%)	Table
	S. F. Lau, B. Wunderlich, *et al.* (1984) [32]	13.	Semicrystalline$^{a\ d,a\ e}$ ΔH_f = 0.703 kJ/mol w^c = 0.171	200–700	DSC-2 (0.5%)	Table
		14.	Semicrystalline$^{a\ d,a\ f}$ w^c = 0.95–0.99	220–570	DSC-2 (0.5%)	Table
Polytetrafluoroethylene	S. F. Lau, B. Wunderlich, *et al.* (1984) [32]	15.	Branched PTFE$^{a\ d,a\ g}$	220–570	DSC-2 (0.5%)	Table
Polyglycolide	Lebedev *et al.* (1978) [8]	1.	$\bar{M}_v$ = 38,000 w^c = 0.67	13–550	Adiabatic (from 13.8 to 30 K 1%) (from 30 to 90 K 0.5%)	Table$^{a\ h}$
					Adiabatic (from 90 to 370 0.25%) (from 370 to 550 K 1%)	Table$^{a\ h}$
	Lebedev *et al.* (1984) [35]	1.	$\bar{M}_w$ = 1.0 × 10^6 ΔH_f = 10.519 kJ/mol	13.8–550	″	Table$^{a\ h}$
poly(β-Propiolactone)	Lebedev *et al.* (1984) [35]	1.	$\bar{M}_w$ = 3.0 × 10^4 $\bar{M}_n$ = 8.0 × 10^3 ΔH_f = 8.058 kJ/mol w^c = 0.79	13.8–400	″	Table$^{a\ h}$
poly(γ-Butyrolactone)	Lebedev *et al.* (1984) [35]	1.	$\bar{M}_n$ = 3.0 × 10^3 ΔH_f = 8.844 kJ/mol w^c = 0.67	13.8–350	″	Table$^{a\ h}$
poly(δ-Valerolactone)	Lebedev *et al.* (1984) [35]	1.	$\bar{M}_w$ = 3.6 × 10^3 $\bar{M}_n$ = 1.4 × 10^3 ΔH_f = 12.74 kJ/mol w^c = 0.70	13.8–350	″	Table$^{a\ h}$
Polycaprolactone	Lebedev *et al.* (1974) [8] and	1.	Melt crystallized $\bar{M}_w$ = 29,000 ΔH_f = 12.27 kJ/mol w^c = 0.76	13.8–350	″	Table$^{a\ h}$
	Lebedev *et al.* (1984) [35]	2.	$\bar{M}_w$ = 29,000 w^c = 0.63	13.8 – 350	″	

Table 2. Heat capacity measurements of various linear macromolecules — Continued

Polymer	Investigator	Samplenumber, characterization		Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Polyundecanolactone	Lebedev *et al.* (1984) [35]	1.	$\overline{M}_w = 3.4 \times 10^4$ $\overline{M}_n = 1.0 \times 10^4$ $\Delta H_f = 27.122$ J/mol $w^c = 0.71$	13.8 – 400	"	Table[a] [h]
Polytridecanolactone	Lebedev *et al.* (1984) [35]		$[\eta] = 0.82$ dℓ/g in $CHCl_3$ at 298.15 K. $\Delta H_f = 34.5$ kJ/mol $w^c = 0.75$	13.8 – 370	"	Table[a] [h]
Polypropiolactone	Lebedev *et al.* (1984) [35]		$[\eta] = 0.93$ dℓ/g in $CHCl_3$ at 298.15 K. $\Delta H_f = 42$ kJ/mol $w^c = 0.75$	13.8 – 370	"	Table[a] [h]
poly(Ethylene oxalate)	Lebedev *et al.* (1982) [36]	1.	$\overline{M}_n = 2 \times 10^5$ Quenched sample (amorphous)	8 – 360	Adiabatic (±0.2%)	Table[a] [i]
poly(Butylene adipate)	Rabinonvich *et al.* (1984) [37]	1.	$\overline{M}_n = 1912$ $\overline{D}_p = 9.1$ $\Delta H_f = 20.83$ kJ/mol $w^c = 0.84$	80–470	Adiabatic (80–320 K 0.3%) (320–470 K 0.8%)	Table[a] [j]
poly(Trimethylene adipate)	Pan (1987) [38]	1.	Semicrystalline[a] [k]	310–360	DSC–2 (0.1%)	Equation[a] [l]
poly(Hexamethylene sebacate)	Pan (1987) [38]	1.	Semicrystalline[a] [k]	340–400	DSC–2 (0.1%)	Equation[a] [m]
poly(Trimethylene succinate)	Pan (1987) [38]	1.	Semicrystalline[a] [k]	310–360	DSC–2 (0.1%)	Equation[a] [n]
poly(Ethylene-sebacate)	Wunderlich and Dole (1958) [8]	1.	Semicrystalline $\rho = 1.167$ Mg m^{-3} $\Delta H_f = 72.8$ J/g $w^c = 0.54$	250–410	Adiabatic (1%)	250–310 K: Equation[a] [o] 350–410 K: Equation[a] [p]
	S. Lim and B. Wunderlich (1987) [39]	2.	Semicrystalline, Five samples of different crystallinities (w^c unknown)	120–220	DSC (0.1%)	120–220 K: Equation[a] [q]
Nylon 6	Wunderlich *et al.* (1989) [40]	1.	Semicrystalline[a] [r]	230–600	DSC–2 (0.1%)	230–320 K: Table of smoothed solid data 500–600 K: smoothed melt data
Nylon 11	Wunderlich *et al.* (1989) [40]	1.	Semicrystalline[a] [r]	230–550	DSC–2 (0.1%)	Table of smoothed data below 320 K 470–550 K: smoothed melt data
Nylon 12	Wunderlich *et al.* (1989)	1.	Semicrystalline[a] [r]	230–540	DSC–2 (0.1%)	Table of smoothed data below 320 K 460–540 K: smoothed melt data

Table 2. Heat capacity measurements of various linear macromolecules – Continued

Polymer	Investigator	Samplenumber,	characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Nylon 6.6	Wunderlich *et al.* [40] (1989)	1.	Semicrystalline$^{a\ r}$	230–620	DSC-2 (0.1%)	Table of smoothed data below 320 K 540–620 K smoothed melt data
Nylon 6.9	Wunderlich *et al.* (1989) [40]	1.	Semicrystalline$^{a\ r}$	230–590	DSC-2 (0.1%)	Table of data smoothed data below 320 K 500–590 K: smoothed melt data
Nylon 6.10	Wunderlich *et al.* (1989) [40]	1.	Semicrystalline$^{a\ r}$	230–590	DSC-2 (0.1%)	Table of smoothed data below 320 K: 510–590 K smoothed melt data
Nylon 6.12	Wunderlich *et al.* (1989) [40]	1.	Semicrystalline$^{a\ r}$	230–590	DSC-2 (0.1%)	Table of smoothed data below 320 K: 500–590 K smoothed melt data
poly(Diethylsiloxane)	Beatty and Karasz (1975) [9]	1.	Semicrystalline $\overline{M}_w$ = 112,000	50–300	Adiabatic (not reported)	Equation$^{a\ s}$
	Turdakin *et al.* (1976) [9]	2.	Semicrystalline $\overline{M}_w$ = 1,530	55–330	Adiabatic (0.3%)	Table
	Lebedev *et al.* (1984) [41]	3.	Semicrystalline T_d = 203 K ΔH_d = 2.63 kJ/mol$^{a\ u}$ T_i = 295 K ΔH_i = 2.62 kJ/mol$^{a\ u}$ ΔC_p = 7.374 J/K mol w^c = 78.6%	10–330	Adiabatic (1%)	Graph and Table
	Wesson *et al.* (1988) [42]	4.	Semicrystalline$^{a\ t}$ Cooled at 1 K min^{-1} w^c = 0.585 ΔC_p = 13.67 J/(K mol) ΔH_d = 0.989 (kJ/mol)$^{a\ u}$ ΔH_i = 0.977 (kJ/mol)$^{a\ u}$	110–360	DSC (1%)	Table
	Wesson *et al.* (1988) [42]	5.	Semicrystalline$^{a\ t}$ Cooled at 10 K/min w^c = 0.469 ΔC_p = 14.13 J/(K mol) ΔH_d = 0.793 (kJ/mol)$^{a\ u}$ ΔH_i = 0.85 (kJ/mol)$^{a\ u}$	110–330$^{a\ v}$	DSC (1%)	Table
	Wesson *et al.* (1988) [42]	6.	Annealed at 264.8 K w^c = 0.759 ΔC_p = 6.92 J/(K mol) ΔH_d = 1.283 (kJ/mol)$^{a\ u}$ ΔH_i = 1.223 (kJ/mol)$^{a\ u}$	110–330$^{a\ v}$	DSC (1%)	Table

Table 2. Heat capacity measurements of various linear macromolecules — Continued

Polymer	Investigator	Samplenumber, characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
	Wesson *et al.* (1988) [42]	7. Semicrystalline, Cooled to 201 K, heated to 223 K and Quenched $w^c = 0.472$ $\Delta C_p = 13.91$ J/(K mol) $\Delta H_d = 0.798$ (kJ/mol)[a u]	110–360[a v]	DSC (1%)	Table
	Wesson *et al.* (1988) [42]	8. Quenched Cooled to 201 K, heated to 223 K Quenched $w^c = 0.431$ $\Delta C_p = 21.12$ J/(K mol) $\Delta H_d = 0.729$ (kJ/mol)	110–360[a v]	DSC (1%)	Table
	Wesson *et al.* (1988) [42]	9. Quenched $\Delta C_p = 31.67$ J/(K mol)	110–350[a v]	DSC (1%)	Table
poly-p-Fluorostyrene	Wunderlich *et al.* (1986) [43]	1. Amorphous $\bar{M}_n = 363{,}400$ $\bar{M}_w/\bar{M}_n = 2.9$	130–350	DSC–2 (0.1%)	Equations[a x]
poly-p-Chlorostyrene	Wunderlich *et al.* (1986) [43]	2. Amorphous $\bar{M}_n = 140{,}400$ $\bar{M}_w/\bar{M}_n = 1.9$	300–550	DSC–2 (0.1%)	Equations[a x]
poly-p-Bromostyrene	Wunderlich *et al.* (1986) [43]	1. Amorphous $\bar{M}_n = 80{,}100$ $\bar{M}_w/\bar{M}_n = 6.3$	300–550	DSC–2 (0.1%)	Equations[a x]
poly-p-Iodostyrene	Wunderlich *et al.* (1986) [43]	1. Amorphous $\bar{M}_n = 84{,}800$ $\bar{M}_w/\bar{M}_n = 4.3$	300–550	DSC–2 (0.1%)	Equations[a x]
poly-p-Methylstyrene	Wunderlich *et al.* (1986) [43]	1. Amorphous $\bar{M}_n = 43{,}900$ $\bar{M}_w/\bar{M}_n = 1.9$	300–550	DSC–2 (0.1%)	Equations[a x]
poly(Dimethylitaconate)	Cowie *et al.* (1983) [44]	1. Quenched from 470 K at 320 K min^{-1} $\bar{M}_n = 7.1 \times 10^4$	110–450	DSC–2 (not reported)	Graph
poly(di-*n*-Propylitaconate)	Cowie *et al.* (1983) [44]	1. Quenched from 470 K at 320 K min^{-1} $\bar{M}_n = 8.3 \times 10^4$	110–410	DSC–2 (not reported)	Graph
poly(di-*n*-Heptylitaconate)	Cowie *et al.* (1983) [44,45]	1. Quenched from 470 K at 320 K min^{-1} $\bar{M}_n = 9.7 \times 10^4$	110–170	DSC–2 (not reported)	Graph
poly(di-*n*-Octylitaconate)	Cowie *et al.* (1983) [44,45]	1. Quenched from 470 K at 320 K min^{-1} $\bar{M}_n = 11.7 \times 10^4$	110–170	DSC–2 (not reported)	Graph
poly(di-*n*-Nonylitaconate)	Cowie *et al.* (1983) [44,45]	1. Quenched from 470 K at 320 K min^{-1} $\bar{M}_n = 12.2 \times 10^4$	110–180	DSC–2 (not reported)	Graph
poly(Didodecylitaconate	Cowie *et al.* (1983) [45]	1. Quenched from 470 K at 320 K min^{-1}	110–200	DSC–2 (not reported)	Graph
poly(Dicyclooctylitaconate	Cowie *et al.* (1982) [46]	1. Quenched from 470 K at 320 K min^{-1} $\bar{M}_n = 1.8 \times 10^5$	110–440	DSC–2	Graph

Table 2. Heat capacity measurements of various linear macromolecules – Continued

Polymer	Investigator	Samplenumber, characterization		Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
poly(Dicyclo-decyl-itaconate	Cowie *et al.* (1983) [47]	1.	Quenched from 470 K at 320 K min^{-1}	110–280	DSC–2	Graph
poly(Dicyclo-dodecyl-itaconate)	Cowie *et al.* (1983) [47]	1.	Quenched from 470 K at 320 K min^{-1}	110–280	DSC–2	Equation[b] [a]
poly(*p*-Metha-cryloloxy-benzoic acid)	Lebedev *et al.* (1984) [48]	1.	Amorphous $\overline{M}_v = 3 \times 10^5$	10–310	Adiabatic (~0.5%)	10–80 K: Table 90–310 K: Graph
poly(*p*-Pheny-lene)	Rabinovich *et al.* (1981) [49]	1.	Semicrystalline	80–300	Adiabatic	Table
poly(Thio-1,4-phenylene)	Wunderlich *et al.* (1987) [50]	1.	Semicrystalline[b] [b] $w^c = 0.43 - 0.59$ $\overline{M}_n = 0.91 \times 10^4$	220–600	DSC–2 (0.1%)	220–340 K: Equation[b] [c]
		2.	Quenched[b] [c]	220–600	DSC–2 (0.1%) Equation[b] [e]	540–600 K:
poly(*p*-Xylylene)	Wunderlich *et al.* (1986) [51]	1.	Semicrystalline[b] [f] $w^c = \sim 90\%$	220–410	DSC–2 (0.1%)	Table [b] [g]
poly(Oxy-2,6-dimethyl-5-bromo-1,4-phenylene)	Wunderlich *et al.* (1982) [29]	2.	Amorphous $\overline{M}_n = 16{,}800$ $\overline{M}_w = 57{,}400$	310–530	DSC–2 (0.1%)	Table[b] [h]
poly[Oxy-2,6-*bis*(1-methyl-ethyl)-1,4-phenylene]	Jauhiainen (1983) [52]	1.	State not reported $\overline{M}_n = 5630 \pm 60\text{g/mol}$	270–450	DSC–2 (1%)	(i)270–410 K: Equation[b] [i] (ii) 430–450 K: Graph
poly(Ethylene terephtha-late)	Collocot (1987) [53]	1.	Amorphous, Quenched	0.4–15	Adiabatic heat pulse (1% above 1.5 K, 2% < 1.5 K)	Graph
		2.	Semicrystalline			
			(i) Annealed at 100 °C for 100 min $w^c = 14.5\%$	"	"	"
			(ii) Annealed at 140 °C for 1560 min $w^c = 33.6\%$	"	"	"
			(iii) Annealed at 210 °C 20 h $w^c = 53.6\%$	"	"	"
			(iv) Annealed at 160 °C for 26 h, 240 °C for 4 h $w^c = 63.6\%$	"	"	"
poly(Butylene-terephthalate)	Cheng *et al.* (1988) [54]	1.	Semicrystalline[b] [j] $\overline{M}_n = 46{,}000$ Isothermally crystallized at 480 K for 48 h, then cooled to 220 K at 0.31 K/min	220–540	DSC–2 (0.1%)	220–280 K: Equation[b] [k] 340–460 K: Graph 490–540 K: Equation[b] [l]

Table 2. Heat capacity measurements of various linear macromolecules – Continued

Polymer	Investigator	Samplenumber, characterization		Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
		2.	Quenched$^{b\,j}$ in a glass bead cooling bath	220–540	DSC-2 (0.1%)	Graph
poly(Butylene-terephthalate)	Aleman (1985) [55]	3.	Semicrystalline$^{b\,m}$ $\overline{M}_n = 19{,}600$ Crystallized at 473 K for 20 min followed by cooling to 143 K with liquid N_2	150–600	DSC (0.1%)	Graph
	Menczel and Wunderlich (1986) [56]	4.	Semicrystalline$^{b\,n}$ $w^c = 0.47$	270–570	DSC-7	Graph
		5.	Semicrystalline$^{b\,n}$ $w^c = 0.31$	270–570	DSC-7	Graph
		6.	Semicrystalline$^{b\,n}$ $w^c = 0.37$	270–570	DSC-7	Graph
poly(4-Hydroxy-benzoic acid)	Wunderlich *et al.* (1985) [58]	1.	Semicrystalline$^{b\,o}$ (i) Samples kept at 500 K (below T_d) for 2 min, cooled at 20 K/min.	170–215	Mettler DSC (not reported)	170–280 K: Equation$^{b\,q}$
			(ii) Samples kept at 630 K (above T_d) for 2 min, cooled at 20 K/min. $T_d{}^{bp} = 616.5 \pm 4$ K $\Delta H_d = 3.8 \pm 1.1$ kJ/mol	215–480	DSC-2	290–480 K: Table
poly(2,6-Hydroxy-naphthoic acid)	Wunderlich *et al.* (1985) [58]	1.	Semicrystalline^{b} (i) Sample kept at 500 K (below T_d) for 2 min, cooled at 20 K/min.	170–215	Mettler DSC (not reported)	170–280 K: Equation$^{b\,t}$
			(ii) Sample kept at 630 K (above T_d) for 2 min, cooled at 20 K/min. $T_d{}^{bp} = 614.5$ K $\Delta H_d = 0.4$ kJ/mol $\pm$ 0.2	215–480	DSC-2 (not reported)	290–480 K: Table$^{b\,u}$
		2.	Melt	500–650		500–650 K: Equation$^{b\,v}$
poly(Ethylene-2,6-naphthalene dicarboxylate)	Cheng and Wunderlich (1988) [59]	1.	Semicrystalline, a. Isothermally crystallized from melt. T_c and t_c varied between 450–520 K and 0.5–15 h respectively. $w^c = 0.3 - 0.51$	220–360 (below T_g) 330–450 (Glass transition region)	DSC-2 (0.1%)	220–300 K: Equation$^{b\,w}$ 400–450 K: Graph
			b. Isothermally crystallized from glass T_c and T_c varied between 450–520 K and 0.5–15 h respectively. $w^c = 0.28\ 0.50$			
		2.	Quenched with liquid N_2	220–600	DSC-2 (0.1%)	220–300 K: Equation$^{b\,w}$ 400–460 K: Graph

Table 2. Heat capacity measurements of various linear macromolecules — Continued

Polymer	Investigator	Samplenumber, characterization		Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
		3.	Melt	540–600	DSC–2 (0.1%)	540–600 K: Equation[b][x]
poly(Oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)	Kemmish *et al.* (1985) [61]	1.	Amorphous[b][y] (Quenched with ice/water) $\overline{M}_w = 3.9 \times 10^4$ $\overline{M}_n = 1.7 \times 10^4$	340–570 (not reported)	DSC–2 Equation[b][z]	(i) 340–420 K: (ii) 440–570 K:
		2.	Melt	610–680	DSC–2 (not reported)	Table
	Cheng and Wunderlich (1986) [62]	3.	Semicrystalline[c][a] Isothermally crystallized from melt and glass at various T_c (463.2–593.2 K) followed by cooling at −0.31 K/min to below T_g $w^c = 0.30 - 0.51$	130–570	DSC–2 (0.1%)	(i) 130–200 K: Equation[c][b] (ii) 200–240 K: Equation[c][c] (iii)340–410 K: Graph (iv)430–570 K: Graph
poly(Oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)	Cheng and Wunderlich (1986) [62]	4.	Amorphous (Quenched with liquid N_2)	340–570	DSC–2 (0.1%) (not reported)	(i) 130–200 K: Equation[c][b] (ii) 200–240 K: Equation[c][c] (iii)340–410 K: Graph
	Cheng and Wunderlich (1986) [63]	5.	Melt	430–680	DSC–2 (0.1%)	(i) 430–680 K: Equation[c][d]
poly[Oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene]	Richardson *et al.* (1979) [21]	1.	Amorphous	380–540	DSC (1%)	380–440 K: Equation[c][e] 480–540 K: Equation[c][f]
	Novoselova *et al.* (1985) [64]	2.	Amorphous	10–480	10–480 K: Adiabatic 330–480 K: DSC (5%)	Table of smoothed data

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[a] Atatic polystyrene – NBS samples – 1478

[b] Commercial sample from Polysciences, Inc.

[c] Average of 6 runs. $C_p = 65.3320 + 0.06326T$ [± 2%, J/(K mol)].

[d] Author's curve fitted equation: $C_p = 5.933 + 0.263\ T$ [± 5%, J/(K mol)]. Equation is derived by fitting melt data obtained from subtracting contribution of solid heat capacity (calculated using ATHAS computation scheme) from semicrystalline data.

[e] Author's curve fitted equation: $C_p = 77.3227 + 0.058517\ T$ [± 2%, J/(K mol)].

[f] Gift sample from IBM.

[g] Author's curve fitted equation: $C_p = 43.296 + 0.170\ T$ [± 2%, J/(K mol)]. Equation is derived by fitting melt data obtained from subtracting contribution of solid heat capacity (calculated using ATHAS computation scheme) from semicrystalline data.

[h] Author's curve fitted equation: $C_p = 88.0236 + 0.06223\ T$ [± 1.5%, J/(K mol)].

[i] Commercial samples from Celanese (Celcon M90) and duPont (Delrin 500 ×). Later had a M.W 40,000.

[j] Author's curve fitted equation: Average of 36 runs. $C_p = 46.51 + 0.0372\ T$ [± 1.2%, J/(K mol)].

[k] Commercial sample from Polysciences, Inc.

[l] Author's curve fitted equation from an average of 8 runs. $C_p = 67.85 + 0.0668\ T$ [± 0.2%, J/(K mol)].

[m] Gift sample and commercial sample (uncharacterized) from General Electric Company.

[n] Author's curve fitted equation: Average of 10 runs. $C_p = 0.559\ T + 249$ [± 0.1%, J/(K mol)].

[o] Commercial PPO sample from General Electric Company.

[p] Author's curve fitted equation: $C_p = \exp[-0.13222\,(\ln T)^3 + 2.2301\,(\ln T)^2 - 11.1681\,(\ln T) + 23.614]$ [± 1.6%, J/(K mol)]. Average of 30 runs.

[q] Author's curve fitted equation: $C_p = 0.2282\ T + 141.6$ [± 1.5%, J/(K mol)].

[r] Sample obtained from Polysciences Inc.

[s] Author's curve fitted equation: $C_p = 52.63 + 0.178$ [± 0.2%, J/(K mol)].

[t] Sample obtained from Chemische Werke Hüls.

[u] Sample obtained from the General Tire and Rubber Co., Research Division, Akron, OH, USA.

[v] Sample obtained from Firestone, Central Research Laboratories, Akron, OH, USA.

[w] Teflon is the trade name for polytetrafluoroethylene manufactured by E. I. duPont de Nemours Co., Inc.

[x] $C_p = 10^{-5}T^3$ cal g^{-1} K^{-1}

[y] $C_p = 98\ T^3$ erg K^{-1} cm^{-3}

[z] $C_p = 0.54268 + 1.345\times10^{-3}\ T + 208/(603.4-T)^2$ J g^{-1} K^{-1}

[aa] $C_p = 0.54921 + 1.45154 \times 10^{-3}T + 410.8/(608-T)^2$ J g^{-1} K^{-1}

[ab] $C_p = 0.61488 + 1.949 \times 10^{-3}\ T$ J g^{-1} K^{-1}

[ac] $C_p = \exp[-0.174744\ (\ln T)^3 + 0.128498\ (\ln T)^2 + 3.13938\ (\ln T) + 5.85181]$ erg g^{-1} K^{-1}

[ad] Gift samples from duPont Research Laboratories (Polymer Products and Central Research Departments)

[ae] PTFE contains 12 ± 2 wt% hexafluoropropylene or 4 CF_3 branches per 100 carbon backbone atoms.

[af] X-ray, IR and NMR indicate complete crystallinity. A series of four samples analyzed to determine heat of fusion and heat capacity of the melt.

[ag] PTFE has a perfluoroether group of 2–5 carbon atoms per branch (1.4 branches per 100 backbone atoms).

[ah] Tabulated smoothed data presented by the author from 10 to 200 K or 150 K was interpolated using the spline function technique to determine heat capacity. For PGL from 210 K and for all other polylactones from 160 K up to just below the glass transition temperature, the C_p data were curve fitted into the linear equations listed in Table 11.

[ai] Author has tabulated the smoothed data. In order to retrieve the data at the standard data bank intervals, interpolation was done using spline function technique and curve fitting the presented data into linear equations at temperatures close to the glass transition (see text).

[aj] Author has tabulated the smoothed data. In order to retrieve the data at the standard data bank intervals, the data was refitted into equations described in the text.

[ak] Commercial samples obtained from Polysciences Inc., Sample no. 1, 2 and 3 are *poly*(trimethylene adipate), *poly*(hexamethylene sebacate) and *poly*(trimethylene succinate) respectively.

[al] Author's curve fitted equation: $C_p = 0.397038\ T + 225.3193$ J/(K mol)

[am] Author's curve fitted equation: $C_p = 0.755081\ T + 309.156$ J/(K mol)

[an] Author's curve fitted equation: $C_p = 0.253009\ T + 212.5816$ J/(K mol)

[ao] Author's curve fitted equation: $C_p = 0.159 + 1.26 \times 10^{-8}\ T^3$ cal/g.C

[ap] Author's curve fitted equation: $C_p = 0.444 + 5.81 \times 10^{-4}\ T$ cal/g.C

[aq] Author's curve fitted equation: $C_p = 52.11 + 0.8269\ T$ J/(K mol)

[ar] Commercial samples from Scientific Polymer Products, Inc.,

[as] Authors tabulated data were curve fitted into the following equations:
60–140 K: $1.0987 \times 10^{-4}\ T^2 - 0.016778\ T + 1.297$ J g^{-1} K^{-1} (RMS dev. 2.3%)
150–190 K: $1.1864 \times 10^{-4}\ T^2 - 0.033338\ T + 3.505$ J g^{-1} K^{-1} (RMS dev. 2.4%)
200–230 K: $3.2433 \times 10^{-4}\ T^2 - 0.1382\ T + 16.17$ J g^{-1} K^{-1} (RMS dev. 1.6%)
270–300 K: $2.8756 \times 10^{-3}\ T + 0.7695$ J g^{-1} K^{-1} (RMS dev. 2.1%)

[at] Heat capacity data of semicrystalline samples provided by Boyer (Midland Macromolecular Institute) show a rigid crystal to condis crystal transition at T_d 206 K and condis crystal to liquid crystal transition at T_i = 272 K and a final isotropization to melt at ~ 300 K. w^c is the crystallinity of rigid crystal.

[au] ΔH_d = and ΔH_i = are the heats of transitions of the two transitions.

[av] Author has curve fitted the data from 290 to 360 K into the equation: $C_p = 93.75 + 0.2365\ T$ which represents melt C_p data.

[aw] For the structure and abbreviations used see the Table given in Appendix.

[ax] Author's curve fitted equations are listed in Table 25.

[ay] The structure and abbreviations used are given in the Table in Appendix.

[az] The structure and abbreviations are given in the table in Appendix.

[ba] Author's curve fitted equation: $C_p = 103.3 + 0.8635\ T + 0.003429\ T^2$ [± 2.6%, J/(K mol)].

[bb] Sample obtained from Polysciences Inc. Semicrystalline samples were prepared by the author by isothermal and non-isothermal crystallization from melt and glass.

[bc] Average of 15 runs on 10 samples. $C_p = \exp\ [0.109038\ (\ln T)^3 - 1.7846\ (\ln T)^2 + 10.7735\ (\ln T) - 18.9156]$ [± 1.5%, J/(K mol)]

[bd] $C_p = 0.12574\ T + 119.\ 73$

[be] Samples had a crystallinity of about 5%.

[bf] Annealed sample.

[bg] Table of smoothed data.

[bh] Table of smoothed data.

[bi] Author's curve fitted equation: $C_p = 0.258337 + 0.003835\ T$ in J/(K g).

[bj] Commercial sample from Eastman Kodak (Valox, Lot 6 P6D).

[bk] Author's curve fitted equation: $C_p = 52.16 + 0.5203\ T + 0.000713\ T^2$ J/(K mol) from an average of 5 measurements.

[bl] Author's curve fitted equation: $C_p = 219.6479 + 0.452209\ T$ J/(K mol) from an average of 7 measurements.

[bm] Commercial sample from Ciba-Geigy AG (Germany).

[bn] Commercial sample from GAF Corporation: Gafite 1600.

[bo] Commercial samples supplied by Celanese Research Company.

[bp] Disordering transition peak temperature.

[bq] Author's curve fitted equation: $C_p = 3.1526 + 0.3977\ T$ [± 0.03%, J/(K mol)].

[br] Commercial samples supplied by Celanese Research Company.

[bs] Disordering transition peak temperature.

[bt] Author's curve fitted equation: $C_p = 3.1514 + 0.5951\ T$ [± 0.02%, J/(K mol)].

[bu] Author's tabulated smoothed data used as such.

[bv] Author's curve fitted equation: $C_p = 0.340361\ T + 138.336$ [± 0.1 %, J/(K mol)].

[bw] Author's curve fitted equation: $C_p = 0.0001616\ T^2 + 0.7544\ T + 29.256$ J/(K mol), average of 18 measurements of semicrystalline PEN and 5 of amorphous PEN with RMS deviation being 0.8%.

[bx] Author's curve fitted equation: $C_p = 0.40941\ T + 268.35$ J/(K mol) average of 15 measurements.

[by] Commercial sample from ICI Co.

[bz] Author's curve fitted equation: $C_p = (0.1036 \pm 0.017) + (3.34 \pm 0.05) \times 10^{-3}\ T$ in J/(K g)

[ca] Commercial sample from ICI Co.

[cb] Author's curve fitted equation: $C_p = \exp[0.1695\ (\ln T)^3 - 2.193\ (\ln T)^2 + 10.08\ (\ln T) - 11.63]$ [± 2.5%, J/(K mol)].

[cc] Author's curve fitted equation: $C_p = 0.00005455\ T^2 + 1.057\ T + 9.631$ [± 1.2%, J/(K mol)].

[cd] Author's curve fitted equation: $C_p = 0.4955\ T + 308.15$ [± 0.1%, J/(K mol)].

[ce] Author's curve fitted equation: $C_p = 0.309 + 0.00288\ T$ J/(K g).

[cf] Author's curve fitted equation: $C_p = 0.926 + 0.00204\ T$ J/(K g).

TABLE 3: Recommended heat capacity data for molten fluorinated polymers

Temp (K)	Heat capacity [J/(K mol)] PVF	Heat capacity [J/(K mol)] PVF2	Heat capacity [J/(K mol)] P3FE
220.00	NA	73.304	NA
230.00	NA	74.529	NA
240.00	NA	75.753	NA
250.00	NA	76.978	NA
260.00	NA	78.202	NA
270.00	NA	79.427	NA
273.15	NA	79.812	NA
280.00	NA	80.651	90.494
290.00	NA	81.876	91.916
298.15	NA	82.873	93.075
300.00	NA	83.100	93.338
310.00	NA	84.325	94.760
320.00	74.916	85.549	96.183
330.00	75.942	86.774	97.605
340.00	76.969	87.998	99.027
350.00	77.996	89.223	100.449
360.00	79.023	90.447	101.872
370.00	80.049	91.672	103.294
380.00	81.076	92.896	104.716
390.00	82.103	94.120	106.138
400.00	83.130	95.345	107.561
410.00	84.156	96.570	108.983
420.00	85.183	97.794	110.405
430.00	86.210	99.019	111.827
440.00	87.236	100.243	113.250
450.00	88.263	101.468	114.672
460.00	89.290	102.692	116.094
470.00	90.317	103.917	117.516
480.00	91.344	105.141	118.939
490.00	92.160	105.634	119.107
500.00	92.942	106.345	119.747
510.00	93.725	107.056	120.386
520.00	94.507	107.767	121.026
530.00	95.290	108.478	121.665
540.00	96.072	109.189	122.305
550.00	96.855	109.900	122.944
560.00	97.637	110.611	123.584
570.00	98.420	111.322	124.223
580.00	99.202	112.033	124.863
590.00	99.985	112.744	125.502
600.00	100.767	113.455	126.142

TABLE 4: Recommended heat capacity data for molten polyoxymethylene and polyoxyethylene

Temp (K)	Heat capacity [J/(K mol)] POM	Heat capacity [J/(K mol)] POE
190.00 (T_g) POM	53.578	NA
200.00	53.950	NA
206.00 (T_g) POE	54.173	81.611
210.00	54.322	81.878
220.00	54.694	82.546
230.00	55.066	83.214
240.00	55.438	83.882
250.00	55.810	84.550
260.00	56.182	85.218
270.00	56.554	85.886
273.15	56.671	86.096
280.00	56.926	86.554
290.00	57.298	87.222
298.15	57.601	87.766
300.00	57.670	87.890
310.00	58.042	88.558
320.00	58.414	89.226
330.00	58.786	89.894
340.00	59.158	90.562
350.00	59.530	91.230
360.00	59.902	91.898
370.00	60.274	92.566
380.00	60.646	93.234
390.00	61.018	93.902
400.00	61.390	94.570
410.00	61.762	95.238
420.00	62.134	95.906
430.00	62.506	96.574
440.00	62.878	97.242
450.00	63.250	97.910
460.00	63.622	98.578
470.00	63.994	99.246
480.00	64.366	99.914
490.00	64.738	100.582
500.00	65.110	101.250
510.00	65.482	101.918
520.00	65.854	102.586
530.00	66.226	103.254
540.00	66.598	103.922

3. Recommended Heat Capacities of Polymers Added to the Data Bank

3.1. Other Carbon Backbone Polymers

3.1.1. Introduction

In the following subsections all newly recommended heat capacities are discussed using the prior established criteria.[1] Overall, only one new polymer is included in this listing together with recommendations on two polymers described earlier.[7] A summary and quick reference to the location of the description of all heat capacities is contained in the appendix.

3.1.2. *poly*(2-Methyl-1,3-pentadiene)

Only one investigation is reported in the literature for heat capacities of *poly*(2-methyl-1,3-pentadiene) (PMP).[17] The details of the measurements are given in Table 2. Heat capacity of PMP over the range over which data were recovered from the graph is given in Table A13. The preliminary recommended heat capacities below and above the glass transition temperature at 277.8 K (T_g) are given in Table 5. The change in heat capacity at 277.8 K (T_g) thus obtained agrees within 1.5% with that reported by the authors.[17] Below the glass transition temperature the data recovered from the graph from 220 to 250 K were curve-fit into the equation:

$$C_p = -0.8438 + 0.0088767\ T - 0.0000166811\ T^2 \quad (\pm\ 0.3\%)\ \mathrm{J/(K\ mol)} \qquad (3)$$

and from 240 to 270 K the data were fitted into the equation:

$$C_p = 0.1450 + 0.0007507\ T\ (\pm\ 0.35\%)\ \mathrm{J/(K\ mol)} \qquad (4)$$

Equation (4) was used to extrapolate the data up to T_g. Melt heat capacities were obtained from T_g up to 320 K by curve fitting the data from 280 to 320 K into the equation:

$$C_p = 0.2575 + 0.0007148\ T\ (\pm\ 0.4\%)\ \mathrm{J/(K\ mol)} \qquad (5)$$

3.1.3. *poly*(1-Butenylene)

In the ATHAS data bank (1983),[7] the heat capacities on *cis* and *trans poly*(1-butenylene) also reffered to as 1,4-polybutadiene were based on only one investigation for semicrystalline samples of unknown crystallinity. Since then a detailed investigation was carried out by Wunderlich *et al.*[31] on both isomers. The heat capacities of both isomers of polybutadiene are given in Table A14 and A15. The details of the measurement are given in Table 2. The glass transitions of *cis poly*(1-butenylene) and *trans poly*(1-butenylene) were established at 171 K and 190 K, respectively. The *trans*-isomer exhibits a condis phase (conformationally disordered and mobile) above 356 K.[31] The melting temperature was established at 284.7 K for the *cis*-isomer and 437 K for *trans*-isomer. Below the glass transition the data of semicrystalline samples (1 and 2) were used to represent the solid state. From 30 to 100 K, tabulated data[7] for the *cis*-isomer were used as such. Equation (6) represents the heat capacity data of the *cis*-isomer from 110 to 171 K (T_g) and was obtained by curve fitting the experimental data reported earlier[7] from 120 to 130 K.

$$C_p = 6.945004 + 0.2761\ T\ (\pm\ 0.02\%)\ \mathrm{J/(K\ mol)} \qquad (6)$$

For the *trans*-isomer, C_p data were reported earlier.[7] The data from 30 to 120 K were used as such, while the data from 130 to 170 K were curve-fit into the equation:

$$C_p = 7.856993 + 0.2743\ T\ (\pm\ 0.04\%)\ \mathrm{J/(K\ mol)} \qquad (7)$$

Equation (7) was used from 130 to 190 K (T_g).

Above the glass transition temperature the data on samples 1 and 2 were not considered, as the new data were based on a more extensive investigation. Heat capacities of melt of both, the *cis* and *trans*-isomers could be represented by the smoothed equation given by the authors[31]:

$$C_p = 52.63 + 0.178\ T\ (\pm\ 0.02\%)\ \mathrm{J/(K\ mol)} \qquad (8)$$

Since the condis phase of the *trans*-isomer was shown by the authors to have heat capacities close to that of the extrapolated melt, Eq. (8) was used to extend the heat capacities to 190 K for *trans poly*(1-butenylene) and up to 171 K for *cis*-butadiene. The recommended heat capacities of *cis poly*(1-butenylene) and *trans poly*(1-butenylene) are given in Tables 6 and 7 and are plotted in Fig. 1.

TABLE 5: Recommended heat capacity data for *poly*(2-methyl-1,3-pentadiene)

Temp (K)	Heat capacity [J/(K mol)]
230.00	105.565
240.00	109.034
250.00	111.387
260.00	113.878
270.00	116.391
273.15	117.182
277.80 (T_g)	118.350
277.80 (T_g)	152.649
280.00	153.176
290.00	155.568
298.15	157.518
300.00	157.961
310.00	160.353
320.00	162.746

TABLE 6a. Recommended heat capacity data for cis *poly*(1-butenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
30.00	11.790
40.00	16.150
50.00	19.980
60.00	23.180
70.00	26.160
80.00	29.070
90.00	31.870
100.00	34.630
110.00	37.316
120.00	40.077
130.00	42.838
140.00	45.599
150.00	48.360
160.00	51.121
170.00	53.882
171.00 (T_g)	54.158

TABLE 6b. Recommended heat capacity data for molten cis *poly*(1-butenylene)

Temp (K)	Heat capacity [J/K mol)]
171.00 (T_g)	83.068
180.00	84.670
190.00	86.450
200.00	88.230
210.00	90.010
220.00	91.790
230.00	93.570
240.00	95.350
250.00	97.130
260.00	98.910
270.00	100.690
273.15	101.251
280.00	102.470
290.00	104.250
298.15	105.701
300.00	106.030
310.00	107.810
320.00	109.590
330.00	111.370
340.00	113.150
350.00	114.930
360.00	116.710
370.00	118.490
380.00	120.270
390.00	122.050
400.00	123.830
410.00	125.610
420.00	127.390
430.00	129.170
440.00	130.950
450.00	132.730

TABLE 7a. Recommended heat capacity data for trans *poly*(1-butenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
30.00	9.704
40.00	14.390
50.00	18.740
60.00	22.560
70.00	25.890
80.00	29.000
90.00	32.020
100.00	34.980
110.00	37.860
120.00	40.700
130.00	43.516
140.00	46.259
150.00	49.002
160.00	51.745
170.00	54.488
180.00	57.231
190.00 (T_g)	59.974

TABLE 7b. Recommended heat capacity data for molten trans *poly*(1-butenylene)

Temp (K)	Heat capacity [J/(K mol)]
190.00 (T_g)	86.450
200.00	88.230
210.00	90.010
220.00	91.790
230.00	93.570
240.00	95.350
250.00	97.130
260.00	98.910
270.00	100.690
273.15	101.251
280.00	102.470
290.00	104.250
298.15	105.701
300.00	106.030
310.00	107.810
320.00	109.590
330.00	111.370
340.00	113.150
350.00	114.930
360.00	116.710
370.00	118.490
380.00	120.270
390.00	122.050
400.00	123.830
410.00	125.610
420.00	127.390
430.00	129.170
440.00	130.950
450.00	132.730

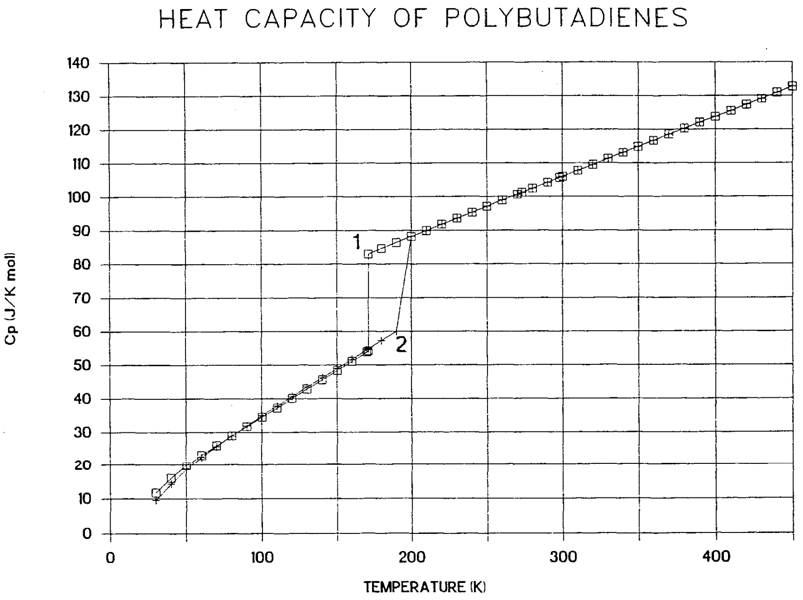

FIG. 1. Recommended heat capacities for: 1. *cis poly*(1-butenylene); 2. *trans poly*(1-butenylene).

3.1.4. Polytetrafluoroethylene

Eleven investigations have been reported in the literature for the heat capacity of PTFE. Eight investigations which meet our standards of acceptability are listed in Table 2. The investigations not included are given in Table 8. Heat capacity data on the first six investigations had already been deposited (Table A15, Ref., 7) with the Physics Auxillary Publication Service of the American Institute of Physics. The new data are given in Table A16. In the ATHAS data bank (1980), heat capacity of PTFE could not be recommended as at that time no definite information on the glass transition temperature and room temperature transitions was available. A detailed investigation on heat capacity of PTFE was carried out in our laboratory[32] on samples of widely ranging crystallinities (w^c = 0.17–0.95). This investigation permits us to recommend experimental heat capacities for completely crystalline and completely amorphous PTFE [obtained by the two phase model, assuming $C_p = w^c C_p{}^c + (1\text{–}w^c)\ C_p{}^a$].

Recommended heat capacities for crystalline PTFE were obtained as follows: From 0.3 to 4 K data on sample 9 was used as the uncertainty claimed by the authors is only 2%. Heat capacities of sample 4 were 14% higher at 1.4 K and 23% at 4 K than sample 9 and the data on sample 5 were higher by 24% and 34%, respectively. From 5 to 25 K the data on sample 8 (crystallinity 0.9) were smoothed by fitting into the equation:

$$C_p = \exp[-7.839547 + 5.168145\,(\ln T) - 0.8187535\,(\ln T)^2 + 0.03979258\,(\ln T)^3]\ (\pm\ 0.0\%)\ \mathrm{J/(K\ mol)} \qquad (9)$$

The heat capacities from 30 to 100 K of sample 8 and 1 were averaged in the region of overlap (the standard deviation is 0.7%) and together with data on sample 1 up to 170 K were fit into the equation.

$$C_p = 0.12087 + 0.2145618\,T - 0.0002071\,T^2\ (\pm\ 0.43\%)\ \mathrm{J/(K\ mol)} \qquad (10)$$

Above 170 K the solid heat capacity in the ATHAS data bank (1980) is not considered since PTFE shows a glass transition in the 160–240 K region (T_g = 200 K) and two room-temperature transitions at 292 and 303 K.[32] Between 180 and 210 K the C_p was obtained using Eq. (10). From 220 to 280 K the heat capacity of sample 14 is taken as the recommended data. Equations (11) and (12) represent the smoothed C_p data from 220 to 240 K and 250 to 280 K, respectively.

$$C_p = 29.52984 - 0.06640669\,T + 0.000466798\,T^2\ (\pm\ 0.04\%)\ \mathrm{J/(K\ mol)} \qquad (11)$$

$$C_p = 157.3948 - 1.099639\,T - 0.0025538687T^2\ (\pm\ 0.13\%)\ \mathrm{J/(K\ mol)} \qquad (12)$$

At 292 K and 303 K PTFE undergoes two transitions (rigid crystal-condis crystal), hence the heat capacities above 270 K cannot be recommended at this stage.

The heat capacity determinations on practically completely crystalline sample 14 (average of two to four measurements) showed an internal standard deviation of only 0.3%. Between 390 and 480 K, the data on samples 11 and 12 showed a standard deviation of 0.1% (claimed by the authors). This agreed closely with the data on sample 1 (maximum discrepancy + 0.7%). From 340 to 560 K agreement with data on samples 6 and 7 was also quite good (maximum discrepancy −0.9%).

Heat capacity data for completely amorphous PTFE was obtained by using the crystallinity extrapolated data as reported by Wunderlich *et al.*[32] of the semicrystalline PTFE above the glass transition region (160–240 K). Between 240 K and 480 K the data on samples 10–14 were extrapolated to get 100% amorphous heat capacities. This was further smoothed by curve fitting into the equation:

$$C_{pa} = 29.51 + 0.06917\,T + 0.00001292\,T^2 \quad (\pm\ 0.4\%)\ \mathrm{J/(K\ mol)} \tag{13}$$

Between 560 and 700 K the C_p data of melt was smoothed by curve fitting into the equation:

$$C_p = 49.45 + 0.0332\,T\ (\pm\ 0.2\%)\ \mathrm{J/(K\ mol)} \tag{14}$$

Equation (13) was used to obtain C_p data from 240 K to 470 K and from 480 to 700 K the heat capacities were obtained using Eq. (14). Between 180 K and 240 K the heat capacities were obtained by making a linear connection between amorphous and crystalline heat capacity. Between 180 K and perhaps 50 K the amorphous and crystalline heat capacities can be assumed to be the same, as in this region heat capacity is usually almost independent of crystallinity. Recommended experimental data of crystalline and amorphous PTFE are given in Tables 9 and 10, respectively.

TABLE 8. Investigations for polytetrafluoroethylene not included in this study

References	Reason(s) for exclusion
Terziiska *et al.* (1981) [33]	Sample characterization not reported. Data shows higher error limits.
Vargha-Butler *et al.* (1982) [18]	Sample characterization not reported for semicrystalline data.
Fritzsch (1983) [13]	Data could not be retrieved accurately from small graphs. Polymer was made by glow discharge polymerization and had uncertain chemical structure.
Boyer *et al.* (1983) [34]	Heat capacity of commercial grade PTFE has been measured by heat pulse technique. Very large deviations observed from recommended data. Up to 5 K data are within the experimental error of Choy's data and show deviations of nearly 10–15 % from Salinger's data discussed in ref. [7].

TABLE 9. Recommended heat capacity data for crystalline polytetrafluoroethylene

Temp (K)	Heat capacity [J/(K mol)]
0.30	0.000065
0.40	0.000125
0.50	0.000223
0.60	0.000370
0.70	0.000582
0.80	0.000871
0.90	0.001252
1.00	0.001740
1.20	0.003094
1.40	0.005041
1.60	0.007687
1.80	0.011110
2.00	0.015380
3.00	0.051
4.00	0.109
5.00	0.228
6.00	0.376
7.00	0.554
8.00	0.759
9.00	0.985
10.00	1.228
15.00	2.565
20.00	3.915
25.00	5.155
30.00	6.371
40.00	8.372
50.00	10.331
60.00	12.249
70.00	14.125
80.00	15.960
90.00	17.754
100.00	19.506
110.00	21.217
120.00	22.886
130.00	24.514
140.00	26.100
150.00	27.645
160.00	29.149
170.00	30.611
180.00	32.032
190.00	33.411
200.00	34.749
210.00	36.046
220.00	37.513
230.00	38.950
240.00	40.480
250.00	42.102
260.00	44.130
270.00	46.669
273.15	47.575
280.00	49.719

TABLE 10. Recommended heat capacity data for amorphous polytetrafluoroethylene

Temp (K)	Heat capacity [J/(K mol)]
180.00	32.960
190.00	35.280
200.00 (T_g)	37.590
210.00	39.910
220.00	42.220
230.00	44.980
240.00	46.855
250.00	47.610
260.00	48.368
270.00	49.128
273.15	49.368
280.00	49.891
290.00	50.656
298.15	51.282
300.00	51.424
310.00	52.194
320.00	52.967
330.00	53.743
340.00	54.521
350.00	55.302
360.00	56.086
370.00	56.872
380.00	57.660
390.00	58.451
400.00	59.245
410.00	60.042
420.00	60.840
430.00	61.642
440.00	62.446
450.00	63.253
460.00	64.062
470.00	64.874
480.00	65.386
490.00	65.718
500.00	66.050
510.00	66.382
520.00	66.714
530.00	67.046
540.00	67.378
550.00	67.710
560.00	68.042
570.00	68.374
580.00	68.706
590.00	69.038
600.00	69.370
610.00	69.702
620.00	70.034
630.00	70.366
640.00	70.698
700.00	72.690

3.2. Recommended Heat Capacities of Heteroatom Backbone Polymers

3.2.1. Introduction

Recommended heat capacities for polyesters derived by substitution of the COO− group in the backbone chain of polyethylene were available in the ATHAS data bank 1980 for polyglycolide, polycaprolactone and *poly*(ethylene terephthalate). Since then Lebedev *et al.*[35] have reported heat capacities on a series of polylactones covering polyglycolide and polycaprolactone, polypriopiolactone, polybutyrolactone, polyvalerolactone, polyundecanolactone, polytridecanolactone and polypentadecanolactone. In addition, heat capacities are also available for *poly*(ethylene oxalate),[36] *poly*(butylene adipate),[37] *poly*(trimethylene adipate),[38] *poly*(ethylene sebacate),[39] *poly*(hexamethylene sebacate)[38] and *poly*(trimethylene sebacate).[38] All the investigations were reevaluated and found to meet our standards of acceptability. The various investigations are discussed individually and the data listed as recommended heat capacities.

3.2.2. Polylactones

The reported data of Lebedev *et al.*[35] on polyglycolide were very high and did not fit into any addition scheme with other polymers. The author had suggested (CH2 − COO −)x as the repeating unit. Since PGL is synthesized, however, from the bimolecular lactide instead of the unstable 3-atom lactone, the heat capacities given by the authors must have referred to (CH2 − COO − CH2 − COO −) and not (CH2 − COO −). Hence, the reported data were halved at all temperatures and the recommended data given in Tables 12 and 13 fit now the addition scheme of all the other polylactones. The details of the measurements on the various polylactones are given in Table 2.

Data were retrieved at the standard data bank intervals from the tabulated, smoothed data presented by the author. For this, the heat capacities from 10 to 200 K (in case of PGL) and 150 K for all other polylactones was interpolated using the spline-function technique. Above these temperatures up to just below T_g, the already smoothed data were curve-fitted into linear equations which are listed in Table 11 along with the equations for the melt. The recommended experimental data are given in Tables 12 and 13 and are plotted in Figs. 2 and 3. Heat capacity increases from PGL to PPDL, while the glass transition temperatures (Table 14) decrease up to PVL and then increase up to PPDL, reaching a value close to that of polyethylene.

3.2.3. *poly*(Ethylene Oxalate)

One investigation has been reported that deals with the heat capacity of *poly*(ethylene oxalate).[36] Details of this investigation which meets our data standards of acceptable data (discussed in Ref. 1), are given in Table 2. Heat capacity of an amorphous sample has been measured over the temperature range of 8 to 360 K. The data on these samples are given in Table A19.

To obtain the recommended data, the author's tabulated, smoothed data from 10 to 240 K were interpolated using the Spline function technique. From 250 K up to 300 K, C_p was curve-fitted into a linear equation:

TABLE 11. Results of curve fitting literature data on heat capacities of polylactones to derive the recommended data

Polymer[a]	State	Equation[b]	Temperature range (K)[c]
PGL	Solid	$C_p = 13.89503 + 0.171812\,T$	210 - 318
	Molten	$C_p = 100.8 + 0.0380966\,T$	318 - 550
PPL	Solid	$C_p = 15.70001 + 0.2480\,T$	160 - 249
	Molten	$C_p = 91.4315 + 0.146407\,T$	249 - 400
PBL	Solid	$C_p = 18.93358 + 0.3295356\,T$	160 - 214
	Molten	$C_p = 124.817 + 0.103469\,T$	214 - 350
PVL	Solid	$C_p = 24.80002 + 0.3741713\,T$	160 - 207
	Molten	$C_p = 131.310 + 0.17399\,T$	207 - 350
PCL	Solid	$C_p = 25.98002 + 0.454714\,T$	160 - 209
	Molten	$C_p = 119.595 + 0.291496\,T$	209 - 350
PUDL	Solid	$C_p = 36.8026 + 0.8141549\,T$	160 - 227
	Molten	$C_p = 241.226 + 0.400712\,T$	227 - 400
PTDL	Solid	$C_p = 40.08001 + 0.97025\,T$	160 - 229
	Molten	$C_p = 323.459 + 0.370269\,T$	229 - 370
PPDL	Solid	$C_p = 50.80290 + 1.067743\,T$	160 - 251
	Molten	$C_p = 389.612 + 0.387217\,T$	251 - 370

[a] The structure and abbreviations of the polymers are given in the appendix.
[b] C_p is in J/(K mol).
[c] Temperature range over which the equation is valid.

$$C_p = 37.04763 + 0.3088571\,T \text{ J/(K mol)} \qquad (15)$$

The RMS deviation was ±0.04%. This equation was used to extend the data up to the glass transition temperature (306 K). To obtain melt data, the results above the glass transition were curve-fitted into the equation:

$$C_p = 133.003 + 0.179037\,T \text{ J/(K mol)} \qquad (16)$$

The RMS deviation was ±0.2%. Melt data from 306 (T_g) up to 360 K were obtained from this equation. The recommended heat capacities above and below T_g are given in Table 15.

3.2.4. *poly*(Butylene Adipate)

One investigation has been reported in the literature, which deals with the heat capacity of *poly*(butylene adipate).[37] The reported heat capacities for both the solid and liquid appear somewhat higher than what is expected if one doubles the C_p data for *poly*(δ-valerolactone) considering that PBA is actually double the repeat unit of this polymer. However, since these are the only available data, they are incorporated in the data bank as preliminary data. The details of the measurement are given in Table 2. The data on the semicrystalline sample are given in Table A20 and 21. Heat capacity of a semicrystalline sample has been reported. Below the glass transition temperature (T_g 199 K), heat capacity of amorphous and crystalline polymers can be assumed to be the same. To obtain the preliminary recommended data from 80 to 199 K (T_g), the author's tabulated data were refitted to the equation:

$$C_p = \exp[-9.1043 \times 10^{-3}\,(\ln T)^3 + 0.216717\,(\ln T)^2 - 0.674235\,(\ln T) + 4.24806] \text{ J/(K mol)} \qquad (17)$$

In the molten state (199 to 450 K), heat capacity data were obtained by curve fitting the data into the linear equation:

$$C_p = 296.844 + 0.325835\,T \text{ J/(K mol)} \qquad (18)$$

The preliminary recommended data below and above the glass transition temperature were obtained using Eqs. (17) and (18), respectively, and are given in Tables 16 and 17.

3.2.5. *poly*(Trimethylene Adipate), *poly*(Hexamethylene Sebacate) and *poly*(Trimethylene Succinate)

Only one investigation[38] is reported in the literature that deals with the heat capacities of the melts of *poly*(-trimethylene adipate), *poly*(hexamethylene sebacate)

TABLE 12. Recommended heat capacity data for semicrystalline polylactones below the glass transition temperature in [J/(K mol)]

Temp (K)	PGL	PPL	PBL	PVL	PCL	PUDL	PTDL	PPDL
0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10.00	0.780	1.390	1.470	1.510	2.420	3.380	3.300	3.470
15.00	2.184	3.240	4.316	4.313	6.130	8.349	9.408	9.829
20.00	3.980	5.650	7.870	8.000	10.720	14.811	17.360	18.480
25.00	5.960	8.374	11.612	12.103	15.667	22.157	26.169	28.415
30.00	8.020	11.200	15.300	16.330	20.660	29.932	35.260	38.890
40.00	12.120	16.560	22.220	24.570	30.170	45.563	53.210	59.660
50.00	16.040	21.220	28.410	32.160	37.950	60.180	70.450	79.330
60.00	19.570	25.540	33.990	39.080	45.740	73.610	86.320	97.580
70.00	22.720	29.600	39.050	45.370	53.020	86.010	100.700	114.400
80.00	25.550	33.400	43.650	51.100	59.610	97.450	113.900	129.900
90.00	28.110	36.910	47.870	56.320	65.620	108.000	126.000	144.100
100.00	30.470	40.130	51.760	61.110	71.140	117.800	137.200	157.200
110.00	32.670	43.050	55.400	65.520	76.250	126.900	147.700	169.200
120.00	34.740	45.710	58.850	69.630	81.020	135.400	157.700	180.400
130.00	36.690	48.190	62.140	73.520	85.550	143.500	167.200	190.900
140.00	38.530	50.550	65.340	77.250	89.910	151.300	176.500	200.900
150.00	40.280	52.840	68.480	80.910	94.190	158.900	185.600	210.800
160.00	41.960	55.370	71.580	84.668	98.734	167.080	195.330	221.640
170.00	43.580	57.850	74.900	88.409	103.281	175.220	205.030	232.320
180.00	45.150	60.330	78.220	92.151	107.829	183.360	214.730	243.000
190.00	46.690	62.820	81.540	95.893	112.376	191.500	224.430	253.670
200.00	48.220	65.300	84.860	99.635	116.923	199.630	234.130	264.350
210.00	49.976	67.780	88.170	NA	NA	207.770	243.830	275.030
220.00	51.694	70.260	NA	NA	NA	215.917	253.535	285.710
230.00	53.412	72.740	NA	NA	NA	NA	NA	296.380
240.00	55.130	75.220	NA	NA	NA	NA	NA	307.060
250.00	56.848	NA	NA	NA	NA	NA	NA	317.739
260.00	58.566	NA	NA	NA	NA	NA	NA	NA
270.00	60.284	NA	NA	NA	NA	NA	NA	NA
273.15	60.825	NA	NA	NA	NA	NA	NA	NA
280.00	62.002	NA	NA	NA	NA	NA	NA	NA
290.00	63.721	NA	NA	NA	NA	NA	NA	NA
298.15	65.121	NA	NA	NA	NA	NA	NA	NA
300.00	65.439	NA	NA	NA	NA	NA	NA	NA
310.00	67.157	NA	NA	NA	NA	NA	NA	NA

The abbreviations used for the polymer names have been described in the appendix.

and *poly*(trimethylene succinate). The details of the measurements are given in Table 2. The heat capacity data is given in Table A22. The only available heat capacities are given in Table 18 as preliminary, recommended data.

3.2.6. *poly*(Ethylene sebacate)

In the ATHAS data bank (1980)[8] heat capacities of semicrystalline *poly*(ethylene sebacate) were available only above the glass transition temperature (T_g = 245 K) and a recommendation could, therefore, not been made. Since then, Wunderlich *et al.*[39] have measured heat capacities of five differently crystallized samples, extending the range of measurement to 120 K. The details of the measurements are given in Table 2. The new data are given in Table A23. To obtain the recommended heat capacities below T_g (245 K), the equation given by the authors for the data, curve-fitted between 120 and 220 K, was used. Heat capacities of the melt were obtained from the equation of the curve-fitted melt data between 350–410 K. The recommended heat capacities below and above T_g are given in Table 19.

3.2.7. Aliphatic Polyamides

In the ATHAS data bank (1980)[8] heat capacities of nylon 6, nylon 6.6 and nylon 6.12 were listed. Since then Wunderlich *et al.*[40] have reported heat capacities of nylon 6, nylon 6.6, nylon 11, nylon 12, nylon 6.9, nylon 6.10, and nylon 6.12. Heat capacities of nylon 6 and nylon 6.6 already recommended in the 1980 data bank remain unaltered, as the new measurements showed a deviation of only about 2% from the previous data which is considered within the experimental error. The details of the new measurements on semicrystalline samples are given in Table 2. All new heat capacities are based on only one investigation[40] and are given in Table A24 and A25. Table 20 lists the recommended heat capacities for the solid

TABLE 13. Recommended heat capacity data for molten polylactones in [J/(K mol)]

Temp (K)	PGL	PPL	PBL	PVL	PCL	PUDL	PTDL	PPDL
210.00	NA	NA	NA	167.848	180.809	NA	NA	NA
220.00	NA	NA	147.580	169.588	183.724	NA	NA	NA
230.00	NA	NA	148.615	171.328	186.639	333.390	408.620	NA
240.00	NA	NA	149.650	173.068	189.554	337.397	412.323	NA
250.00	NA	128.033	150.684	174.808	192.469	341.404	416.026	NA
260.00	NA	129.497	151.719	176.547	195.384	345.411	419.728	490.288
270.00	NA	130.961	152.754	178.287	198.299	349.418	423.431	494.161
273.15	NA	131.423	153.080	178.835	199.217	350.680	424.597	495.380
280.00	NA	132.425	153.788	180.027	201.214	353.425	427.134	498.033
290.00	NA	133.890	154.823	181.767	204.129	357.432	430.836	501.905
298.15	NA	135.083	155.666	183.185	206.505	360.698	433.854	505.061
300.00	NA	135.354	155.858	183.507	207.044	361.440	434.539	505.777
310.00	NA	136.818	156.892	185.247	209.959	365.447	438.242	509.649
320.00	112.991	138.282	157.927	186.987	212.874	369.454	441.944	513.521
330.00	113.372	139.746	158.962	188.727	215.789	373.461	445.647	517.394
340.00	113.753	141.210	159.996	190.467	218.704	377.468	449.350	521.266
350.00	114.134	142.674	161.031	192.207	221.619	381.475	453.052	525.138
360.00	114.515	144.138	NA	NA	NA	385.482	456.755	529.010
370.00	114.896	145.602	NA	NA	NA	389.489	460.458	532.882
380.00	115.277	147.066	NA	NA	NA	393.497	NA	NA
390.00	115.658	148.530	NA	NA	NA	397.504	NA	NA
400.00	116.039	149.994	NA	NA	NA	401.511	NA	NA
410.00	116.420	NA	NA	NA	NA	NA	NA	NA
420.00	116.801	NA	NA	NA	NA	NA	NA	NA
430.00	117.182	NA	NA	NA	NA	NA	NA	NA
440.00	117.563	NA	NA	NA	NA	NA	NA	NA
450.00	117.943	NA	NA	NA	NA	NA	NA	NA
460.00	118.324	NA	NA	NA	NA	NA	NA	NA
470.00	118.705	NA	NA	NA	NA	NA	NA	NA
480.00	119.086	NA	NA	NA	NA	NA	NA	NA
490.00	119.467	NA	NA	NA	NA	NA	NA	NA
500.00	119.848	NA	NA	NA	NA	NA	NA	NA
510.00	120.229	NA	NA	NA	NA	NA	NA	NA
520.00	120.610	NA	NA	NA	NA	NA	NA	NA
530.00	120.991	NA	NA	NA	NA	NA	NA	NA
540.00	121.372	NA	NA	NA	NA	NA	NA	NA
550.00	121.753	NA	NA	NA	NA	NA	NA	NA

The abbreviations used for the polymer names have been described in the appendix.

and for the melt. Solid heat capacity data are the smoothed experimental data. Recommended melt data were obtained from the equation:

$$C_p = N_C(7.4506 + 0.0745\,T) + N_N(86.8483 - 0.0226\,T)\ (\pm\ 1.22\%)\ \mathrm{J/(K\ mol)} \qquad (19)$$

where N_N is the number of amide groups and N_C is the number of methylene groups developed from an addition scheme on melt heat capacities of all aliphatic homopolyamides and copolymers. The equation describes the experimental results with an accuracy of ~ 1%. Using this equation heat capacities were extrapolated up to the glass transition temperature as between T_g and T_m heat capacity varies with thermal history of the sample.

The glass transition temperatures show no definite pattern of change on going from nylon 6 to nylon 6.12. It is 313 K for nylon 6; nylon 11 and nylon 12 have a value of 316 K and 314 K, respectively; while nylon 6.6, nylon 6.9, nylon 6.10 and nylon 6.12 have their glass transition temperatures at 323 K, 331 K, 323 K and 319 K, respectively. The recommended value of ΔC_p for 100% amorphous nylons obtained by subtracting solid C_p data (calculated from an approximate vibrational spectrum fitted to experimental heat capacities)[40] from the recommended melt data was 68, 74, 110, 118, 141 for nylon 11, nylon 12, nylon 6.9, nylon 6.10 and nylon 6.12 respectively.

TABLE 14. Heat capacity change at the glass transition temperature of the various polylactones

Polymer	T_g (K)	ΔC_p [J/(Kmol)]
Polyglycolide	318	44.4
Polypropiolactone	249	50.4
Polybutyrolactone	214	57.4
Polyvalerolactone	207	65.1
Polycaprolactone	209	59.5
Polyundecanolactone	227	110.6
Polytridecanolactone	229	146.0
Polypentadecanolactone	251	168.0

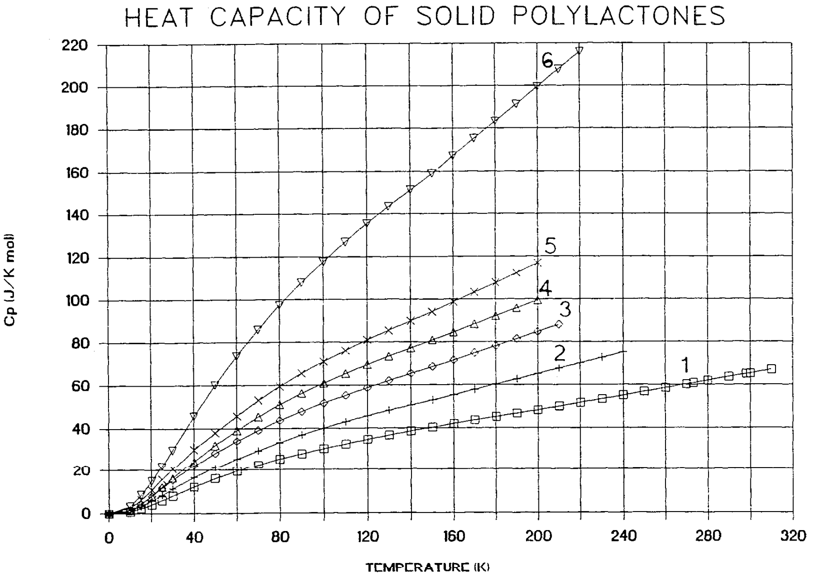

FIG. 2. Recommended heat capacities below the glass transition temperature for the following polylactones: 1. polyglycolide, 2. *poly*(β-propiolactone), 3. *poly*(γ-butyrolactone), 4. *poly*(δ-valerolactone), 5. *poly*(ε-caprolactone), and 6. polyundecanolatone.

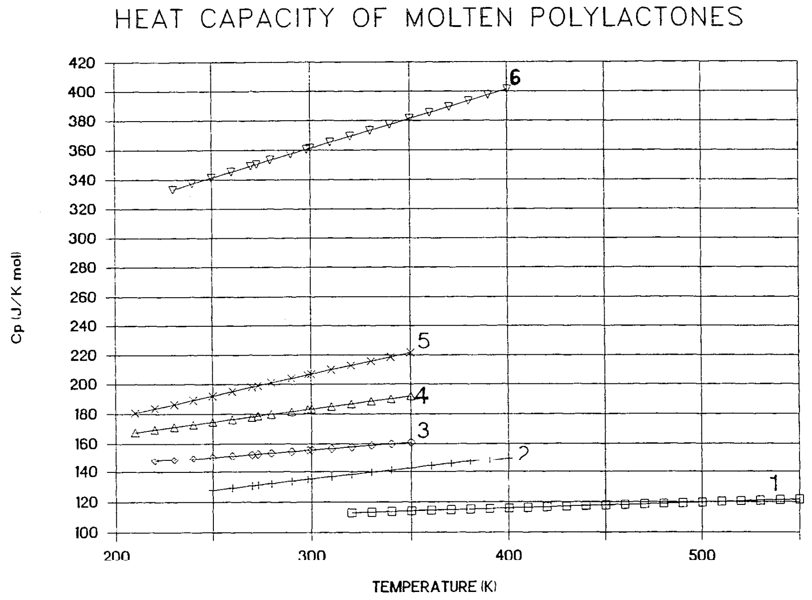

FIG. 3. Recommended heat capacities for the following molten polylactones: 1. polyglycolide, 2. *poly*(β-propiolactone), 3. *poly*(γ-butyrolactone), 4. *poly*(δ-valerolactone), 5. *poly*(ε-caprolactone), and 6. polyundecanolactone.

TABLE 15a. Recommended heat capacity data for amorphous *poly*(ethylene oxalate) below the glass transition

0.00	0.000
10.00	1.830
15.00	5.223
20.00	9.180
25.00	13.175
30.00	17.070
40.00	24.630
50.00	31.850
60.00	37.950
70.00	43.320
80.00	48.350
90.00	53.210
100.00	57.930
110.00	62.480
120.00	66.850
130.00	71.050
140.00	75.060
150.00	78.900
160.00	82.570
170.00	86.110
180.00	89.580
190.00	93.030
200.00	96.530
210.00	100.100
220.00	103.700
230.00	107.300
240.00	110.800
250.00	114.262
260.00	117.350
270.00	120.439
273.15	121.412
280.00	123.528
290.00	126.616
298.15	129.133
300.00	129.705
306.00 (T_g)	131.558

TABLE 15b. Recommended heat capacity data for molten *poly*(ethylene oxalate)

Temp (K)	Heat capacity [J/K mol)]
306.00 (T_g)	187.788
310.00	188.504
320.00	190.295
330.00	192.085
340.00	193.876
350.00	195.666
360.00	197.456

TABLE 16. Recommended heat capacity data for semicrystalline *poly*(butylene adipate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
80.00	108.734
90.00	118.245
100.00	127.737
110.00	137.217
120.00	146.690
130.00	156.161
140.00	165.632
150.00	175.107
160.00	184.587
170.00	194.074
180.00	203.570
190.00	213.075
199.00 (T_g)	221.639

TABLE 17. Recommended heat capacity data for molten *poly*(butylene adipate)

Temp (K)	Heat capacity [J/(K mol)]
199.00 (T_g)	361.685
200.00	362.011
210.00	365.269
220.00	368.528
230.00	371.786
240.00	375.044
250.00	378.303
260.00	381.561
270.00	384.819
273.15	385.846
280.00	388.078
290.00	391.336
298.15	393.992
300.00	394.595
310.00	397.853
320.00	401.111
330.00	404.370
340.00	407.628
350.00	410.886
360.00	414.145
370.00	417.403
380.00	420.661
390.00	423.920
400.00	427.178
410.00	430.436
420.00	433.695
430.00	436.953
440.00	440.211
450.00	443.470

3.2.8. *poly*(Diethyl Siloxane)

In the ATHAS data bank (1980)[9] no recommendation of experimental heat capacities could be made as the data reported by Karasz *et al.*[9] on sample 1 and Turdakin *et al.*[9] on sample 2 differed by 2–9%. Since then additional heat capacity measurements have been reported and the details of these are given in Table 2. The crystallinity reported by the authors[41] on sample 3 was found to be in error since an incorrect value of ΔC_p for the sample reported was used. Hence, before proceeding with the comparison of the C_p data, it was considered necessary to reevaluate the crystallinity. The value of ΔC_p for sample 3 was recalculated to be 7.374 J/(K mol) and this together with the ΔC_p for 100% amorphous PDES (obtained from the author's melt data and data for the solid calculated from an approximate vibrational spectrum fitted to author's data) results in a crystallinity for the semicrystalline PDES of 78.6% as listed in Table 2.

The heat capacity data for samples 3 to 9 over the different temperature ranges are given in Tables A26–A27. Table A26 lists the heat capacity data below the glass transition temperature. For samples 1 and 2 data have already been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics as described in Ref. 9. Table A27 shows the data for the condis crystal, liquid crystal and the melt.

Recommended experimental heat capacities below 40 K were obtained by curve-fitting the tabulated data points reported by Lebedev *et al.*[41] From 10 to 20 K C_p was obtained from the equation of the smoothed data.

$$C_p = \exp[-18.90025 + 18.16324 \ln T - 5.681586 \ln T^2 + 0.6641430 \ln T^3] \ (\pm\ 0.6\%)\ \mathrm{J/(K\ mol)} \quad (20)$$

From 25 to 40 K curve-fitted data were obtained from the equation:

$$C_p = -8.0921 + 0.9564671\ T + 4.187165 \times 10^{-4}\ T^2 \ (\pm\ 2.2\%),\ \mathrm{J/(K\ mol)} \quad (21)$$

Heat capacities reported by Karasz[9] were higher than both Lebedev[41] and Turdakin's[9] data in the temperature range 70 to 100 K. At 70 K, for example, it was ~ 9% higher while at 90 K it was ~ 3% higher. Therefore, to determine the recommended experimental data from 50 K–135 K (T_g), an average of only Turdakin and Lebedev's data over the temperature of overlap (60–100 K), together with the heat capacity data of Lebedev at 50 K and 110 K was fit into the equation:

$$C_p = -7.778002 + 1.064166\ T - 0.00230083\ T^2 \ (\pm\ 0.2\%)\ \mathrm{J/(K\ mol)} \quad (22)$$

The data of Turdakin at 110 K and 120 K appeared to be associated with the glass transition, as it was 1–2% higher than that of Lebedev. Hence, only Lebedev's data at 120 and 130 K were fit into a linear equation:

$$C_p = 6.418823 + 0.6749153\ T \ (\pm\ 0.4\%)\ \mathrm{J/(K\ mol)} \quad (23)$$

and this equation was used to obtain the heat capacity from 120 to 135 K (T_g).

The recommended data for molten *poly*(diethyl siloxane) were obtained by averaging the melt data reported by Lebedev from 300 to 330 K and the work carried out in our laboratory[42] from 290–360 K. Averaged data were fit into a linear equation:

$$C_p = 96.87783 + 0.2284644\ T \ (\pm\ 0.2\%)\ \mathrm{J/(K\ mol)} \quad (24)$$

This equation was used to extend the data to the glass transition temperature. Recommended heat capacities below T_g (from 10 to 135 K) were obtained using Eqs. 20 to 23 (Table 21). The heat capacities above T_g, up to 360 K can be represented by Eq. (24) (Table 22). The use of Eq. (24) to approximate the heat capacities of the condis and liquid crystalline state is a reasonable approximation.[42]

TABLE 18. Recommended heat capacity data for molten *poly*(trimethylene adipate), *poly*(hexamethylene sebacate) and *poly*(trimethylene succinate)

Temp (K)	Heat capacity [J/(K mol)] PTMA	PHMS	PTMS
310.00	348.401	NA	291.014
320.00	352.371	NA	293.544
330.00	356.341	NA	296.074
340.00	360.312	565.884	298.604
350.00	364.282	573.434	301.134
360.00	368.252	580.985	303.664
370.00	NA	588.536	NA
380.00	NA	596.087	NA
390.00	NA	603.638	NA
400.00	NA	611.188	NA

TABLE 19a. Recommended heat capacity data for semicrystalline *poly*(ethylene sebacate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
120.00	151.338
130.00	159.607
140.00	167.876
150.00	176.145
160.00	184.414
170.00	192.683
180.00	200.952
190.00	209.221
200.00	217.490
210.00	225.759
220.00	234.028
230.00	242.297
240.00	250.566
245.00 (T_g)	254.701

TABLE 19b. (cont'd.): Recommended heat capacity data for molten *poly*(ethylene sebacate)

Temp (K)	Heat capacity (J/K.mol)
245.00 (T_g)	408.760
250.00	411.540
260.00	417.100
270.00	422.660
273.15	424.411
280.00	428.220
290.00	433.780
298.15	438.311
300.00	439.340
310.00	444.900
320.00	450.460
330.00	456.020
340.00	461.580
350.00	467.140
360.00	472.700
370.00	478.260
380.00	483.820
390.00	489.380
400.00	494.940
410.00	500.500

3.3. Recommended Heat Capacities of Carbon Backbone Polymers with Pendant Aromatic/Aliphatic Groups

3.3.1. Introduction

The series of polymers covered under this section include p-substituted polystyrenes and series of polyitaconates having aliphatic as well as cyclic pendant side chains. In the ATHAS data bank (1980) heat capacity of polystyrene has already been critically evaluated.[5] An update on this was described in Sec. 2. New heat capacity data are reported for *poly*(p-fluorostyrene), *poly*(p-chlorostyrene), *poly*(p-bromostyrene), *poly*(p-iodostyrene) and *poly*(p-methyl styrene) and will be discussed in the next section. The change in heat capacity at T_g (Table 23) for *poly*(p-chlorostyrene) and *poly*(p-bromostyrene) is close to that of polystyrene [ΔC_p = 30.8 J/(K mol)]. *poly*(p-iodostyrene) and *poly*(p-methyl styrene) have a slightly higher T_g as expected due to the bulky substituted group.[43]

Heat capacity determinations have also been reported on a series of *poly*(di-n-alkyl itaconates) with side chain lengths varying from 1 to 10 carbon atoms and for *poly*(dicyclo-alkyl itaconates). Polyitaconates having linear side chains exhibit two jumps in the heat capacity. The low-temperature inflection in the heat capacity curves of *poly*(di-n-heptyl itaconate) to *poly*(di-n-decyl itaconate) has been referred to as $T_g{}^L$ and attributed to the independent motions of the side chains.[44] $T_g{}^U$ has been assigned to the temperature at which the polymer softens and is about 60–70 K above the $T_g{}^L$ (Table 24). The heat capacity data will be discussed in the subsequent sections.

3.3.2. Substituted Polystyrenes

Wunderlich *et al.*[43] have carried out a detailed analysis of heat capacities of the various substituted polystyrenes and unsubstituted polystyrenes. The details of this investigation which meet our standards of acceptable data are listed in Table 2. The equations of the curve-fitted data are given in Table 25, and heat capacity data are given in Tables A28 and A29. The recommended experimental heat capacities based on only one investigation are given in Tables 26 and 27, and plotted in Figs. 4 and 5.

3.3.3. Polyitaconates

Only two investigations are reported in the literature[44,45] which deal with the heat capacities of *poly*(di-n-alkyl itaconates). The details of the measurements which meet our standards of acceptable data are given in Table 2. Heat capacities retrieved from the graphs are given in Tables A30–A32. Table 28 gives the various curve-fitted equations. The preliminary recommended data for *poly*(dimethyl itaconate) and *poly*(di-n-propyl itaconate) are given in Tables 29 and 30 and are plotted in Fig. 6. Heat capacities of all other available solid *poly*(di-n-alkyl itaconates) are given in Table 31 and are plotted in Fig. 7.

Heat capacity measurements have also been reported by Cowie and coworkers[46,47] for *poly*(dicycloalkyl itaconates) with cycloalkyl groups such as cyclooctyl, cyclodecyl and cyclododecyl. The details of the measurements which meet our standards of acceptable data are given in Table 2. Tables A33 to A34 give the heat capacities for the three itaconates. The curve-fitted equations of the smoothed data are given in Table 32. The preliminary recommended heat capacities for *poly*(dicylodecyl itaconate) and *poly*(dicyclo dodecyl itaconate) are given in Table 31 and in Fig. 7 while the heat capacity data for *poly*(dicyclooctyl itaconate) are given in Table 33.

3.3.4. *poly*(p-Methacryloyloxybenzoic acid)

Only one investigation[48] is reported for the heat capacity of *poly*(p-methacryloyloxy benzoic acid). The details of the measurements which meets our standards of acceptable data are given in Table 2. Heat capacities for an amorphous sample have been reported. The data below the glass transition temperature (T_g 316 K) are given in Table A35. The experimental data are directly used from 10 to 80 K, while the heat capacities from 80 to 310 K were fit into the equation:

$$C_p = \exp[0.0840357\,(\ln T)^3 - 1.17815\,(\ln T)^2 + 6.33259\,(\ln T) - 7.81629]\ (\pm\ 0.4\%)\ \mathrm{J/(K\ mol)} \quad (25)$$

The preliminary, recommended heat capacities from 10 to 310 K are given in Table 34.

TABLE 20. Recommended heat capacity data for nylons

Temp (K)	Nylon 11	Nylon 12	Nylon 6.9	Nylon 6.10	Nylon 6.12
Below T_g					
230.00	238.210	254.020	321.530	340.870	381.780
240.00	249.260	264.100	332.440	354.280	395.570
250.00	259.990	273.910	343.660	368.180	410.520
260.00	271.300	283.950	355.330	381.970	425.770
270.00	282.660	294.770	368.400	395.520	439.750
280.00	294.130	305.980	381.850	409.720	458.630
290.00	306.970	318.560	395.270	426.590	475.420
300.00	320.910	334.490	408.080	441.820	494.480
310.00	342.100	358.690	425.330	463.600	520.210
320.00	NA	NA	454.510	497.000	NA
330.00	NA	NA	469.639	NA	NA
Melt					
320.00	392.522	423.813	NA	NA	659.882
330.00	399.746	431.782	NA	607.279	671.350
340.00	406.970	439.751	584.476	617.257	682.818
350.00	414.194	447.720	593.709	627.235	694.286
360.00	421.418	455.689	602.942	637.213	705.754
370.00	428.642	463.658	612.175	647.191	717.222
380.00	435.866	471.627	621.408	657.169	728.690
390.00	443.090	479.596	630.641	667.147	740.158
400.00	450.314	487.565	639.874	677.125	751.626
410.00	457.538	495.534	649.107	687.103	763.094
420.00	464.762	503.503	658.340	697.081	774.562
430.00	471.986	511.472	667.573	707.059	786.030
440.00	479.210	519.441	676.806	717.037	797.498
450.00	486.434	527.410	686.039	727.015	808.966
460.00	493.658	535.379	695.272	736.993	820.434
470.00	500.882	543.348	704.505	746.971	831.902
480.00	508.106	551.317	713.738	756.949	843.370
490.00	515.330	559.286	722.971	766.927	854.838
500.00	522.554	567.255	732.204	776.905	866.306
510.00	529.778	575.224	741.437	786.883	877.774
520.00	537.002	583.193	750.670	796.861	889.242
530.00	544.226	591.162	759.903	806.839	900.710
540.00	551.450	599.131	769.136	816.817	912.178
550.00	558.674	607.100	778.369	826.795	923.646
560.00	565.898	615.069	787.602	836.773	935.114
570.00	573.122	623.038	796.835	846.751	946.582
580.00	580.346	631.007	806.068	856.729	958.050
590.00	587.570	638.976	815.301	866.707	969.518
600.00	594.794	646.945	824.534	876.685	980.986

3.4. Recommended Data on Heat Capacity of Polymers with Aromatic Groups in the Backbone

3.4.1. *poly*(*p*-Phenylene)

Only one investigation[49] is reported in the literature which deals with the heat capacity of *poly*(*p*-phenylene). The heat capacity of a semicrystalline sample has been measured from 80 to 300 K. The details of the measurements are given in Table 2 and the heat capacity data are given in Table A36. The glass transition temperature of *poly*(*p*-phenylene) is unknown, while the melting temperature is believed to be above 1000 K. The preliminary recommended heat capacities were obtained by curve-fitting the data from 80 to 300 K into Eq. (26). and are given in Table 35:

$$C_p = \exp[8.080832 - 3.371739\,(\ln T) + 0.6658902\,(\ln T)^2 - 0.03270898\,(\ln T)^3]\ \text{J/(K mol)} \qquad (26)$$

Figure 8 shows the plot of the heat capacity over this temperature range.

3.4.2. *poly*(Thio-1,4-Phenylene)

Only one investigation is reported in the literature which deals with heat capacities of *poly*(thio-1,4-phenylene).[50] The details of the measurements are given in Table 2. Heat capacity of PTP over the range of measurement is given in Tables A37 and A38. The recommended data below the glass transition temperature (363 K) were obtained by extrapolating the author's curve-fitted data from 220 up to T_g. Both semicrystalline and amorphous heat capacities were reported to be in close agreement. Above T_g, a rigid amorphous fraction dependence of heat capacity was reported for the semicrystalline polymers obtained by isothermal and non-isothermal crystallization. Hence, the melt data from 540 to 600 K were extrapolated down to T_g and represent the recommended data above the glass transition temperature. The recommended data for the solid and melt are given in Tables 36 and 37. The solid heat capacities are plotted in Figure 8.

3.4.3. *poly*(*p*-Xylylene)

Only one investigation is reported in the literature which deals with heat capacities of *poly*(*p*-xylylene).[51] The details of the measurements are given in Table 2. The data are given in Table A39. The preliminary recommendated data for a sample of high crystallinity ~ 90%, below and above the glass transition temperature (286 K) is given in Table 38. Above T_g, the semicrystalline data is included as it is the only available data and it is for a sample of high crystallinity. Figure 8 shows the heat capacities when compared with *poly*(*p*-phenylene) and *poly*(thio-1,4-phenylene).

TABLE 21. Recommended heat capacity data for semicrystalline *poly*(diethyl siloxane) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
0.00	0.000
10.00	2.477
15.00	6.112
20.00	10.789
25.00	16.081
30.00	20.979
40.00	30.837
50.00	39.678
60.00	47.789
70.00	55.440
80.00	62.630
90.00	69.360
100.00	75.630
110.00	81.440
120.00	87.409
130.00	94.158
135.00 (T_g)	97.532

TABLE 22. Recommended heat capacity data for molten *poly*(diethyl siloxane)

Temp (K)	Heat capacity [J/(K mol)]
135.00 (T_g)	127.721
140.00	128.863
150.00	131.147
160.00	133.432
170.00	135.717
180.00	138.001
190.00	140.286
200.00	142.571
210.00	144.855
220.00	147.140
230.00	149.425
240.00	151.709
250.00	153.994
260.00	156.279
270.00	158.563
273.15	159.283
280.00	160.848
290.00	163.133
298.15	164.994
300.00	165.417
310.00	167.702
320.00	169.986
330.00	172.271
340.00	174.556
350.00	176.840
360.00	179.125

TABLE 23. Heat capacity change at the glass transition temperature of the various substituted polystyrenes

Polymer[a]	T_g (K)	ΔC_p [J/(K mol)]
PS	273	30.8[b]
PFS	384	33.3[c]
PCS	406	31.1[d]
PBS	410	31.9[d]
PIS	424	37.9[d]
PMS	380	34.6[d]

[a] For the structure and abbreviations used for the various polymers see the table given in appendix.

[b] Data from reference 5.

[c] Data obtained with the DuPont DSC at a heating rate of 20 K/min.

[d] Data obtained with Perkin-Elmer DSC-2 at a heating rate of 10 K/min.

TABLE 24. Transitions in *poly*(*di*-*n*-alkyl itaconates)

Polymer[a]	T_g^L (K)	C_p^L [J/(K mol)]	T_g^u (K)	ΔC_p^u [J/(K mol)]
PDMI	–	–	377	54.23
PDPI	–	–	304	57.84
PDHI	172	45.64	248	13.04
PDOI	178	99.12	240	14.16
PDNI	187	183.36	245	11.46

[a] For the structure and abbreviations used for the various polymers see the table given in appendix.

TABLE 25. Equations used to derive the recommended heat capacities of various substituted polystyrenes

Polymer[a]	State	Equation[b] (RMS dev.)	Temperature range (K)[c]	Number of measurements
PFS	Solid	$C_p = 44.84 + 5.21 \times 10^{-3} T + 7.476 \times 10^{-4} T^2$ (0.9%)	130 – 384	3
PCS	Solid	$C_p = -4.20 + 0.4866\,T$ (0.3%)	300 – 406	3
	Molten	$C_p = 112.57 + 0.2775\,T$ (0.3%)	406 – 550	3
PBS	Solid	$C_p = 6.33 + 0.4649\,T$ (1.5%)	300 – 410	4
	Molten	$C_p = 113.94 + 0.2801\,T$ (1.2%)	410 – 550	4
PIS	Solid	$C_p = 7.18 + 0.4945\,T$ (0.5%)	300 – 424	4
	Molten	$C_p = 139.02 + 0.2730\,T$ (0.5%)	424 – 550	4
PMS	Solid	$C_p = -3.54 + 0.5138\,T$ (0.2%)	300 – 380	2
	Molten	$C_p = 90.85 + 0.3564\,T$ (0.3%)	380 – 500	2

[a] The structure and abbreviations of the polymers are given in the appendix.
[b] C_p is in J/(K mol).
[c] Temperature range over which the equation is valid.

TABLE 26. Recommended heat capacity data for amorphous substituted polystyrenes below the glass transition temperature in [J/(K mol)]

Temp (K)	PS	PFS	PCS	PBS	PIS	PMS
130.00	57.887	58.152	NA	NA	NA	NA
140.00	61.426	60.222	NA	NA	NA	NA
150.00	65.009	62.443	NA	NA	NA	NA
160.00	68.650	64.812	NA	NA	NA	NA
170.00	72.358	67.331	NA	NA	NA	NA
180.00	76.142	70.000	NA	NA	NA	NA
190.00	80.011	72.818	NA	NA	NA	NA
200.00	83.971	75.786	NA	NA	NA	NA
210.00	88.028	78.903	NA	NA	NA	NA
220.00	92.187	82.170	NA	NA	NA	NA
230.00	95.992	85.586	NA	NA	NA	NA
240.00	100.140	89.152	NA	NA	NA	NA
250.00	104.428	92.868	NA	NA	NA	NA
260.00	108.836	96.732	NA	NA	NA	NA
270.00	113.346	100.747	NA	NA	NA	NA
273.15	114.785	102.042	NA	NA	NA	NA
280.00	117.944	104.911	NA	NA	NA	NA
290.00	122.617	109.224	NA	NA	NA	NA
298.15	126.475	112.850	NA	NA	NA	NA
300.00	127.357	113.687	141.780	145.800	155.530	150.600
310.00	132.154	118.299	146.646	150.449	160.475	155.738
320.00	137.001	123.061	151.512	155.098	165.420	160.876
330.00	141.893	127.973	156.378	159.747	170.365	166.014
340.00	146.825	133.034	161.244	164.396	175.310	171.152
350.00	151.791	138.245	166.110	169.045	180.255	176.290
360.00	156.788	143.605	170.976	173.694	185.200	181.428
370.00	161.813	149.114	175.842	178.343	190.145	186.566
380.00	NA	154.773	180.708	182.992	195.090	NA
390.00	NA	NA	185.574	187.641	200.035	NA
400.00	NA	NA	190.440	192.290	204.980	NA
410.00	NA	NA	NA	NA	209.925	NA
420.00	NA	NA	NA	NA	214.870	NA

The abbreviations used for the polymer names have been described in the appendix.

3.4.4. *poly*(Oxy-3-bromo-2,6-dimethyl-1,4-phenylene)

Only one investigation[29] is reported in the literature which deals with the measurement of heat capacities of *poly*(oxy-3-bromo-2,6-dimethyl-1,4-phenylene). The details of the measurement are given in Table 2 and the only available heat capacity data are given in Table A40. The preliminary recommended heat capacities are given in Table 39 and plotted in Fig. 9. To extend the heat capacities up to T_g (559 K) the data from 480 to 520 K were curve-fitted into the equation:

$$C_p = 52.15326 + 0.396001\,T \text{ (J/K mol)} \qquad (27)$$

and, using this equation, extended to 559 K (T_g). The ΔC_p at T_g has been reported by the authors[29] as 18 J/(K mol) and is much lower than *poly*(oxy-2,6-dimethyl-1,4-phenylene) whose ΔC_p is 28.3 J/(K mol) at 482 K.

3.4.5. *poly*[Oxy-2,6-*bis*(1-methylethyl)-1,4-phenylene]

Only one investigation is reported in the literature which deals with heat capacities of *poly* [oxy-2,6-*bis*(1-methylethyl)-1,4-phenylene].[52] The details of the measurement are given in Table 2. Heat capacity data on samples whose state has not been identified by the authors can thus be used only as a preliminary set of data. Table A41 gives the heat capacities below and above the glass transition temperature. Recommended heat capacities below the glass transition temperature (425.5 K) were obtained by extrapolating the author's curve-fitted equation from 270 to 425.5 K (Table 40). Figure 9 shows the heat capacities when compared with that of *poly*(oxy-2,6-dimethyl-1,4-phenylene) and *poly*(oxy-3-bromo-2,6-dimethyl-1,4-phenylene).

3.4.6. *poly*(Ethylene Terephathate)

In the ATHAS data bank (1980),[8] the recommended heat capacity was evaluated for only amorphous *poly*(ethylene terephthate) as the available data was limited to samples of either low crystallinity or completely amorphous samples. Since then Collocot *et al.*[53] have reported heat capacities below 15 K. The heat capacity data retrieved from the graph are given in Table A42. Based on the author's extrapolated data for 100% crystalline and 100% amorphous PET it is now possible to obtain recommended heat capacities for the two limiting states in the low temperature range where amorphous heat capacity is usually higher than the crystalline data.

The new low temperature amorphous data were found to be in close agreement with Choy's data (sample 15, Ref., 8) while Assfalg's (sample 8, Ref., 8) showed larger deviations. Therefore, to arrive at a better recommended set of heat capacities in the low temperature region (1.2–15 K) for amorphous PET, the data of Collocot and Choy were averaged in the region of overlap and curve-fitted into the equation:

$$C_{pa} \ \exp[-4.879994 + 3.464046\,(\ln T) - 0.1205552\,(\ln T)^2 - 0.06363761\,(\ln T)^3]$$
$$(\pm\ 0.94\%) \text{ J/(K mol)} \qquad (28)$$

This equation represents the new C_p data from 1.2 to 15 K. Above 15 K up to 590 K heat capacities of 100% amorphous PET were recommended earlier.[8]

For crystalline PET, the smoothed heat capacity data retrieved from the graph were used. From 1.2 to 15 K the smoothed data can be represented by the equation:

$$C_{pc} = \exp[-4.790307 + 3.27316\,(\ln T) + 0.03140159\,(\ln T)^2 - -0.100217\,(\ln T)^3]$$
$$(\pm\ 2\%) \text{ J/(Kmol)} \qquad (29)$$

An attempt was also made to arrive at a recommended set of heat capacities for crystalline PET above 110 K. From 20 to 110 K the heat capacities can be assumed to be close to that for amorphous PET, as only amorphous PET data is available in the literature. Between 110 K and 230 K heat capacities for only one semicrystalline sample (no 24, Ref., 8, crystallinity 0.39) were available. These data seem to be in error as they are much lower than the heat capacity for other samples of comparable crystallinities at temperatures of overlap above 240 K. Hence, it was not possible to arrive at a recommended of heat capacity for crystalline PET between 110 and 240 K. From 240 K to 520 K heat capacities were available for semicrystalline PET where crystallinity ranged between 0.01 to 0.52. Above 240 K the heat capacity of crystalline PET obtained from the two-phase model $C_p = w^c C_p{}^c + (1 - w^c)\,C_p{}^a$, showed erratic variations. This indicates that in order to determine heat capacity for crystalline PET at temperatures above 110 K, data for samples of higher crystallinities are needed. The new recommended heat capacities from 1.2 to 15 K for 100% crystalline and 100% amorphous PET are given in Table 41.

3.4.7. *poly*(Butylene Terephthalate)

Four investigations have been reported in the literature on the heat capacity measurements of five semicrystalline and one quenched sample of *poly*(butylene terephthalate) (PBT).[54–57] Details of the three investigations[54–56] which meet our standards of acceptability are given in Table 2. Data on these samples below and above the glass transition and for the melt are given in Tables A43 to A46. Heat capacity data on semicrystalline PBT reported by Bair *et al.*[57] has not been included, as a very high heating rate of 40 °C/min has been used and the reported data are much higher than those reported by other authors.

A detailed study on PBT carried out in our laboratory[54] has revealed the existence of rigid amorphous fractions of the semicrystalline samples crystallized from glass and from melt between 275 and 490 K. The glass transition temperatures of amorphous PBT samples quenched in a

TABLE 27. Recommended heat capacity data for molten substituted polystyrenes in [J/(K mol)]

Temp (K)	PS	PFS	PCS	PBS	PIS	PMS
380.00	195.934	NA	NA	NA	NA	NA
390.00	198.587	NA	NA	NA	NA	229.846
400.00	201.240	NA	NA	NA	NA	233.410
410.00	203.893	NA	226.345	NA	NA	236.974
420.00	206.546	NA	229.120	231.582	NA	240.538
430.00	209.199	NA	231.895	234.383	256.410	244.102
440.00	211.852	NA	234.670	237.184	259.140	247.666
450.00	214.505	NA	237.445	239.985	261.870	251.230
460.00	217.158	NA	240.220	242.786	264.600	254.794
470.00	219.811	NA	242.995	245.587	267.330	258.358
480.00	222.464	NA	245.770	248.388	270.060	261.922
490.00	225.117	NA	248.545	251.189	272.790	265.486
500.00	227.770	NA	251.320	253.990	275.520	269.050
510.00	230.423	NA	254.095	256.791	278.250	NA
520.00	233.076	NA	256.870	259.592	280.980	NA
530.00	235.729	NA	259.645	262.393	283.710	NA
540.00	238.382	NA	262.420	265.194	286.440	NA
550.00	241.035	NA	265.195	267.995	289.170	NA
560.00	243.688	NA	NA	NA	NA	NA
570.00	246.341	NA	NA	NA	NA	NA
580.00	248.994	NA	NA	NA	NA	NA
590.00	251.647	NA	NA	NA	NA	NA
600.00	254.300	NA	NA	NA	NA	NA

The abbreviations used for the polymer names have been described in the appendix.

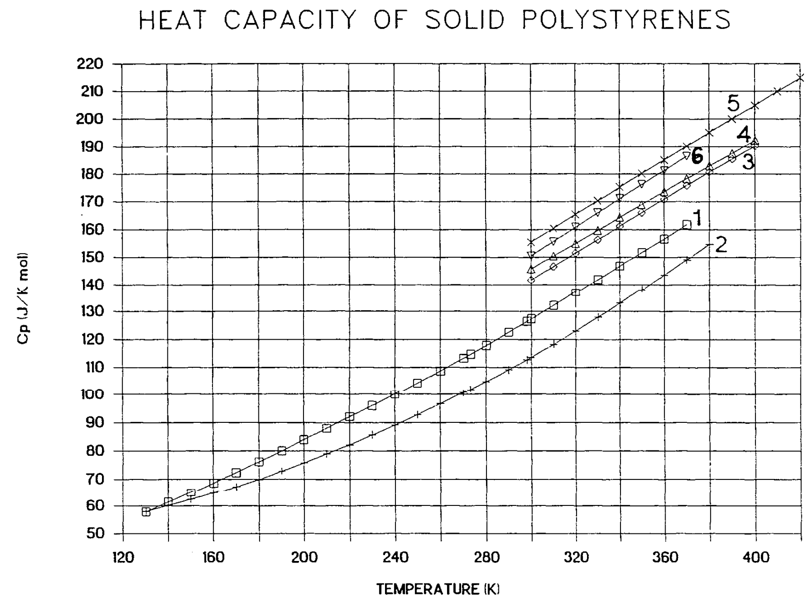

FIG. 4. Recommended heat capacities for the following solid polymers: 1. polystyrene, 2. *poly*(*p*-fluorostyrene), 3. *poly*(*p*-chlorostyrene), 4. *poly*(*p*-bromostyrene), 5. *poly* (*p*-iodostyrene), and 6. *poly*(*p*-methyl styrene).

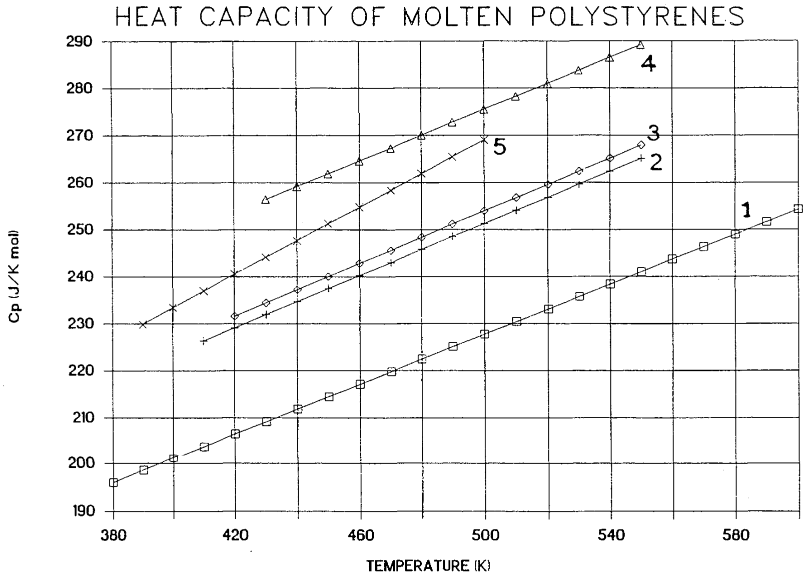

FIG. 5. Recommended heat capacities for the following molten polymers: 1. polystyrene, 2. *poly*(*p*-fluorostyrene), 3. *poly*(*p*-chlorostyrene), 4. *poly*(*p*-bromostyrene), 5. *poly* (*p*-iodostyrene), and 6. *poly*(*p*-methyl styrene).

cooling bath of glass beads was found to be 248 K, which is much lower than that reported for semicrystalline samples, where T_g varies between 310–325 K. Amorphous samples showed a second T_g at about 310 K with a ΔC_p of 20 J/(K mol). Since the lower limit of the DSC used by us was 220 K and amorphous samples showed a T_g at 248 K, C_p data below the first T_g could not be retrieved. Due to the presence of a crystallization exotherm before the second T_g, the heat capacities above T_g are no longer due to the amorphous melt.

As a preliminary set of heat capacities of semicrystalline PBT (below the glass transition at 320 K) the data for samples 1 and 3 from 150–240 K were averaged over the region of overlap and fit into the equation:

$$C_p = -6.938805 + 0.9502766\,T - 4.876461 \times 10^{-5}\,T^2\ (\pm\ 0.11\%)\ \mathrm{J/(K\,mol)} \qquad (30)$$

Between 240 to 310 K the averaged data for samples (1,4–6) were smoothed by fitting into the equation:

$$C_p = 13.13337 + 0.8544043\,T\ (\pm\ 0.15\%)\ \mathrm{J/(K\,mol)} \qquad (31)$$

To obtain heat capacities of the melt, the data of sample 1 (which is an average of 7 measurements) were fit into the equation:

$$C_p = 219.6479 + 0.452209\,T\ (\pm\ 0.1\%)\ \mathrm{J/(K\,mol)} \qquad (32)$$

and this equation was used to extrapolate the data up to T_g. The data on samples 2–6 have not been included, due to deviations above 1% introduced during the retrieval of data from the graph. Heat capacity data on amorphous PBT (sample 2) is not recommended, since it is associated with crystallization and shows the dependence of heat capacity on the rigid amorphous fraction.

Preliminary recommended data below T_g (248 K) obtained from Eq. (30), between 1st T_g and 2nd T_g at 320 K obtained from Eq. (31) and heat capacities of the melt obtained from Eq. (32) are given from 248 K up to 570 K in Tables 42 and 43 respectively.

3.4.8. *poly*(4-Hydroxybenzoic Acid)

Only one investigation is reported in the literature[58] which deals with heat capacities of commercial, semicrystalline *poly*(4-hydroxybenzoic acid). The details of the measurement are given in Table 2. Heat capacities are given for a semicrystalline sample below the glass transition region and in the glass transition region in Tables A47 and A48. The recommended heat capacities (Table 44) from 170 to T_g (434 K) are included in the ATHAS data bank as a preliminary set of data as from 290 K up to 420 K the reported heat capacities are associated already with the beginning of a broad glass transition. The data from 390 to 420 K were curve-fitted into the equation:

$$C_p = 19.28989 + 0.362003\,T\ (\pm\ 0.04\%)\ \mathrm{J/(K\,mol)} \qquad (33)$$

This was used to obtain C_p data from 390 to 434 K (T_g). From 500 to 650 K the author has reported C_p data of the melt obtained from an empirical addition scheme in

TABLE 28. Results of curve fitting literature data on heat capacity of *poly*(*di*-*n*-alkyl itaconates) to derive the recommended data

Polymer[a]	State		Equation[b] (RMS dev.)	Temperature range (K)[c]
PDMI	Solid	(i)	$C_p = -6.68519 + 1.038724\,T - 0.0010872\,T^2$ (0.8%)	110–290
		(ii)	$C_p = 64.5583 + 0.47983\,T$ (0.3%)	300–377
	Molten		$C_p = 213.0095 + 0.22989\,T$ (0.2%)	377–450
PDPI	Solid	(i)	$C_p = 29.5446 + 1.284867\,T - 0.00099196\,T^2$ (0.6%)	110–210
		(ii)	$C_p = 75.4368 + 0.84752\,T$ (0.4%)	220–304
	Molten		$C_p = 283.0105 + 0.35491\,T$ (0.1%)	304–410
PDHI	Solid		$C_p = 215.2651 - 0.8023134\,T + 0.00795689\,T^2$ (0.6%)	110–170
PDOI	Solid		$C_p = 74.58574 + 1.67328\,T$ (0.7%)	110–170
PDNI	Solid		$C_p = 19.2201 + 2.033779\,T$ (0.2%)	110–180
PDDI	Solid		$C_p = 100.2314 + 1.6497\,T$ (1.0%)	110–170

[a] The structure and abbreviations of the polymers are given in the appendix.

[b] C_p is in J/(Kmol).

[c] Temperature range over which the equation is valid.

TABLE 29a. Recommended heat capacity data for amorphous *poly*(-dimethyl itaconate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
110.00	94.419
120.00	102.306
130.00	109.975
140.00	117.427
150.00	124.661
160.00	131.678
170.00	138.477
180.00	145.059
190.00	151.424
200.00	157.571
210.00	163.500
220.00	169.212
230.00	174.707
240.00	179.984
250.00	185.044
260.00	189.887
270.00	194.512
273.15	195.923
280.00	198.919
290.00	203.109
298.15	207.619
300.00	208.507
310.00	213.305
320.00	218.104
330.00	222.902
340.00	227.700
350.00	232.499
360.00	237.297
370.00	242.095
377.00 (T_g)	245.454

TABLE 29b. Recommended heat capacity data for molten *poly*(dimethyl itaconate)

Temp (K)	Heat capacity [J/(K mol)]
377.00 (T_g)	299.680
380.00	300.370
390.00	302.669
400.00	304.968
410.00	307.267
420.00	309.566
430.00	311.865
440.00	314.164
450.00	316.463

which C_p data of several copolymers of POB and PON are evaluated.

$$C_p = n\mathrm{ON}(173.65 + 0.285\,T) + n\mathrm{OB}(132.31 + 0.179\,T) \quad (34)$$

Since this is not truly experimental, the data are not recommended. The recommended heat capacities are plotted in Figure 10.

3.4.9. *poly*(2,6-Hydroxynaphthoic Acid)

Only one investigation[58] is reported in the literature which deals with heat capacities of commercial, semicrystalline *poly*(2,6-hydroxynaphthoic acid). The details of the measurements are given in Table 2. Heat capacity data are given in Tables A49 (below T_g), A50 (in the glass transition region) and A51 (melt). To obtain recommended heat capacities up to glass transition (399 K), the data between 170 and 280 K were extrapolated as above 290 K the reported data are associated with the beginning of the glass transition.Heat capacity of the melt from 399 K (T_g) up to 650 K was obtained by extrapolating author's curve-fitted data between 500 and 640 K. The recommended heat capacities are given in Table 45 and 46 and are plotted in Fig. 10.

3.4.10. *poly*(Ethylene-2,6-naphthalene Dicarboxylate)

Only one investigation[59] is reported in the literature which deals with the heat capacity measurement of *poly*(ethylene-2,6-naphthalene dicarboxylate) (PEN). Heat capacity of semicrystalline samples crystallized from the melt and from the glassy state under widely ranging crystallization conditions, and of amorphous samples prepared with different cooling rates have been reported. The details of this investigation are given in Table 2. Heat capacity data below T_g and of the melt are given in Tables A52 and A53.The author's curve-fitted equation for the heat capacity data between 220–300 K was used to obtain the heat capacity of semicrystalline PEN from 220 up to 390 K (glass transition temperature). The glass transition temperature on cooling changes logarithmically ($T_g = 382.3 + 2.03 \ln q$, q in K/min). Amorphous PEN shows a higher heat capacity above 300 K up to the glass transition. The authors have reported the difference to be ~ 3% [9–10 J/(K/mol)] above 340 K. Between T_g and T_m a rigid amorphous fraction (up to 0.2) dependent on the crystallinity was reported. This fraction starts to gain mobility at 430 K and decreases in amount, to reach zero after melting of the low melting crystals. Since amorphous samples were associated with crystallization which occurred between 460–510 K, recommended heat capacity of the melt were obtained from 390 K (T_g) up to 600 K by extrapolating the author's curve-fitted equation (540–600 K) for the melt. The change in heat capacity at the glass transition was found to be 81.57 J/(K mol), close to the value of 80.1 J/(K mol) estimated by the authors. The recommended heat capacity below and above T_g are given in Tables 47 and 48.

TABLE 30a. Recommended heat capacity data for amorphous *poly(di-n-*propyl itaconate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
110.00	158.877
120.00	169.444
130.00	179.813
140.00	189.983
150.00	199.955
160.00	209.729
170.00	219.304
180.00	228.681
190.00	237.859
200.00	246.839
210.00	255.621
220.00	261.892
230.00	270.367
240.00	278.842
250.00	287.318
260.00	295.793
270.00	304.268
273.15	306.938
280.00	312.743
290.00	321.219
298.15	328.126
300.00	329.694
304.00 (T_g)	333.084

TABLE 30b. Recommended heat capacity data for molten *poly*(*di-n*-propyl itaconate)

Temp (K)	Heat capacity [J/(K mol)]
304.00 (T_g)	390.902
310.00	393.032
320.00	396.581
330.00	400.130
340.00	403.679
350.00	407.228
360.00	410.777
370.00	414.326
380.00	417.875
390.00	421.424
400.00	424.973
410.00	428.522

TABLE 31. Recommended heat capacity data for amorphous polyitaconates below the glass transition temperature in (J/K.mol)

Temp (K)	PDHI	PDOI	PDNI	PDDI	PDCYDI	PDCYDDI
110.00	223.289	258.647	242.936	281.698	203.786	239.776
120.00	233.567	275.380	263.274	298.195	225.792	256.298
130.00	245.436	292.113	283.611	314.692	247.952	273.505
140.00	258.896	308.846	303.949	331.189	270.265	291.398
150.00	273.948	325.578	324.287	347.686	292.730	309.978
160.00	290.591	342.311	344.625	364.183	315.348	329.242
170.00	308.826	359.044	364.963	380.680	338.119	349.193
180.00	NA	NA	385.300	397.177	361.043	369.830
190.00	NA	NA	NA	413.674	384.120	391.152
200.00	NA	NA	NA	430.171	407.350	413.160
210.00	NA	NA	NA	NA	430.733	435.854
220.00	NA	NA	NA	NA	454.268	459.234
230.00	NA	NA	NA	NA	475.543	483.299
240.00	NA	NA	NA	NA	496.822	508.050
250.00	NA	NA	NA	NA	518.101	533.488
260.00	NA	NA	NA	NA	539.380	559.610
270.00	NA	NA	NA	NA	560.659	586.419
273.15	NA	NA	NA	NA	567.362	595.006
280.00	NA	NA	NA	NA	581.938	613.914

The abbreviations used for the polymer names have been described in the appendix.

3.4.11. *poly*(Oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)

Four investigations[60–63] have been reported in the literature which deal with heat capacities of *poly*(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (PEEK). Three[61–63] meet our standards of acceptable data. The details of the measurements are given in Table 2. Table A54 lists the heat capacity data below T_g (419 K) while A55 gives the melt data. Heat capacities of semicrystalline samples crystallized at a wide range of conditions, and quenched with liquid N_2 were measured by Cheng and Wunderlich.[62] Below 240 K the heat capacities of semicrystalline and amorphous samples were identical, and from 340 to 410 K the heat capacity showed dependence on crystallinity. Heat capacity of amorphous PEEK reported on sample 4 by Kemmish *et al.*[61] agree below T_g to ~ 1% with Cheng and Wunderlich.[62] Above T_g (419 K) and below T_m the heat capacity showed dependence on the rigid-amorphous fraction (fraction of amorphous material that does not contribute to the increase in C_p at T_g). To obtain the recommended heat capacity data below T_g the author's[62] curve-fitted data from 130 to 240 K were used.

From 340 to 410 K the data for 100% crystalline and 100% amorphous were retrieved from the graph of heat capacity vs crystallinity. Table 49 shows the heat capacity as a function of crystallinity from 340 to 410 K and this was smoothed further by curve-fitting into the following equations:

$$C_p^c = 52.56964 + 0.8790476\, T\, [\pm\ 0.2\%,\ \mathrm{J/(K\ mol)}] \quad (35)$$

$$C_p^a = 28.74449 + 0.9758333\, T\, [\pm\ 0.13\%,\ \mathrm{J/(K\ mol)}] \quad (36)$$

Equation (35) was used to obtain the heat capacity of crystalline PEEK from 250 K to 410 K and Eq. (36) was used to obtain heat capacity of amorphous PEEK from 250 to 419 K (T_g).

Melt heat capacities reported by Wunderlich and Cheng (sample 4) and Kemmish (sample 1) agreed to ~2%. Since the measurements on sample 4 were more extensive (average of 14 runs in the temperature range of 600–680 K), their data were used as recommended heat capacities from 419 K (T_g) up to 680 K. The recommended set of data below and above T_g are listed in Table 50 and Table 51 and are plotted in Fig. 11.

3.4.12. *poly*[Oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene]

Recommended experimental heat capacity data of this bisphenol based amorphous polysulfone are based on two out of three investigations reported in the literature.[21,64,65] Details of the investigations included are given in Table 2. Heat capacities have also been measured by Privalko *et al.*[65] from 308 to 523 K, but only graphical data of polysulfone (chemical structure not revealed) has been presented for the temperature dependence of a reduced heat capacity. Data on the two samples discussed here in the temperature regions below and above the glass transition are given in Tables A56 and A57. To obtain the recommended data below T_g (458.5 K), the tabulated data on sample 2 from 10 to 350 K were smoothed by curve fitting into the following equations:

$$\text{From 10–30 K:}\quad C_p = \exp[-5.947623 + 4.872284\,(\ln T) - 0.7156859\,(\ln T)^2 + 0.04178513\,(\ln T)^3]\ (\pm\ 0.4\%) \quad (37)$$

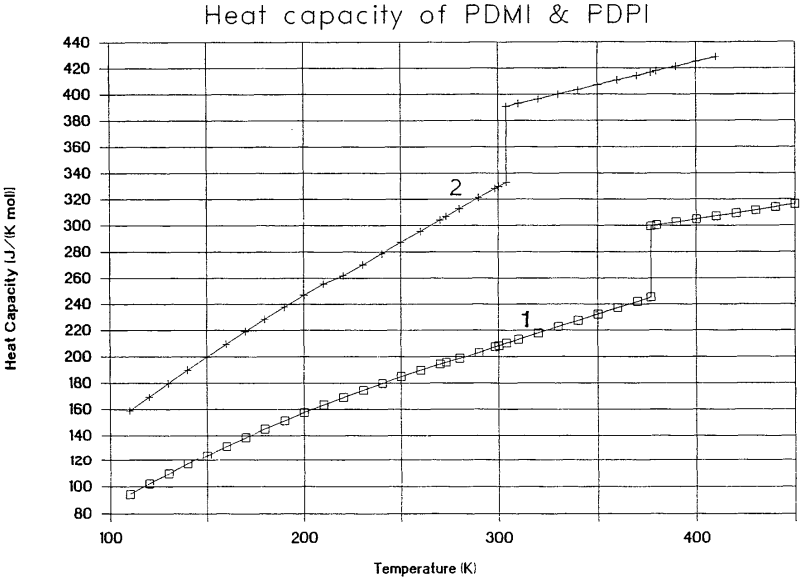

FIG. 6. Recommended heat capacies for the following two polymers: 1. *poly*(dimethyl itaconate) and 2. *poly*(di-*n*-propyl itaconate).

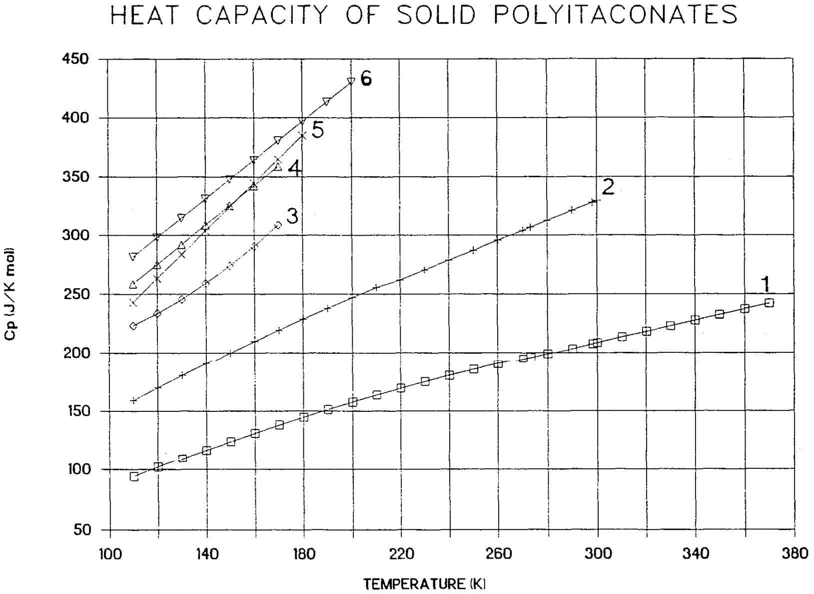

FIG. 7. Recommended heat capacities for several solid polyitaconates: 1. *poly*(dimethyl itaconate), 2. *poly*(di-*n*-propyl itaconate), 3. *poly*(di-*n*-hexyl itaconate, 4. *poly*(di-*n*-octyl itaconate), 5. *poly*(di-*n*-nonyl itaconate), and 6. *poly*(di-*n*-decyl itaconate).

TABLE 32. Results of curve fitting literature data on heat capacity of *poly*(dicycloalkyl itaconates) to derive the recommended data

Polymer[a]	State		Equation[b] (RMS dev.)	Temperature range (K)[c]
PDCyOI	Solid	(i)	$C_p = 9.00687 + 1.896353\,T - 0.00011835\,T^2$ (0.6%)	110 -200
		(ii)	$C_p = 17.34212 + 1.99247\,T - 0.00082074\,T^2$ (0.4%)	210 - 310
		(iii)	$C_p = 119.4146 + 1.41202\,T$ (0.2%)	320 - 390
	Molten		$C_p = 423.197 + 0.80616\,T$ (0.1%)	390 - 440
PDCyDI	Solid	(i)	$C_p = -28.2002 + 2.02489\,T - 0.00076432\,T^2$ (O.8%)	110 - 230
		(ii)	$C_p = -13.876 + 2.1279\,T$ (0.3%)	240 - 280

[a] The structure and abbreviations of the polymers are given in the appendix.

[b] C_p is in J/(K mol).

[c] Temperature range over which the equation is valid.

From 40–60 K:
$$C_p = -64.21593 + 5.459890\,T - 0.0586861\,T^2 + 0.000291628\,T^3\ (\pm\ 0.47\%) \quad (38)$$

From 70–190 K:
$$C_p = 26.148 + 1.43144\,T + 0.001090276\,T^2 - 2.558776 \times 10^{-6}\,T^3\ (\pm\ 0.8\%) \quad (39)$$

From 200–310 K:
$$C_p = -50.30969 + 2.162671\,T - 0.001161756\,T^2\ (\pm\ 0.17\%) \quad (40)$$

From 320–350 K:
$$C_p = -239.516 + 3.3455461\,T - 0.003009135\,T^2\ (\pm\ 0.4\%) \quad (41)$$

From 360–450 K:
$$C_p = 271.6364 + 0.8409091\,T\ (\pm\ 1.6\%) \quad (42)$$

The heat capacities reported by Richardson[21] on sample 1 were higher than that of sample 2 in the region of overlap. For example at 380 K it was ~ 5% higher while at 440 K it was higher by ~ 8%. Since the error limit of the measurements on sample 2 above 330 K was 5%, the data on sample 1 from 380–440 K and the data points from 340 to 370 K of sample 2 were further smoothed by curve-fitting into the equation:

$$C_p = 59.02983 + 1.460377\,T\ (\pm\ 0.6\%) \quad (43)$$

Recommended heat capacities below the glass transition were obtained as follows. From 10 to 30 K Eq. (37), 40–60 K Eq. (38), 70–190 K Eq. (39), 200–310 Eq. (40), 320–330 K Eq. (41) and from 340 to 458.5 K (T_g) Eq. (42) was used. Heat capacities of molten polysulfone [Eq. (43)] are recommended. The data below and above T_g are listed in Tables 52 and 53, and plotted in Fig. 12.

TABLE 33a. Recommended heat capacity data for amorphous *poly*(dicyclo octyl itaconate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
110.00	216.174
120.00	234.865
130.00	253.533
140.00	272.177
150.00	290.797
160.00	309.394
170.00	327.966
180.00	346.516
190.00	365.041
200.00	383.543
210.00	399.566
220.00	415.961
230.00	432.193
240.00	448.260
250.00	464.163
260.00	479.902
270.00	495.477
273.15	500.349
280.00	510.887
290.00	526.134
298.15	538.438
300.00	541.216
310.00	556.134
320.00	571.259
330.00	585.380
340.00	599.500
350.00	613.620
360.00	627.740
370.00	641.860
380.00	655.980
390.00 (T_g)	670.100

TABLE 33b. Recommended heat capacity data for molten *poly*(dicyclooctyl itaconate)

Temp (K)	Heat capacity [J/(K mol)]
390.00 (T_g)	737.599
400.00	745.660
410.00	753.722
420.00	761.784
430.00	769.845
440.00	777.907

TABLE 34 Recommended heat capacity data for *poly*(p-methacryloyloxy benzoic acid) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
10.00	3.800
15.00	9.112
20.00	15.150
25.00	21.383
30.00	27.630
40.00	40.050
50.00	49.950
60.00	60.870
70.00	70.890
80.00	79.950
90.00	88.272
100.00	96.346
110.00	104.249
120.00	112.040
130.00	119.765
140.00	127.461
150.00	135.160
160.00	142.887
170.00	150.663
180.00	158.505
190.00	166.429
200.00	174.448
210.00	182.575
220.00	190.820
230.00	199.191
240.00	207.699
250.00	216.350
260.00	225.152
270.00	234.112
273.15	236.967
280.00	243.235
290.00	252.529
298.15	260.233
300.00	261.999
310.00	271.650

TABLE 35. Recommended heat capacity data for semicrystalline *poly*(*p*-phenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
80.00	28.220
90.00	30.312
100.00	32.486
110.00	34.729
120.00	37.031
130.00	39.387
140.00	41.792
150.00	44.241
160.00	46.733
170.00	49.263
180.00	51.831
190.00	54.434
200.00	57.071
210.00	59.740
220.00	62.440
230.00	65.171
240.00	67.930
250.00	70.717
260.00	73.531
270.00	76.371
273.15	77.271
280.00	79.236
290.00	82.126
298.15	84.499
300.00	85.040

TABLE 36. Recommended heat capacity data for semicrystalline *poly*(thio-1,4-phenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
220.00	80.263
230.00	84.053
240.00	87.848
250.00	91.651
260.00	95.466
270.00	99.297
273.15	100.507
280.00	103.147
290.00	107.019
298.15	110.193
300.00	110.916
310.00	114.840
320.00	118.794
330.00	122.781
340.00	126.802
350.00	130.860
360.00	134.957
363.00 (T_g)	136.193

TABLE 37. Recommended heat capacity data for molten *poly*(thio-1,4-phenylene)

Temp (K)	Heat capacity [J/(K mol)]
363.00 (T_g)	165.374
370.00	166.254
380.00	167.511
390.00	168.769
400.00	170.026
410.00	171.283
420.00	172.541
430.00	173.798
440.00	175.056
450.00	176.313
460.00	177.570
470.00	178.828
480.00	180.085
490.00	181.343
500.00	182.600
510.00	183.857
520.00	185.115
530.00	186.372
540.00	187.630
550.00	188.887
560.00	190.144
570.00	191.402
580.00	192.659
590.00	193.917
600.00	195.174

TABLE 38 Recommended heat capacity data for semicrystalline (crystallinity = 90%) *poly*(*p*-xylylene)

Temp (K)	Heat capacity [J/(K mol)]
220.00	95.241
230.00	100.179
240.00	105.148
250.00	110.149
260.00	115.181
270.00	120.243
273.15	121.000
280.00	125.337
286.00 (T_g)	128.409
290.00	130.460
298.15	134.664
300.00	135.622
310.00	140.817
320.00	146.045
330.00	151.308
340.00	156.604
350.00	161.933
360.00	167.297
370.00	172.694
380.00	178.125
390.00	183.589
400.00	189.087
410.00	194.619

TABLE 39. Recommended heat capacity data for amorphous *poly*(oxy-2,6-dimethyl,5-bromo-1,4-phenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
310.00	173.811
320.00	177.913
330.00	182.004
340.00	186.086
350.00	190.158
360.00	194.220
370.00	198.272
380.00	202.315
390.00	206.347
400.00	210.370
410.00	214.383
420.00	218.386
430.00	222.379
440.00	226.363
450.00	230.337
460.00	234.300
470.00	238.254
480.00	242.234
490.00	246.194
500.00	250.154
510.00	254.114
520.00	258.074
530.00	262.034
540.00	265.994
550.00	269.954
559.00 (T_g)	273.518

TABLE 40. Recommended heat capacity data for *poly*(oxy-2,6-bis(1-methylethyl)-1,4-phenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
270.00	227.707
273.15	229.833
280.00	234.456
290.00	241.206
298.15	246.707
300.00	247.955
310.00	254.705
320.00	261.455
330.00	268.204
340.00	274.954
350.00	281.703
360.00	288.453
370.00	295.203
380.00	301.952
390.00	308.702
400.00	315.451
410.00	322.201
420.00	328.951
425.50 (T_g)	332.663

TABLE 41. Recommended heat capacity data for *poly*(ethylene terephthalate)

Temp (K)	Heat capacity [J/(K mol)]	
	Crystalline	Amorphous
1.2	0.014180	0.014224
1.4	0.021517	0.023980
1.6	0.030947	0.037436
1.8	0.042689	0.055108
2.0	0.056945	0.077458
3.0	0.172138	0.271379
4.0	0.373338	0.619381
5.0	0.672904	1.124794
6.0	1.078123	1.774736
7.0	1.592487	2.548069
8.0	2.216689	3.420507
9.0	2.949358	4.367650
10.0	3.787629	5.366644
15.0	9.404000	10.51606

TABLE 42. Heat capacity data for semicrystalline *poly*(butylene terephthalate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
150.00	134.505
160.00	143.857
170.00	153.199
180.00	162.531
190.00	171.853
200.00	181.166
210.00	190.469
220.00	199.762
230.00	209.045
240.00	218.190
248.00 (T_g)	225.026
250.00	226.734
260.00	235.278
270.00	243.823
273.15	246.514
280.00	252.367
290.00	260.911
298.15	267.874
300.00	269.455
310.00	277.999
320.00 (T_g)	286.543

TABLE 43. Recommended heat capacity data for molten *poly*(butylene terephthalate)

Temp (K)	Heat capacity [J/(K mol)]
248.00 (T_g)	331.796
250.00	332.700
260.00	337.222
270.00	341.744
273.15	343.169
280.00	346.266
290.00	350.789
298.15	354.474
300.00	355.311
310.00	359.833
320.00	364.355
330.00	368.877
340.00	373.399
350.00	377.921
360.00	382.443
370.00	386.965
380.00	391.487
390.00	396.009
400.00	400.532
410.00	405.054
420.00	409.576
430.00	414.098
440.00	418.620
450.00	423.142
460.00	427.664
470.00	432.186
480.00	436.708
490.00	441.230
500.00	445.752
510.00	450.274
520.00	454.797
530.00	459.319
540.00	463.841
550.00	468.363
560.00	472.885
570.00	477.407

TABLE 44. Recommended heat capacity data for semicrystalline *poly*(4-hydroxybenzoic acid) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
170.00	70.762
180.00	74.739
190.00	78.716
200.00	82.693
210.00	86.670
220.00	90.647
230.00	94.624
240.00	98.601
250.00	102.578
260.00	106.555
270.00	110.532
273.15	111.784
280.00	114.509
290.00	118.400
298.15	121.835
300.00	122.600
310.00	126.700
320.00	131.800
330.00	135.100
340.00	139.500
350.00	144.100
360.00	148.500
370.00	152.600
380.00	156.900
390.00	160.471
400.00	164.091
410.00	167.711
420.00	171.331
430.00	174.951
434.00 (T_g)	176.399

TABLE 45. Recommended heat capacity data for semicrystalline *poly*(2,6-hydroxynaphthoic acid) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
170.00	104.318
180.00	110.269
190.00	116.220
200.00	122.171
210.00	128.122
220.00	134.073
230.00	140.024
240.00	145.975
250.00	151.926
260.00	157.877
270.00	163.828
273.15	165.703
280.00	169.779
290.00	175.730
298.15	180.580
300.00	181.681
310.00	187.632
320.00	193.583
330.00	199.534
340.00	205.485
350.00	211.436
360.00	217.387
370.00	223.338
380.00	229.289
390.00	235.240
399.00 (T_g)	240.596

TABLE 46. Recommended heat capacity data for molten *poly*(2,6-hydroxynaphthoic acid)

Temp (K)	Heat capacity [J/(K mol)]
399.00 (T_g)	274.140
400.00	274.480
410.00	277.884
420.00	281.288
430.00	284.691
440.00	288.095
450.00	291.498
460.00	294.902
470.00	298.306
480.00	301.709
490.00	305.113
500.00	308.517
510.00	311.920
520.00	315.324
530.00	318.727
540.00	322.131
550.00	325.535
560.00	328.938
570.00	332.342
580.00	335.745
590.00	339.149
600.00	342.553
610.00	345.956
620.00	349.360
630.00	352.763
640.00	356.167
650.00	359.571

TABLE 47. Recommended heat capacity data for semicrystalline *poly*(ethylene-2,6-naphthalene dicarboxylate) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]
220.00	203.045
230.00	211.317
240.00	219.620
250.00	227.956
260.00	236.324
270.00	244.725
273.15	247.377
280.00	253.152
290.00	261.633
298.15	268.546
300.00	270.115
310.00	278.596
320.00	287.078
330.00	295.559
340.00	304.041
350.00	312.522
360.00	321.004
370.00	329.485
380.00	337.967
390.00 (T_g)	346.448

TABLE 48. Recommended heat capacity data for molten *poly*(ethylene-2,6-naphthalene dicarboxylate)

Temp (K)	Heat capacity [J/(K mol)]
390.00 (T_g)	428.020
400.00	432.114
410.00	436.208
420.00	440.302
430.00	444.396
440.00	448.490
450.00	452.585
460.00	456.679
470.00	460.773
480.00	464.867
490.00	468.961
500.00	473.055
510.00	477.149
520.00	481.243
530.00	485.337
540.00	489.431
550.00	493.526
560.00	497.620
570.00	501.714
580.00	505.808
590.00	509.902
600.00	513.996

TABLE 49. Results of curve fitting the heat capacity data for *poly*(oxy-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenylene) as a function of crystallinity into the equation $C_p = w^C C_p{}^C + (1-w^C) C_p{}^a$

Temp (K)	Heat capacity [J/(K mol)]	
	crystalline	amorphous
340.00	350.550	360.191
350.00	360.000	370.382
360.00	370.000	380.085
370.00	378.880	390.298
380.00	387.000	400.000
390.00	394.440	409.000
400.00	403.500	418.000
410.00	413.330	429.500

TABLE 50. Recommended heat capacity data for *poly*(oxy-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenylene) below the glass transition

Temp (K)	Heat capacity [J/(K mol)]	
	Crystalline	Amorphous
130.00	152.016	152.016
140.00	161.309	161.309
150.00	171.008	171.008
160.00	181.161	181.161
170.00	191.808	191.808
180.00	202.990	202.990
190.00	212.743	212.743
200.00	223.213	223.213
210.00	234.007	234.007
220.00	244.811	244.811
230.00	255.627	255.627
240.00	266.453	266.453
250.00	272.332	272.703
260.00	281.122	282.461
270.00	289.912	292.219
273.15	292.681	295.293
280.00	298.703	301.978
290.00	307.493	311.736
298.15	314.658	319.689
300.00	316.284	321.494
310.00	325.074	331.253
320.00	333.865	341.011
330.00	342.655	350.769
340.00	351.446	360.528
350.00	360.236	370.286
360.00	369.027	380.044
370.00	377.817	389.803
380.00	386.608	399.561
390.00	395.398	409.319
400.00	404.189	419.078
410.00	412.979	428.836
419.00 (T_g)	NA	437.619

TABLE 51. Recommended heat capacity data for molten *poly*(oxy-1,4-phenylene-oxy-1,4-phenylene carbonyl-1,4-phenylene)

Temp (K)	Heat capacity [J/(K mol)]
419.00 (T_g)	515.765
420.00	516.260
430.00	521.215
440.00	526.170
450.00	531.125
460.00	536.080
470.00	541.035
480.00	545.990
490.00	550.945
500.00	555.900
510.00	560.855
520.00	565.810
530.00	570.765
540.00	575.720
550.00	580.675
560.00	585.630
570.00	590.585
580.00	595.540
590.00	600.495
600.00	605.450
610.00	610.405
620.00	615.360
630.00	620.315
640.00	625.270
650.00	630.225
660.00	635.180
670.00	640.135
680.00	645.090

TABLE 52. Recommended heat capacity data for amorphous *poly*(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene) the glass transition

Temp (K)	Heat capacity [J/(K mol)]
0.00	0.000
10.00	7.290
15.00	16.910
20.00	28.470
25.00	41.010
30.00	54.640
40.00	78.950
50.00	98.520
60.00	115.410
70.00	130.813
80.00	146.331
90.00	161.943
100.00	177.636
110.00	193.393
120.00	209.199
130.00	225.039
140.00	240.898
150.00	256.759
160.00	272.609
170.00	288.430
180.00	304.209
190.00	319.930
200.00	335.754
210.00	352.618
220.00	369.249
230.00	385.648
240.00	401.814
250.00	417.748
260.00	433.450
270.00	448.919
273.15	453.744
280.00	464.157
290.00	479.161
298.15	491.218
300.00	493.934
310.00	508.474
320.00	522.950
330.00	536.819
340.00	554.370
350.00	572.460
360.00	584.600
370.00	601.010
380.00	620.303
390.00	633.032
400.00	645.762
410.00	658.492
420.00	671.221
430.00	683.951
440.00	696.680
450.00	709.410
458.50 (T_g)	720.230

TABLE 53: Recommended heat capacity data for molten *poly*(oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene)

Temp (K)	Heat capacity [J/(K mol)]
458.50 (T_g)	822.712
460.00	824.065
470.00	833.082
480.00	842.098
490.00	851.115
500.00	860.132
510.00	869.149
520.00	878.166
530.00	887.182
540.00	896.199

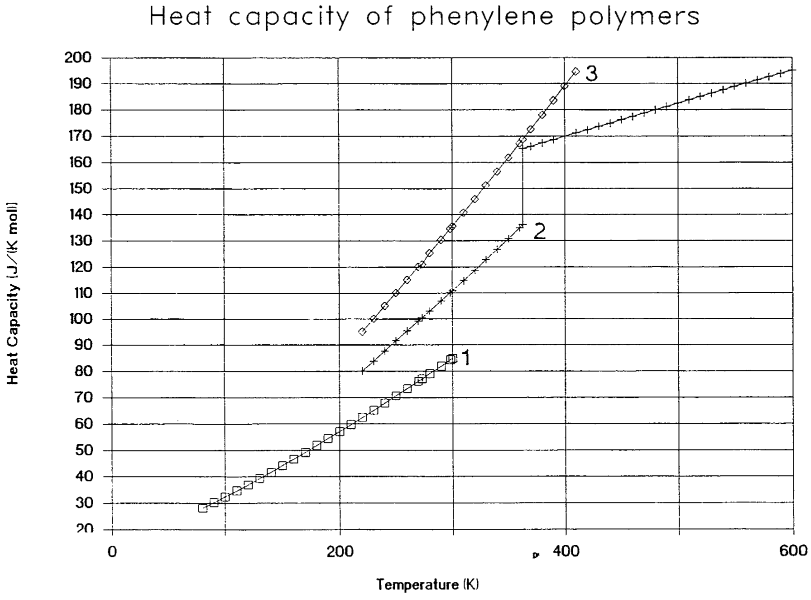

FIG. 8. Recommended heat capacities for several polymers: 1. *poly*(*p*-phenylene), 2. *poly*(thio-1,4-phenylene), and 3. *poly*(*p*-xylylene).

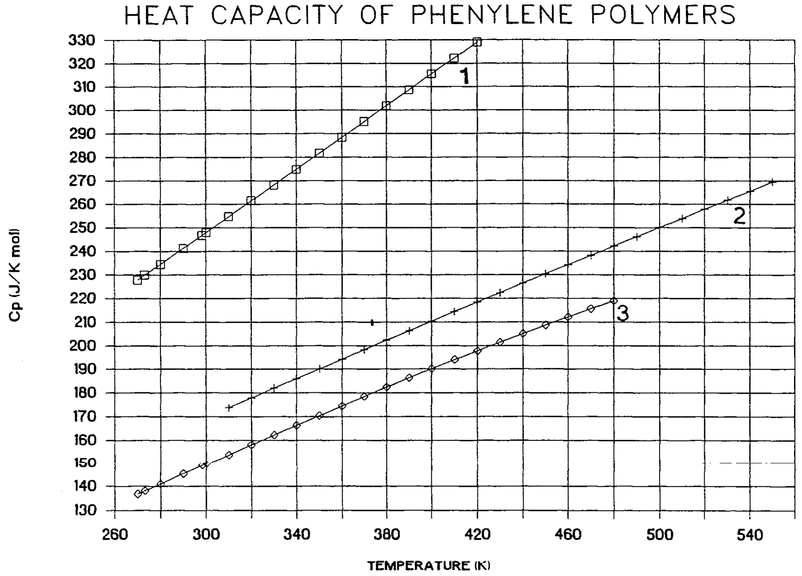

FIG. 9. Recommended heat capacities for several polymers:
1. poly[oxy-2,6-*bis*(1-methyl ethyl)-1,4-phenylene],
2. *poly*(oxy-3-bromo-2,6-dimethyl-1,4-phenylene), and 3. *poly* (oxy-2,6-dimethyl phenylene).

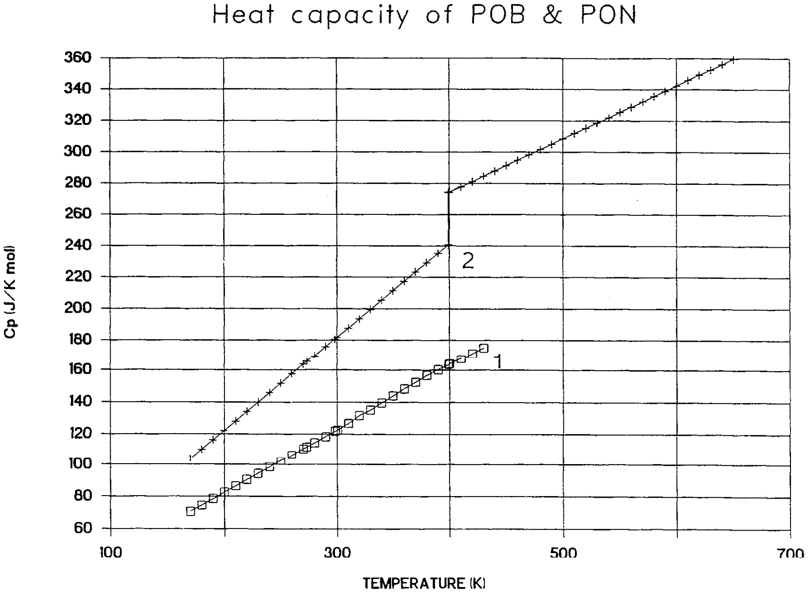

FIG. 10. Recommended heat capacities for two polymers below and above the glass transition:
1. *poly*(4-hydroxybenzoic acid), and 2. *poly*(2,6-hydroxynaphthoic acid).

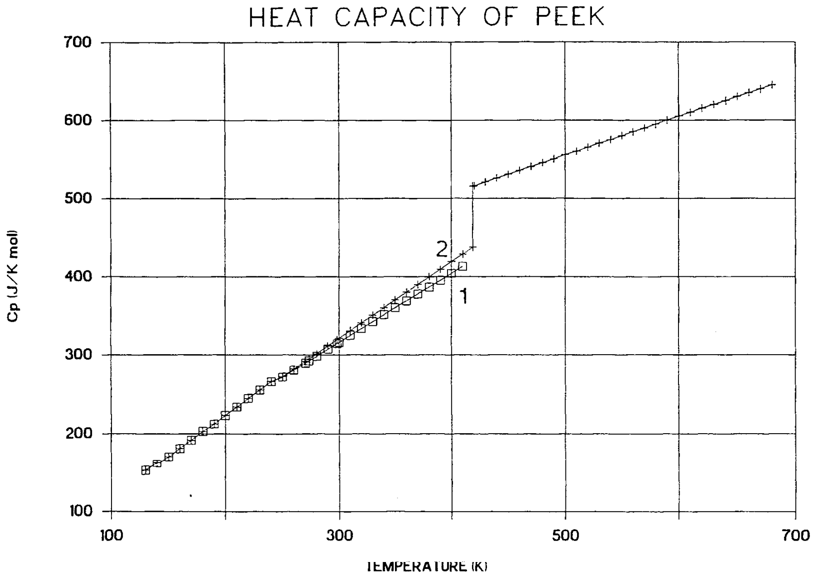

FIG. 11. Recommended heat capacities for 1. crystalline, and 2. amorphous *poly*(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene).

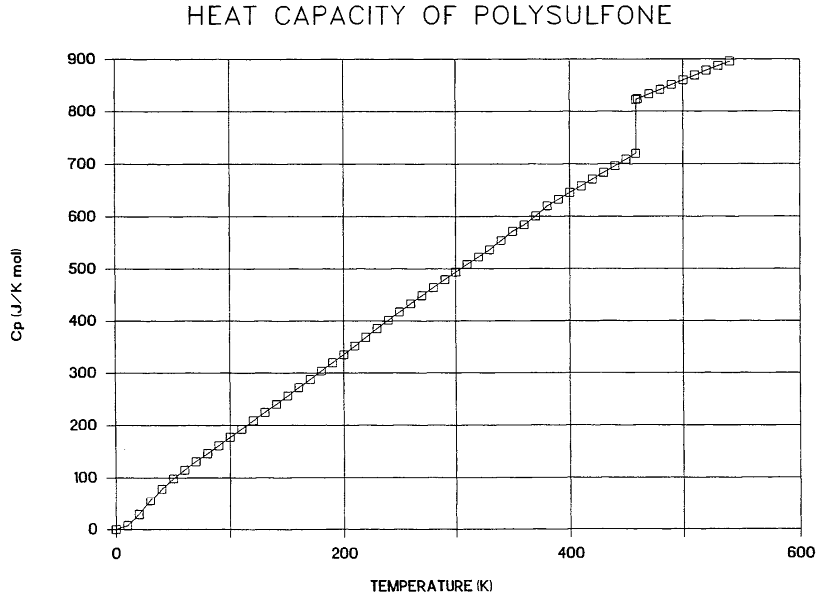

FIG. 12. Recommended heat capacities for amorphous poly[oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene].

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Appendix

ATHAS table of thermal properties of linear macromolecules[a]

Polymer	T_g(K)	ΔC_p[b]	T_m°(K)	ΔH_f[c]	*SHG*[d]	S_o[e]	Θ_1	Θ_3	N[f]	C_p[g]
Polyethylene										
(c)	–	–	414.6	4.11	×	0	519	158	2	0.1–410
(a)	237	10.5(1)	–	–	×	3.0	519	80	2	0.1–600
PE (CH_2-)										
Polypropylene										
(c)	–	–	460.7	8.70	×	0	714	91	7	10.0–460
(a)	270	19.2(2)*	–	–	×	5.2	633	78	7	10.0–600
PP (CH_2-CHCH_3-)										
poly(2-Methyl-1,3-pentadiene)										
(a)	278	34.3(?)	–	–	?	?	?	?	?	230–320
PMP ($CH_2-CCH_3=CH-CCH_3-$)										
poly(1-Butenylene),*cis*										
(c)	–	–	284.7	9.20	×	0	589	87	8	30–171**
(a)	171	27.2(3)*	–	–	×	18	589	?	8	171–350
PBUT *cis* ($CH=CH-CH_2-CH_2-$)										
poly(1-Butenylene),*trans*										
(c)	–	–	437	3.73[h]	×	0	599	95	8	30–180**
(a)	190	28.0(3)*	–	–	×	16	599	?	8	360–500
PBUT *trans* ($CH=CH-CH_2-CH_2-$)										
poly(Vinyl fluoride)										
(c)	–	–	503.2	7.54	×	0	440	105	4	80–314**
(a)	314	17.0(2)*	–	–	×	9.4	440	?	4	480–530i
PVF (CH_2-CHF-)										
poly(Vinylidene fluoride)										
(c)	–	–	483.2	6.70	×	0	346	66	4	5–212**
(a)	212	21.2(2)*	–	–	×	5.1	346	?	4	450–580i
PVF2 (CH_2-CF_2-)										
Polytrifluoroethylene										
(c)	–	–	495.2	5.44	×	0	315	56	4	25–280**
(a)	280	13.8(2)*	–	–	×	12.7	315	?	4	480–600i
PTRIF ($CHF-CF_2-$)										
Polytetrafluoroethylene										
(c)	–	–	605	4.10[j]	×	0	250	54	2	0.3–280
(a)	200	9.4(1)	–	–	×	3.3	250	?	2	180–700
PTFE (CF_2-CF_2-)										
Polyoxymethylene										
(c)	–	–	457.2	9.79	×	0	232	117	2	0.1–390
(a)	190	28.2(2)*	–	–	×	3.4	232	?	2	190–600
POM ($O-CH_2-$)										
Polyoxyethylene										
(c)	–	–	342	8.66	×	0	353	114	4	10–342
(a)	206	38.2(3)*	–	–	×	8.1	353	?	4	206–450
POE ($O-CH_2-CH_2-$)										
Polyglycolide										
(c)	–	–	506	11.1	×	0	521	98	6	10–318**
(a)	318	44.4(?)	–	–	×	7.3	521	?	6	318–550
PGL ($CH_2-CO-O-$)										
poly(β-Propiolactone)										
(c)	–	–	366	10.2	×	0	522	85	8	10–249**
(a)	249	50.4(?)	–	–	×	11	522	?	8	249–400
PPL [$(CH_2)_2-CO-O-$]										

ATHAS table of thermal properties of linear macromolecules[a] – Continued

Polymer	T_g(K)	ΔC_p[b]	T_m°(K)	ΔH_f[c]	SHG[d]	S_o[e]	Θ_1	Θ_3	N[f]	C_p[g]
poly(γ-Butyrolactone)										
(c)	–	–	337.5	13.2	×	0	474	96	10	10–214**
(a)	214	57.5(4)	–	–	×	18	474	?	10	214–350
PBL $[(\mathrm{CH}_2)_3-\mathrm{CO}-\mathrm{O}-]$										
poly(δ-Valerolactone)										
(c)	–	–	331	18.2	×	0	502	101	12	10–207**
(a)	207	65.1(5)	–	–	×	30	502	?	12	207–350
PVL $[(\mathrm{CH}_2)_4-\mathrm{CO}-\mathrm{O}-]$										
poly(ε-Caprolactone)										
(c)	–	–	342.2	19.0	×	0	491	101	14	10–209**
(a)										
PCL $[(\mathrm{CH}_2)_5-\mathrm{CO}-\mathrm{O}-]$										
Polyundecanolactone										
(c)	–	–	365	38.2	×	0	528	105	24	10–227**
(a)	227	110.6(11)	–	–	×	61	528	?	24	227–400
PUDL $[(\mathrm{CH}_2)_{10}-\mathrm{CO}-\mathrm{O}-]$										
Polytridecanolactone										
(c)	–	–	368	46.0	×	0	519	112	28	10–229**
(a)	229	146.0(13)	–	–	×	68	519	?	28	229–370
PTDL $[(\mathrm{CH}_2)_{12}-\mathrm{CO}-\mathrm{O}-]$										
Polypentadecanolactone										
(c)	–	–	370.5	56.0	×	0	525	114	32	10–251**
(a)	251	168.0(15)	–	–	×	93	525	?	32	251–380
PPDL $[(\mathrm{CH}_2)_{14}-\mathrm{CO}-\mathrm{O}-]$										
poly(Trimethylene adipate)										
(a)	?	?	–	–	?	?	?	?	?	310–360
PTMA $[\mathrm{O}-(\mathrm{CH}_2)_3-\mathrm{O}-\mathrm{CO}-(\mathrm{CH}_2)_4-\mathrm{CO}-]$										
poly(Butylene adipate)										
(c)	–	–	328.8	?	×	0	514	(108)	24	80–199**
(a)	199	140.0(?)	–	–	?	?	514	?	24	199–450
PBAD $[\mathrm{O}-(\mathrm{CH}_2)_4-\mathrm{O}-\mathrm{CO}-(\mathrm{CH}_2)_4-\mathrm{CO}-]$										
poly(Ethylene oxalate)										
(c)	–	–	450	23	?	0	533	?	12	?
(a)	306	56.2(?)	–	–	×	?	533	89	12	10–360
PEOL $[\mathrm{O}-(\mathrm{CH}_2)_2-\mathrm{O}-\mathrm{CO}-\mathrm{CO}-]$										
poly(Ethylene sebacate)										
(c)	–	–	356.2	31.9	×	0	514	(125)	28	120–245**
(a)	245	154.0(12)	–	–	×	(22)	514	(80)	28	245–410
PES $[\mathrm{O}-(\mathrm{CH}_2)_2-\mathrm{O}-\mathrm{CO}-(\mathrm{CH}_2)_8-\mathrm{CO}-]$										
poly(Hexamethylene sebacate)										
(a)	?	?	–	–	?	?	?	?	?	340–400
PHMS $[\mathrm{O}-(\mathrm{CH}_2)_6-\mathrm{O}-\mathrm{CO}-(\mathrm{CH}_2)_8-\mathrm{CO}-]$										
poly(Trimethylene succinate)										
(a)	?	?	–	–	?	?	?	?	?	310–360
PTMS $[\mathrm{O}-(\mathrm{CH}_2)_3-\mathrm{O}-\mathrm{CO}-(\mathrm{CH}_2)_2-\mathrm{CO}-]$										
Nylon 11										
(c)	–	–	493	44.7	×	0	420	(67)	24	230–321**
(a)	316	68.4(?)*	–	–	×	78	420	?	24	470–550
NYLON11 $[\mathrm{CH}_2)_{10}-\mathrm{CO}-\mathrm{NH}-]$										
Nylon 12										
(c)	–	–	500	48.4	×	0	455	(67)	26	230–310**
(a)	314	74.3(?)*	–	–	×	82	455	?	26	460–540
NYLON12 $[(\mathrm{CH}_2)_{11}-\mathrm{CO}-\mathrm{NH}-]$										

ATHAS table of thermal properties of linear macromolecules[a] – Continued

Polymer	T_g(K)	ΔC_p[b]	T_m°(K)	ΔH_f[c]	SHG[d]	S_o[e]	Θ_1	Θ_3	N[f]	C_p[g]
Nylon 6,9										
(c)	–	–	500	69	×	0	579	(84)	34	230–332**
(a)	331	109.5(?)*	–	–	×	114	579	?	34	500–590
NYLON6,9 $[NH-(CH_2)_6-NH-CO-(CH_2)_7-CO-]$										
Nylon 6,10										
(c)	–	–	506	71.7	×	0	543	(84)	36	230–322**
(a)	323	118(?)*	–	–	×	120	543	?	36	510–590
NYLON6,10 $[NH-(CH_2)_6-NH-CO-(CH_2)_8-CO-]$										
Nylon 6,12										
(c)	–	–	520	80.1	×	0	533	(84)	40	230–319**
(a)	319	141.4(?)*	–	–	×	124	533	?	40	319–600
NYLON6,12 $[NH-(CH_2)_6-NH-CO-(CH_2)_{10}-CO-]$										
poly(Diethyl siloxane)										
(c)	–	–	282.7	1.84[k]	×	0	480	87	14	10–135**
(a)	135	29.2(?)	–	–	×	8.4	480	?	14	135–360
PDES $[O-Si(CH_2CH_3)_2-]$										
Polystyrene[l]										
(c)	–	–	516.2	10.0	×	0	284	110	6	?
(a)	373	30.8(1+1)	–	–	×	4.4	284	48	6	0.1–600
PS $(CH_2-CHC_6H_5-)$										
poly-p-Fluorostyrene										
(a)	384	33.3(1+1)	–	–	×	?	284	(48)	6	130–384
PFS $[CH_2-CH(C_6H_4F)-]$										
poly-p-Chlorostyrene										
(a)	406	31.1(1+1)	–	–	×	?	284	(48)	6	300–550
PCS $[CH_2-CH(C_6H_4Cl)-]$										
poly-p-Bromostyrene										
(a)	410	31.9(1+1)	–	–	×	?	284	(48)	6	300–550
PBS $[CH_2-CH(C_6H_4Br)-]$										
poly-p-Iodostyrene										
(a)	424	37.9(1+1)	–	–	×	?	284	(48)	6	300–550
PIS $[CH_2-CH(C_6H_4I)-]$										
poly-p-Methylstyrene										
(a)	380	34.6(1+1)	–	–	×	?	284	(48)	6	300–550
PMS $[CH_2-CH(C_6H_4CH_3)-]$										
poly(*p*-Methacryloyloxybenzoic acid)										
(a)	316	60.0(?)	–	–	?	?	?	?	?	10–310
PMAOBZA $[CH_2-CCH_3CO(OC_6H_4COOH)-]$										
poly(Dimethyl itaconate)										
(a)	377	54.2(?)	–	–	?	?	557	(67)	20	110–450
PDMI $[CH_2-C(CH_2COOCH_3)(COOCH_3)-]$										
poly(*di-n*-Propyl itaconate)										
(a)	304	57.8(?)	–	–	?	?	428	(67)	28	110–410
PDPI $[CH_2-C(CH_2COOCH_2CH_2CH_3)(COOCH_2CH_2CH_3)-]$										
poly(*di-n*-Heptyl itaconate)										
(a)	172[m]	43.96(?)	–	–	?	?	582	(67)	44	110–170
PDHI $-CH_2-C[CH_2COO(CH_2)_6CH_3][COO(CH_2)_6CH_3]-$										
poly(*di-n*-Octyl itaconate)										
(a)	178[m]	95.76(?)	–	–	?	?	518	(67)	48	110–170
PDOI $-CH_2-C[CH_2COO(CH_2)_7CH_3][COO(CH_2)_7CH_3]-$										

ATHAS table of thermal properties of linear macromolecules[a] – Continued

Polymer	T_g(K)	ΔC_p[b]	T_m°(K)	ΔH_f[c]	*SHG*[d]	S_o[e]	Θ_1	Θ_3	N[f]	C_p[g]
poly(*di-n*-Nonyl itaconate)										
(a)	187[m]	177.6(?)	–	–	?	?	589	(67)	52	110–180
PDNI $-CH_2-C[CH_2COO(CH_2)_8CH_3][COO(CH_2)_8CH_3]-$										
poly(*di-n*-Decyl itaconate)										
(a)	?	?	–	–	?	?	585	(67)	56	110–200
PDDI $-CH_2-C[CH_2COO(CH_2)_9CH_3][COO(CH_2)_9CH_3]-$										
poly(Dicyclo octyl itaconate)										
(a)	390[m]	67.5(?)	–	–	?	?	?	?	?	110–440
PDCYOI $-CH_2-C[CH_2COO(CH_2)_8][COO(CH_2)_8]-$										
poly(Dicyclo decyl itaconate)										
(a)	?	?	–	–	?	?	?	?	?	110–280
PDCYDI $-CH_2-C[CH_2COO(CH_2)_{10}][COO(CH_2)_{10}]-$										
poly(Dicyclo dodecyl itaconate)										
(a)	?	?	–	–	?	?	?	?	?	100–280
PDCYDDI $-CH_2-C[CH_2COO(CH_2)_{20}][COO(CH_2)_{20}]-$										
poly(*p*-Phenylene)										
(c)	–	–	>1000	?	×	0	544	(54)	3	80–300**
(a)	?	?(0+1)	–	–	?	?	544	(40)	3	?
PPP (C_6H_4-)										
poly(Thio-1,4-phenylene)										
(c)	–	–	593	8.65	×	0	566	(54)	5	220–360**
(a)	363	29.2(0+1)	–	–	×	(4.2)$_5$66	(40)	5		360–600
PTP $(S-C_6H_4-)$										
poly(*p*-Xylylene)										
(c)	–	–	700	10.0[n]	×	0	562	(54)	7	220–410**
(a)	286	37.6(1+1)*	–	–	?	?	562	(40)	7	(286–410)
PPX $(CH_2-C_6H_4-CH_2)$										
poly(Oxy-2,6-dimethyl-1,4-phenylene)										
(c)	–	–	580	5.95	?	0	564	(54)	5	80–482**
(a)	482[o]	31.9(1+1)	–	–	×	(8)	564	(40)	5	482–570
PPO $[O-C_6H_2(CH_3)_2-]$										
poly(Oxy-3-*bromo*-2,6-dimethyl-1,4-phenylene)										
(a)	559 18(?)	–	–	?	?	?	?	?		310–559
PPBO $[O-C_6HBr(CH_3)_2-]$										
poly[oxy-2,6-*bis*(1-methylethyl)-1,4-phenylene]										
(c)	426	17.6(?)	? ?	?	–	?	?	?	?	270–426**
PPPRO $[O-C_6H_2(CH_2CH_2CH_3)_2-]$										
poly(Ethylene terephthalate)										
(c)	–	–	553	26.9	×	0	586	54	15	1.0–10
(a)	342	77.8(4+1)	–	–	×	22	586	44	15	1.0–590
PET $[O-(CH_2)_2-O-CO-C_6H_4-CO-]$										
poly(Butylene terephthalate)										
(c)	–	–	518.2	32.0	×	0	542	(54)	19	150–310**
(a)	248[p] 107(6+1)	–	–	×	(10)	542	(40)	19		248–570
PBT $[O-(CH_2)_4-O-CO-C_6H_4-CO-]$										
poly(4-Hydroxybenzoic acid)										
(c)	–	–	–	q	×	0	823	(54)	7	170–434**
(a)	434	34.0(1+1)	–	–	×	?	823	(25)	–	–
PHBA $(O-C_6H_4-CO-)$										
poly(2,6-Hydroxynaphthoic acid)										
(c)	–	–	–	r	×	0	640	(54)	9	170–399**
(a)	399	33.5(1+1)	–	–	×	?	640	(27) 9		399–650
PHNA $(O-C_{12}H_8-CO-)$										

ATHAS table of thermal properties of linear macromolecules[a] – Continued

Polymer	T_g(K)	ΔC_p[b]	T_m^o(K)	ΔH_f[c]	*SHG*[d]	S_o[e]	Θ_1	Θ_3	N[f]	C_p[g]
poly(Ethylene-2,6-naphthalene dicarboxylate										
(c)	–	–	610	25.0	×	0	600	(54)	17	220–390**
(a)	390	81.6(4+1)	–	–	×	(10)	600	(30)	17	390–600
PEN [O – $(CH_2)_2$ – O – CO – $C_{12}H_8$ – CO –]										
poly(4,4'-Isopropylidene diphenylenecarbonate)										
(c)	–	–	608.2	33.6	×	0	569	(54)	14	?
(a)	424	48.8(2+2)	–	–	×	(25)	569	40	14	0.4–750
PC [C_6H_4 – $C(CH_3)_2$ – C_6H_4 – O – CO – O –]										
poly(Oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)										
(c)	–	–	668.2	37.4	×	0	560	(54)	15	130–419**
(a)	419[s]	78.1(1+3)	–	–	×	(17)	560	(40)	15	419–680
PEEK [O – C_6H_4 – O – C_6H_4 – CO – C_6H_4 –]										
poly(Oxy-1,4-phenylene-sulfonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)--1,4-phenylene)										
(a)	459	102.5(?)	–	–	?	?	708	70	26	10–540
PBISP [O – C_6H_4 – SO_2 – C_6H_4 – O – C_6H_4 – $C(CH_3)_2$ – C_6H_4 –]										

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a. This table includes all the new and updated data collected and measured by Advanced Thermal Analysis Laboratory data bank as of August 31, 1989. The detailed table for all the available polymers in the literature is available with us. Please correspond with us about improvements, new data, errors, etc. In the table, 'a' represents amorphous, and 'c' represents 100% crystalline and '**' represents heat capacity of semicrystalline polymers. The abbreviations used for the polymer names are computer file names. The structure of the repeating unit enclosed within the parenthesis shows one single bond on the right side instead of two half bonds cut by a parenthesis as making this is not possible on our computer.

b. The change in the heat capacity in J/(K mol) at T_g is as available in the ATHAS recommended experimental data bank. '*' represents that the change in the heat capacity is derived from the difference in the experimental liquid C_p and C_p calculated using ATHAS computation scheme. The first number within parenthesis refers to "small" beads. Their heat capacity increase at the glass transition temperature is about 11.3 J/(K mol). The second number refers to "large" beads. Their heat capacity increase at the glass transition temperature is double or triple that of a "small" bead. The average per "small" bead or equivalent of the listed polymers is 11.5 +/– 1.7 J/(K mol).

c. The melting temperature is the "best available estimate" of the equilibrium melting temperature. Heat of fusion in the unit of kJ per mole of repeating units computed for 100% crystallinity.

d. Thermodynamic functions, such as enthalpy, entropy, and Gibbs free energy etc. × represents that the data on these thermodynamic functions is available based on the ATHAS "recommended data."

e. Residual entropy in amorphous state at absolute zero in units of J/(K mol).

f. The number of skeletal vibrational modes used in the Tarasov equation with the theta temperatures of the previous two columns. The value of theta temperature in parentheses is derived from the data on polymers having similar backbone structure. Group vibrations are usually tabulated in the given references.

g. Temperature range of recommended experimental heat capacity data. Computations of heat capacties of solids are usually carried out from 0.1 to 1000 K. For references see columns to the left.

h. PBUT trans has an additional condis state at lower temperature. Crystal/condis crystal transition is at 356 K, and heat of transition is 7.8 kJ/mol, see Refs.(31).

i. Between T_g and T_m melt C_p data is not extrapolated as liquid heat capacities of fluorinated polymers are non-linear. For details see Ref. (25).

j. PTFE has additional room-temperature crystal/crystal/condis crystal transitions at 292 K and 303 K, combined heat of fusion is 850 J/mol, see Ref.(32)

k. PDES has an additional condis state at a lower temperature. Crystal/condis crystal transition is at 206.7 K, and heat of transition is 2.72 kJ/mol. See Refs.(42).

l. For deuterated amorphous solid polystyrene and ring-only deuterated polystyrene heat capacities lead to Tarasov theta 3 and theta 1 temperatues of 55, 244 K and 49, 278 K, respectively. Thermodynamic functions S, H, and G are listed in Ref. (43).

m. The glass transition temperature listed has been assigned to the relaxation process of the *n*-alkyl/cycloalkyl side groups. T_g^U has been assigned to the backbone. For details see Ref.(44–47).

n. PPX has two lower first order transitions leading to condis crystals at 504 K and 560 K with heat of transtiton being 5.0 and 1.5 kJ/mol respectively, see Ref.(51).

o. Semicrystalline PPO shows the existence of a rigid-amorphous phase which governs the thermal properties from T_g to Tm. Fusion, superheating and annealing are directly linked to this. For details see Ref. (30).

p. The glass transition temperature of quenched PBT is 248 K and change in C_p at T_g is 107 J/(K mol). Semicrystalline PBT has a T_g between 310–325 K and change in C_p at 320 K is 77 J/(K mol), and shows the existence of rigid- amorphous fraction. For details see Ref. (38).

q. PHBA shows a disordering transition at 616.5 K and heat of transition is 3.8 kJ/mol. For details see Ref. (58).

r. PHNA shows a disordering transition at 614.5 K and heat of transition is 0.4 kJ/mol. For details see Ref. (58) .

s. Above T_g, poorly crystallized samples show a rigid-amorphous fraction that does not contribute to increase in heat capacity at T_g. For details see Ref. (62).