Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. VII. Other Carbon Backbone Polymers

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The heat capacity of poly-1-butene, poly-1-pentene, poly-1-hexene, polyisobutylene, poly(4-methyl-1-pentene), polybutadiene, *cis*-1, 4-poly(2-methylbutadiene), polycyclopentene, poly(vinyl fluoride), poly(vinylidene fluoride), polytrifluoroethylene, polytetrafluoroethylene, poly(vinyl chloride), poly(vinylidene chloride), polychlorotrifluoroethylene, poly(vinyl alcohol), poly(vinyl acetate), poly(α-methylstyrene), poly(o-methylstyrene), poly(o-chlorostyrene) and a series of poly(vinyl benzoate)s is reviewed on the basis of 62 measurements reported in the literature. A set of recommended data has been derived for each polymer. Entropy and enthalpy functions have been calculated for poly-1-hexene, polyisobutylene, *cis*-1, 4-poly(2-methylbutadiene), poly(vinyl chloride), and poly(α-methylstyrene). This paper is seventh in a series which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: enthalpy; entropy; fusion; glass transition; halogenated polymers; heat capacity; linear macromolecule; polyalkenes; polybenzoates; polystyrenes; vinyl polymers; vinylidene polymers.

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[a]See AIP document no. PAPS JPCRD-12-0029-32 for 32 pages of data tables. Order by PAPS number and journal reference from the American Institute of Physics Auxiliary Publication Service, 335 East 45th Street, New York, N.Y. 10017. The price is $1.50 for a microfiche or $5.00 for photocopies. Airmail is additional. This material also appears in *Current Physics Microform*, the monthly microfilm edition of the complete set of journals published by AIP on frames following the journal article.

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1. Introduction

This is the seventh paper in a series of discussions on the heat capacity of linear macromolecules. In the previous papers,[1-6] the heat capacity of selenium, polyethylene, polypropylene, polystyrene, and series of polyoxides and acrylic polymers were analyzed. In this paper all the remaining carbon backbone polymers on which heat capacity data are available are analyzed. These are poly-1-butene, poly-1-pentene, poly-1-hexene, polyisobutylene, poly(4-methyl-1-pentene), polybutadiene, *cis*-1, 4-poly(2 methylbutadiene), polycyclopentene, poly(vinyl fluoride), poly(vinylidene fluoride), polytrifluoroethylene, polytetrafluoroethylene, poly(vinyl chloride), poly(vinylidene chloride), polychlorotrifluoroethylene, poly(vinyl alcohol), poly(vinyl acetate), poly(α-methylstyrene), poly(o-methylstyrene), poly(o-chlorostyrene), and a series of poly(vinyl benzoate)s. In the subsequent publications, the analysis of the heat capacity of polyamides, polyesters, and linear macromolecules with hetero atoms and aromatic groups in their main and side chains will be reported.

2. Heat Capacity of Other Carbon Backbone Polymers

2.1. Introduction

Heat capacity analyses of carbon backbone polymers with large numbers of measurements available in the literature have been reported earlier. These include polyethylene,[2] polypropylene,[3] polystyrene,[5] and acrylic polymers.[6] All other carbon backbone polymers with fewer data sets available are analyzed in this paper. The repeating unit, formula weight, crystal structure, density, melting temperature, heat of fusion, and glass transition temperature of these polymers are listed in Table 1.[7,8]

Table 1. Crystal structures and thermal properties of various vinyl polymers

Vinyl polymer (formula wt.) Structure of repeat unit.	Crystal syst. Space group Mol. helix	Unit cell axes and angles (nm,deg.)	No. of units	ρ_c (Mg m^{-3})	Cryst. packing density	T_m (K)	ΔH_f (kJ mol^{-1})	ρ_a (Mg m^{-3})	Amorph. packing density	T_g (K)
Poly-1-butene I (56.10) CH_2-CHC_2H_5-	TRIG $R\bar{3}c$ 2*3/1	1.77 1.77 0.65	18	0.951	0.66	411	7.01	0.859	0.60	249
Poly-1-butene II (56.10) CH_2-CHC_2H_5-	TETR $P\bar{4}$ 2*11/3	1.485 1.485	44	0.902	0.63	403		0.859	0.60	249
Poly-1-butene III (56.10) CH_2-CHC_2H_5-	ORTH	1.249 0.896	8			379		0.859	0.60	249
Poly-1-pentene (70.13) CH_2-CHC_3H_7-	MONO 2*3/1	1.135 2.085 0.649 β=99.6	12	0.923	0.65	403	6.31	0.850	0.60	233
Poly-1-hexene (84.16) CH_2-CHC_4H_9-	MONO 2*7/2	2.22 0.889 1.37 γ=94.5	14	0.726						233
Poly(4-methyl-1-pentene) (86.16) CH_2-$CH[CH_2$-$CH(-CH_3)_2]$-	TETR $P\bar{4}$ 2*7/2	1.854 1.384	28	0.822	0.57	523	9.93	0.838	0.58	302
Polyisobutylene (56.10) CH_2-$C(CH_3)_2$-	ORTH $P2_12_12_1$ 2*8/3	0.694 1.196 1.863	16	0.964	0.67	317	12.0	0.915	0.63	200
1,4-Polybutadiene, cis (54.09) CH_2-CH=CH-CH_2-	MONO C2/c 8*1/1	0.460 0.950 0.860 β=109	4	1.011	0.68	284.6	9.20	0.902	0.61	171
1,4-Polybutadiene, trans (54.09) CH_2-CH=CH-CH_2-	MONO $P2_1/a$ 4*1/1	0.863 0.911 0.843 β=114	4	1.036	0.69	415	3.61	-	-	215
1.4-Poly(2-methyl-butadiene), cis (68.12) CH_2-CCH_3=CH-CH_2-	ORTH Pbac 8*1/1	1.246 0.886 0.81	8	1.009	0.68	301	4.36	0.910	0.61	200
1,4-Poly(2-methyl-butadiene), trans β (68.12) CH_2-CCH_3=CH-CH_2-	ORTH $P2_12_12_1$ 4*1/1	0.783 1.187 0.479	4	1.025	0.69	355.4	10.55	0.905	0.61	215

Table 1. Crystal structures and thermal properties of various vinyl polymers--Continued

Vinyl polymer (formula wt.) structure of repeat unit.	Crystal syst. Space group Mol. helix	Unit cell axes and angles (nm, deg.)	No. of units	ρ_c ($Mg\ m^{-3}$)	Crystal packing density	T_m (K)	ΔH_f ($kJ\ mol^{-1}$)	ρ_a ($Mg\ m^{-3}$)	Amorph. packing density	Tg (K)
Polycyclo-pentene, trans (68.12) $CH=CH-(CH_2-)_3$	ORTH Pnam 5*2/1	0.728 0.497 1.190	4	1.051	0.71					159(cis) 183(trans)
Poly(vinyl fluoride) (46.04) CH_2-CHF-	ORTH Cm2m 2*1/1	0.857 0.495 0.252	2	1.430	0.72	503	7.54			314
Poly(vinyl-idene fluoride) (64.04) CH_2-CF_2-	ORTH Cm2m 2*1/1	0.847 0.490 0.256	2	2.002	0.84	483	6.69	1.672	0.70	233
Polytri-fluoro-ethylene (82.02) $CHF-CF_2-$	TRIG	0.559 0.250	1	2.013						304
Polytetra-fluoro-ethylene I (100.02) CF_2-CF_2-	TRIC P1 1*13/6	0.559 0.559 1.688 90 90 119.3	13	2.347	0.80	600	3.42			
Polytetra-fluoro-ethylene II (100.02) CF_2-CF_2-	TRIG ($P3_1$ or $P3_2$) 1*15/7	0.566 0.566 1.950	15	2.302	0.78			2.000	0.68	
Poly(vinyl chloride) (62.50) $CH_2-CHCl-$	ORTH Pbcm 4*1/1	1.040 0.530 0.510	4	1.477	0.68	546	11.0	1.41	0.65	354
Poly(vinyl-idene chloride) (96.95) CH_2-CCl_2-	MONO $P2_1$ 4*1/1	0.673 0.468 1.254 β=123.6	4	1.957	0.76	465		1.66	0.64	255
Polychloro-trifluoro-ethylene-(116.47) $CF_2-CFCl-$	TRIG	0.654 3.5	14	2.222	0.58	495	5.02	2.08	0.54	325
Poly(vinyl alcohol) (44.05) $CH_2-CHOH-$	MONO $P2_1/m$ 2*1/1	0.781 0.251 0.551 β=91.7	2	1.350	0.77	505	6.87	1.291	0.74	358
Poly(vinyl acetate) (86.08) $CH_2-CH(OOCCH_3)-$										305
Poly-α-methyl-styrene (118.17) $CH_2-C(CH_3)-(C_6H_5)-$	TRIG									441

Table 1. Crystal structures and thermal properties of various vinyl polymers--Continued

Vinyl polymer (formula wt.) structure of repeat unit.	Crystal syst. Space group Mol. helix	Unit cell axes and angles (nm, deg.)	No. of units	ρ_c (Mg m^{-3})	Crystal packing density	T_m (K)	ΔH_f (kJ mol^{-1})	ρ_c (M m^{-3})	Amorph. packing density	T_g (K)
Poly-o-methyl-styrene (118.17) CH_2-$CH(C_6H_4CH_3)$-	TETR I4$_1$cd 2*4/1	1.901 0.819	16	1.072	0.65					409
Poly-o-chloro-styrene (138.60) CH_2-$CH(C_6H_4Cl)$-										392
Poly(vinyl benzoate) (148.15) CH_2-$CH(OOC_6H_5)$-										347
Poly(vinyl-p-ethylbenzoate) (176.21) CH_2-$CH(OOCC_6H_4C_2H_5)$-										330
Poly(vinyl-p-isopropyl-benzoate) (190.23) CH_2-$CH(OOCC_6H_4C_3H_7)$-										335
Poly(vinyl-p-tert-butyl-benzoate) (204.26) CH_2-$CH(OOCC_6H_4C_4H_9)$						600				394

2.2. Recommended Heat Capacity Data and Thermodynamic Functions

2.2.1. Poly-1-butene

Three investigations[9,10,11] have been reported in the literature on the heat capacity measurements of poly-1-butene. All the measurements meet our standards of acceptable data (discussed in Ref. 1). Details of these investigations are given in Table 2. Heat capacities of four semicrystalline samples of various crystal forms and a molten sample have been measured from 22 to 630 K.

The data on these samples are given in Tables A1 to A3. Tables A1 to A3 have been deposited with the Physics Auxiliary Publication Service of the American Institute of Phy-

Table 2. Heat capacity measurements of poly-1-butene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Dainton et al. (1962) [9]	9. Isotactic[a] w^c = 0.44	22-310	Adiabatic (1%)	Table
Wilski and Grewer (1964) [10]	10. Isotactic[b] ρ = 0.94 Mg m^{-3}	260-430	Adiabatic (unreported)	Graph
	11. Atactic[c] ΔH_f = 0.85 kJ mol^{-1} ρ = 0.8795 Mg m^{-3} w^c = 0.13	250-420	Adiabatic (Unreported)	Graph
	12. Isotactic[d] ΔH_f = 5.33 kJ mol^{-1} ρ = 0.9294 Mg m^{-3} w^c = 0.76	250-380	Adiabatic (Unreported)	Graph
Bares and Wunderlich (1973) [11]	13. Molten[e], isotactic	410-630	DSC (1%)	Table

[a]The powder used was 44% crystalline (X-rays) and contained 37% trigonal and 7% tetragonal crystals and was probably still converting slowly during the measurements, although no evidence for this was found from the heat capacity measurements.

[b]X-ray analysis shows that the crystalline fraction (w^c unknown) consists of approximately equal parts of trigonal and orthorhombic crystals.

[c]Predominantly atactic sample containing small crystalline (trigonal) portion.

[d]Exclusively trigonal crystals.

[e]Originally tetragonal crystals.

Table 3. Recommended heat capacity data for semicrystalline (w^c = 0.44) poly-1-butene below the glass transition.[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
0.0	0.0
10.0	0.9595
20.0	5.415
30.0	10.20
40.0	14.86
50.0	19.26
60.0	23.27
70.0	27.01
80.0	30.69
90.0	34.30
100.0	37.78
110.0	41.16
120.0	44.35
130.0	47.47
140.0	50.48
150.0	53.38
160.0	56.22
170.0	59.08
180.0	62.06
190.0	65.14
200.0	68.40
210.0	71.88
220.0	75.05
230.0	78.32
240.0	81.59
249.0(T_g)	84.54

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

Table 4. Recommended heat capacity data for molten poly-1-butene[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
249.0(T_g)	107.6
250.0	107.8
260.0	109.7
270.0	111.5
273.15	112.1
280.0	113.3
290.0	115.2
298.15	116.7
300.0	117.0
310.0	118.9
320.0	120.7
330.0	122.6
340.0	124.4
350.0	126.2
360.0	128.1
370.0	129.9
380.0	131.8
390.0	133.6
400.0	135.5
410.0	137.3
411.0(T_m)	137.5
420.0	139.1
430.0	141.0
440.0	142.8
450.0	144.7
460.0	146.5
470.0	148.4
480.0	150.2
490.0	152.0
500.0	153.9
510.0	155.7
520.0	157.6
530.0	159.4
540.0	161.3
550.0	163.1
560.0	164.9
570.0	166.8
580.0	168.6
590.0	170.5
600.0	172.3
610.0	174.2
620.0	176.0
630.0	177.9

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

sics. Since the heat capacity data reported are for various crystal types and the data on these semicrystalline samples overlap over a very limited temperature range (250 to 330 K), the calculation of the heat capacity of crystalline and amorphous poly-1-butene from the crystallinity extrapolations using the two phase model was not attempted. Recommended data for the heat capacity of semicrystalline poly-1-butene (w^c = 0.44) from 0 K to the glass transition temperature (249 K) and of molten poly-1-butene from 249 to 630 K only have been derived.

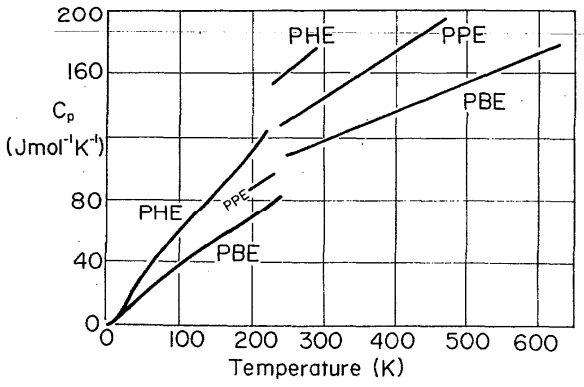

FIG. 1. Recommended heat capacity data for poly-1-butene (PBE), poly-1-pentene (PPE), and poly-1-hexene (PHE).

The heat capacity data on sample 9 are taken as the recommended data from 0 to 210 K. The heat capacity val-

ues from 220 to 240 K are somewhat higher, because they are associated with the beginning of the glass transition. The recommended data from 220 to the glass transition temperature 249 K were determined by linearly extrapolating the data below 220 K. The heat capacity values from 180 to 210 K were curve fitted into the equation

$$C_p = 0.3272\,T + 3.066 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (1)$$

The rms deviation was 0.1%. The recommended values for the heat capacities of poly-1-butene below the glass transition are listed in Table 3 and plotted in Fig. 1.

The recommended data on heat capacity of molten poly-1-butene were determined by curve fitting the data on samples 10, 11, and 13 from 390 to 630 K into the equation

$$C_p = 0.1843\,T + 61.73 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (2)$$

The rms deviation was 0.7%. Equation (2) was used to calculate the heat capacity of molten poly-1-butene from 249 to 630 K. These values are listed in Table 4 and plotted in Fig. 1.

2.2.2. Poly-1-pentene

Only one investigation[12] has been reported in the literature which deals with the heat capacity of poly-1-pentene. The investigation meets our standards of acceptable data (discussed in Ref. 1). Details of this investigation are given in Table 5. Heat capacities of an amorphous atactic and two semicrystalline isotactic samples have been reported from 200 to 460 K. The data on these samples are given in Tables A4 to A6. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Below the glass transition temperature, the heat capacity of amorphous atactic and semicrystalline isotactic samples are in fair agreement. Thus the heat capacity just below the glass transition temperature is largely independent of crystallinity. To derive the recommended data from 200 K to the glass transition temperature (233 K), the data on all the three samples were curve fitted into the equation

$$C_p = 0.296 + 28.7 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (3)$$

The rms deviation was 2.1%. Heat capacity values from 200 to 233 K calculated from Eq. (3) are listed in Table 6 and plotted in Fig. 1.

The recommended data on heat capacity of molten poly-1-pentene were determined by curve fitting the data on the atactic sample above T_g and the isotactic samples above T_m (Table A6) into the equation

$$C_p = 0.294\,T + 56.14 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (4)$$

The rms deviation was 0.7%. Equation (4) was used to calculate the heat capacity of molten poly-1-pentene from 233 to 479 K. These values are listed in Table 7 and plotted in Fig. 1.

Table 5. Heat capacity measurements of poly-1-pentene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Gianotti and Capizzi (1968) [12]	14. Atactic $\bar{M}_w$ = 490,000 w^c = 0	200-410	DSC (1%)	Table[a]
	15. Isotactic (Form I) w^c = 0.42[b]	200-470	DSC (1%)	Table[a]
	16. Isotactic (Form II) w^c = 0.54[b]	210-460	DSC (1%)	Table[a]

[a]Data were interpolated using spline function technique to give heat capacities at every ten degree interval.

[b]Crystallinity estimated from ΔCp at the glass transition.

Table 6. Recommended heat capacity data for poly-1-pentene below the glass transition

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
200.0	87.90
210.0	90.86
220.0	93.82
230.0	96.78
233.0(T_g)	97.67

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

Table 7. Recommended heat capacity data for molten poly-1-pentene.

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
233.0(T_g)	124.7
240.0	126.7
250.0	129.7
260.0	132.6
270.0	135.5
273.15	136.5
280.0	138.5
290.0	141.4
298.15	143.8
300.0	144.4
310.0	147.3
320.0	150.2
330.0	153.2
340.0	156.1
350.0	159.1
360.0	162.0
370.0	165.0
380.0	167.9
390.0	170.8
400.0	173.8
403.0(T_m)	174.7
410.0	176.7
420.0	179.7
430.0	182.6
440.0	185.5
450.0	188.5
460.0	191.4
470.0	194.4

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

2.2.3. Poly-1-hexene

Only one investigation[13,14] has been reported in the literature which deals with the heat capacity of poly-1-hexene. The investigation meets our standards of acceptable data (discussed in Ref. 1). Details of this investigation are given in Table 8. The heat capacity of a quenched, amorphous sample has been measured from 20 to 290 K. The sample was then cooled slowly at 0.15 K h^{-1} and the heat capacity was remeasured from 35 to 250 K. An anomalous behavior just outside the error limits was observed at 80 K. The data on both the samples are given in Table A7. Table A7 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. Heat capacity data on the quenched and slowly cooled samples agree within 0.3%, except in the temperature range from 60 to 100 K.

The heat capacity data on sample 1 are taken as the recommended data from 0 to 190 K. The heat capacity values at 200 to 210 K are somewhat higher, because they are associated with the beginning of the glass transition. The data from 200 to 223 K(T_g) were determined by linearly extrapolating the data below 200 K. The heat capacity values from 170 to 190 K were curve fitted into the equation

$$C_p = 0.5645\ T - 0.8067\ \text{J mol}^{-1}\ \text{K}^{-1}. \quad (5)$$

The rms deviation was 0.1%. The recommended data on the heat capacity of amorphous poly-1-hexene are listed in Table 9 and plotted in Fig. 1.

The recommended data on the heat capacity of molten poly-1-hexene were determined by curve fitting the data on both quenched and slowly cooled samples above the glass transition into the equation

$$C_p = 0.3701\ T + 67.65\ \text{J mol}^{-1}\ \text{K}^{-1}. \quad (6)$$

The rms deviation was 0.6%. Equation (6) was used to calculate the heat capacity of molten poly-1-hexene from 223 to 290 K. These values are listed in Table 9 and plotted in Fig. 1.

Table 8. Heat capacity measurements of poly-1-hexene

Investigator	Sample no. characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Bourdariat et al. (1973) [13, 14]	1. $\bar{M}_n$ = 350,000 $\bar{M}_w$ = 1,050,000 Cooled at 250 K h^{-1} ρ = 0.8540 $Mg\ m^{-3}$ w^c = 0 (X-Ray)	20-290	Adiabatic (0.4%)	Table
	2. Sample 1 cooled at 0.15 K h^{-1}	320-250	Adiabatic (0.4%)	Table

Table 9. Recommended thermodynamic data for amorphous poly-1-hexene[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a - H_0^a$ (J mol^{-1})	$S_T^a - S_0^a$ (J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
20.0	9.091	90.91	4.55
25.0	12.35	144.5	6.92
30.0	16.42	216.4	9.52
40.0	24.00	418.5	15.26
50.0	30.16	689.3	21.27
60.0	36.71	1023	27.35
70.0	42.67	1420	33.46
80.0	48.33	1875	39.52
90.0	53.74	2385	45.53
100.0	59.08	2950	51.47
110.0	64.30	3566	57.35
120.0	69.61	4236	63.17
130.0	74.68	4957	68.94
140.0	79.88	5730	74.67
150.0	84.96	6554	80.35
160.0	89.69	7428	85.99
170.0	95.11	8352	91.59
180.0	100.9	9332	97.19
190.0	106.4	10368	102.8
200.0	112.1	11460	108.4
210.0	117.7	12609	114.0
220.0	123.4	13815	119.6
223.0(T_g)	125.1	14188	121.3
223.0(T_g)	150.2	14188	121.3
230.0	152.8	15248	126.0
240.0	156.5	16794	132.6
250.0	160.2	18378	139.0
260.0	163.9	19998	145.4
270.0	167.6	21655	151.6
273.15	168.7	22185	153.6
280.0	171.3	23349	157.8
290.0	175.0	25081	163.9

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

Enthalpy and entropy of amorphous poly-1-hexene were calculated from 0 to 300 K by numerically integrating the heat capacity data. These thermodynamics functions are listed in Table 9.

2.2.4. Polyisobutylene

Two investigations[15,16] have been reported in the literature on the heat capacity measurements of polyisobutylene. Both the measurements meet our standards of acceptable data (discussed in Ref. 1). Details of these investigations are given in Table 10. The heat capacity data for atactic, amorphous samples have been reported from 14 to 380 K. The data on these samples are given in Table A8. Table A8 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. Heat capacity data associated with somewhat larger error limits have also been reported by Egorov and Kilesso[18] on an uncharacterized sample.

More recent heat capacity data on a sample of higher molecular weight (sample 32) are taken as recommended data from 15 to 180 K. The heat capacity values from 190 to 200 K are somewhat higher, because they are associated with the beginning of the glass transition. The recommended data from 190 to 200 K were determined by linearly extrapolating the data below the glass transition. The recommended data from 160 to 180 K were curve fitted into the equation

$$C_p = 0.3125\,T + 1.842 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (7)$$

The rms deviation was 0.1%. The recommended values for the heat capacity of glassy, amorphous polyisobutylene are listed in Table 11 and plotted in Fig. 2.

The recommended data on the heat capacity of molten polyisobutylene were determined by curve fitting the data on sample 32 from 210 to 380 K into the equation

$$C_p = 0.2446\,T + 36.71 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (8)$$

The rms deviation is below 0.3%. Equation (8) was used to evaluate the heat capacity of molten polyisobutylene from 200 to 380 K. These values are listed in Table 11 and plotted in Fig. 2.

Table 10. Heat capacity measurements of polyisobutylene

Investigator	Sample No. characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Ferry and Park (1936) [15]	31. Atactic $\bar{M}_n$ = 4,900 ρ = 0.9074 mg m^{-3}	120-290	Aneroid (Unreported)	Table
Furukawa and Reilly (1956) [16]	32. Atactic; Vistanex B-100 (Esso Standard Oil) $\bar{M}_v$ = 1,350,000 $\bar{M}_v$ = 1,560,000	14-380	Adiabatic (Unreported)	Table

Table 11. Recommended thermodynamic data for polyisobutylene[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a - H_0^a$ (J mol^{-1})	$S_T^a - S_0^a$ (J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
15.0	3.008	22.56	1.504
20.0	4.663	41.74	2.588
25.0	6.301	69.15	3.801
30.0	7.839	104.5	5.085
40.0	10.76	197.5	7.74
50.0	13.69	319.7	10.45
60.0	16.78	472.1	13.22
70.0	20.10	656.5	16.05
80.0	23.65	875.2	18.97
90.0	27.34	1130	21.96
100.0	30.97	1421	25.03
110.0	34.58	1749	28.15
120.0	38.15	2113	31.31
130.0	41.72	2518	34.56
140.0	45.20	2953	37.78
150.0	48.59	3422	41.01
160.0	51.82	3924	44.25
170.0	55.01	4458	47.49
180.0	58.07	5023	50.72
190.0	61.22	5620	53.94
200.0(T_g)	63.34	6247	57.16
200.0(T_g)	85.63	6247	57.16
210.0	88.07	7116	61.40
220.0	90.52	8009	65.55
230.0	92.97	8926	69.63
240.0	95.41	9868	73.64
250.0	97.86	10835	77.58
260.0	100.3	11825	81.47
270.0	102.7	12840	85.30
273.15	103.5	13164	86.50
280.0	105.2	13880	89.08
290.0	107.6	14944	92.82
298.15	109.6	15828	95.83
300.0	110.1	16032	96.51
310.0	112.5	17145	100.2
320.0	115.0	18283	103.8
330.0	117.4	19445	107.3
340.0	119.9	20631	110.9
350.0	122.3	21842	114.4
360.0	124.8	23078	117.9
370.0	127.2	24338	121.3
380.0	129.7	25622	124.7

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

Enthalpy and entropy of amorphous polyisobutylene were calculated from 0 to 380 K by numerically integrating the heat capacity data. These thermodynamic functions are listed in Table 11.

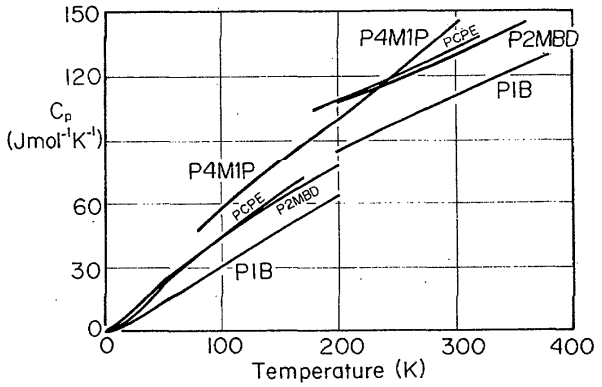

FIG. 2. Recommended heat capacity data for polyisobutylene (PIB), poly(4-methyl-1-pentene) (P4M1P), *cis*-1, 4-poly(2-methylbutadiene) (P2MBD), and polycyclopentene (PCPE).

2.2.5. Poly(4-methyl-1-pentene)

Two investigations[19,20] have been reported in the literature on the heat capacity measurements on poly(4-methyl-1-pentene). Both the investigations meet our standards of acceptable data (discussed in Ref. 1). Details of these investigations are given in Table 12. Heat capacities of four samples of crystallinity from 0.28 to 0.65 have been measured over a temperature range of 85 to 540 K. The data on these samples are given in Tables A9 to A11. Tables A9 to A11 have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Below the glass transition temperature, the heat capacity has very limited dependence on the crystallinity. The recommended data on the heat capacity of poly(4-methyl-1-pentene) below the glass transition were determined by curve fitting the data on samples 5, 6, 7, and 8 from 80 to 290 K into the equation

$$C_p = \exp[0.158247(\ln T)^3 - 2.35568(\ln T)^2 + 12.468(\ln T) - 18.862] \text{ J mol}^{-1}\text{ K}^{-1}. \quad (9)$$

The rms deviation was 0.5%. Equation (9) was used to calculate the recommended values from 80 to 303 K. These data are listed in Table 13 and plotted in Fig. 2.

Above the glass transition the heat capacity data (Table A10) are available for samples of very similar crystallinity only. The data are in quite good agreement, but cannot be extrapolated with respect to crystallinity to determine the heat capacity of completely crystalline and amorphous poly(4-methyl-1-pentene)s.

The heat capacity data for molten poly(4-methyl-1-pentene) (Table A11) are available over a very limited temperature range (520 to 540 K). Since the heat capacity–temperature slope is not well established, it would not be very accurate to extrapolate the molten heat capacity values down to the glass transition temperature.

Table 12. Heat capacity measurements of poly(4-methyl-1-pentene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Karasz et al. (1967) [19]	5. Powder (P4MP; Union Carbide) $\bar{M}_v$ = 140,000 ρ = 0.8325 Mg m^{-3}	80-420	Adiabatic (0.4%)	Table[a]
	6. Sample 5 cooled from 423 K at 10K h^{-1} ΔH_f = 3.01 kJ mol^{-1} w^c = 0.29	270-540	Adiabatic (0.4%)	270-420 K:Table[a] 520-540 K: Equation[b]
	7. Sample 5 cooled from 538 K at 10 K h^{-1} ΔH_f = 2.89 kJ mol^{-1} w^c = 0.28	100-540	Adiabatic (0.4%)	100-480 K:Table[a] 520-540: Equation[b]
Melia and Tyson (1967) [20]	8. Commercial Research Sample (I.C.I.) ρ = 0.83 Mg m^{-3} w = 0.65 (x rays)	80-310	Adiabatic (Unreported)	Table

[a]Data were interpolated using the spline function technique to give heat capacities at every ten degree intervals.

[b]Data above the melting transition on samples 6 and 7 were curve fitted into the equation C_p = 0.3368 T + 74.51 J mol^{-1}K^{-1} (RMS dev. = 0.2%). This equation was used to calculate the heat capacity of molten poly(4-methyl-1-pentene) listed in table All.

Table 13. Recommended heat capacity data for poly(4-methyl-1-pentene) below the glass transition[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
80.0	47.21
90.0	52.54
100.0	57.52
110.0	62.22
120.0	66.72
130.0	71.06
140.0	75.29
150.0	79.45
160.0	83.57
170.0	87.66
180.0	91.75
190.0	95.87
200.0	100.0
210.0	104.2
220.0	108.4
230.0	112.8
240.0	117.1
250.0	121.6
260.0	126.2
270.0	130.8
273.15	132.3
280.0	135.6
290.0	140.4
298.15	144.5
300.0	145.4
303.0(T_g)	147.0

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

Table 14. Heat capacity measurements of 1,4-polybutadiene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Dainton et al. (1962) [9]	45. trans-1,4-polybutadiene 96.2% pure 3.8% 1,2 addition	22-340	Adiabatic (1%)	Table
	46. cis-1,4-polybutadiene 94% pure 3% trans isomer 3% 1,2 addition	22-310	Adiabatic (1%)	Table

Table 15. Heat capacity of two 1,4-polybutadienes[d] in J $mol^{-1}K^{-1}$

	45	46
10	(0.8005)[a]	(1.179)[b]
20	(4.819)	(6.523)
30	9.704	11.79
40	14.39	16.15
50	18.74	19.98
60	22.56	23.18
70	25.89	26.16
80	29.00	29.07
90	32.02	31.87
100	34.98	34.63
110	37.86	37.34
120	40.70	40.05
130	43.55	42.82
140	46.26	45.62
150	48.99	48.50
160	51.71	53.93
		glass transition
170	54.52	69.72
180	57.88	73.78
	glass transition	
190		75.83
200	68.80	79.62
210	74.21	
220	78.76	
230	83.46	
240	88.60	
250	94.39	
260	100.6	melting
270	107.2	95.79
280	114.3	97.52
290	121.9	99.09
300	133.0	100.6
310	182.3[c]	101.8
320	124.1	
330	135.5	
340	147.5	

[a]Heat capacities above 22 K were fitted into the Debye function $C_p = 18.79\ D(\frac{122}{T})$ to obtain data at 10 and 20 K.

[b]Heat capacities above 22 K were fitted into the Debye function $C_p = 21.53\ D(\frac{112}{T})$ to obtain data at 10 and 20 K.

[c]Planar zig-zag chain conformation to helical conformational transition.

[d]Sample numbers correspond to the samples described in table 14.

2.2.6. 1,4-Polybutadiene

1,4-polybutadiene has several stereochemical modifications. Heat capacity measurements have been made for the two geometrical isomers *cis*-1,4-polybutadiene and *trans*-1, 4-polybutadiene by Dainton *et al.*[9] The measurements meet our standards of acceptable data (discussed in Ref. 1). Details of their investigation are given in Table 14. The data on these samples are given in Table 15.

Earlier measurements by Furukawa and McCoskey[21] were made on impure samples and are thus not included here. Yagfarov[22] and Stellman *et al.*[23] have also measured heat capacity of various 1, 4-polybutadienes, but only over a very limited temperature range.

Heat capacity measurements of Dainton *et al.*[9] were made on slowly cooled, semicrystalline samples of unknown crystallinity. Below 80 K, the *cis*-1, 4-polybutadiene has a higher heat capacity (decreasing from 20% at 20 K to zero at 80 K). From 80 K to the glass transition temperature the heat capacities are about equal. Above the glass transition the *cis*-1, 4-polybutadiene shows signs of defect rearrangement and melting.

2.2.7. cis-1, 4-Poly(2-methylbutadiene)

Perhaps the first heat capacity measurement on any polymer was made on natural rubber in 1889 by Gee and Terry.[24] Later measurements were made by LeBlanc and Kröger in 1928.[25] High precision heat capacity measurements on natural rubber were made in 1935 by Bekkedahl and Matheson[26] between 14 and 320 K, who discussed other early measurements on rubber. After several decades, a review by Gehman[27] on the thermal diffusivity of natural rubber showed discrepancies in Bekkedahl and Matheson's data. Wood and Bekkedahl[28] found on reexamination of heat capacity data on many rubberlike substances that above the glass transition temperature (200 K), between 213 and 298 K, slow crystallization changed their original data to lower values. Qualitative data on filled rubber by Hellwege *et al.*[29] support this conclusion. Based upon newer knowledge of crystallization in rubber, Wood and Bekkedahl proposed adjustments to their original data of 1935 to provide more refined data for *cis*-1, 4-poly(2-methylbutadiene). Chang and Bestul[33] have reported heat capacity values for a synthetic sample of the polymer. Synthetic *cis*-1, 4-poly(2-methylbutadiene) crystallizes much more slowly than natural rubber.

Table 16. Heat capacity measurements of cis-1,4-poly(2-methylbutadiene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Chang and Bestul (1971) [33]	26. Contains 3% cis-3,4-polyisoprene and 1% additives. Dried at 253 K under vacuum for 24 h. Cooled through T_g at 1 K h^{-1} and annealed at 195 K for 48 h.	20-200	Adiabatic (0.05% above 15 K)	2-9 K: Equation[a] 10-200 K: Table
	27. Sample 26 quenched through T_g at 5 K min^{-1}.	2.0-360	Adiabatic (0.05% above 15 K)	2-9 K: Equation[b] 10-360 K: Table

[a] Authors tabulated data from 2.5 to 10.6 K were curve fitted into the equation

$C_p = \exp[0.0116251\ (\ln T)^3 - 0.603157\ (\ln T)^2 + 4.6949\ (\ln T) - 6.88471]$ J $mol^{-1}K^{-1}$

(RMS dev. = 0.3%).

[b] Authors tabulated data from 2.2 to 10.7 K was curve fitted into the equation

$C_p = \exp[-0.0535849\ (\ln T)^3 - 0.255451\ (\ln T)^2 + 4.08355\ (\ln T) - 6.51616]$ J $mol^{-1}K^{-1}$

(RMS dev. = 0.9%)

Heat capacity of natural rubber has also been analyzed as a function of elongation. Mayor[30] and Mayor and Boissonnas[31] have reported the heat capacity of stretched rubber up to several hundred percent elongation at 286 and 298 K. No change in heat capacity was discovered as long as no crystallization occurred during elongation. Dynamic heat capacity measurements to study the effects during elongation have been made by Dick and Müller.[32]

Heat capacity of quenched and annealed *cis*-1, 4-poly(2-methylbutadiene) has been measured by Chang and Bestul.[33] The details of the measurements from 2 to 360 K are given in Table 16. The data on these samples are given in Table A12. Table A12 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Table 17. Recommended thermodynamic data for amorphous cis-1, 4-poly(2-methylbutadiene)[a]

T(K)	C_p (J $mol^{-1}K^{-1}$)	$H_T^a - H_0^a$ (J mol^{-1})	$S_T^a - S_0^a$ (J $mol^{-1}K^{-1}$)
0.0	0.0	0.0	0.0
2.0	.0218	0.0218	0.0109
3.0	.0899	0.0777	0.0313
4.0	.226	0.236	0.0746
5.0	.437	0.567	0.147
6.0	.721	1.14	0.250
7.0	1.07	2.03	0.385
8.0	1.48	3.31	0.554
9.0	1.92	5.01	0.753
10.0	2.41	7.17	0.981
15.0	5.23	26.27	2.45
20.0	8.32	60.15	4.37
25.0	11.36	109.3	6.54
30.0	14.24	173.3	8.87
40.0	19.54	342.2	13.68
50.0	24.34	561.6	18.56
60.0	28.83	827.5	23.39
70.0	33.06	1136	28.16
80.0	37.07	1487	32.84
90.0	40.90	1877	37.43
100.0	44.58	2304	41.93
110.0	48.12	2768	46.34
120.0	51.57	3266	50.68
130.0	54.93	3799	54.94
140.0	58.23	4365	59.13
150.0	61.48	4963	63.26
160.0	64.70	5594	67.33
170.0	67.89	6257	71.35
180.0	71.06	6952	75.32

Table 17. Recommended thermodynamic data for amorphous cis-1,4-poly(2-methylbutadiene)--Continued[a]

T(K)	C_p (J $mol^{-1}K^{-1}$)	$H_T^a - H_0^a$ (J mol^{-1})	$S_T^a - S_0^a$ (J $mol^{-1}K^{-1}$)
190.0	74.85	7681	79.27
200.0(T_g)[b]	78.03	8446	83.19
200.0(T_g)[b]	108.9	8446	83.19
210.0	111.0	9545	88.55
220.0	112.8	10664	93.76
230.0	114.7	11802	98.82
240.0	116.7	12959	103.7
250.0	118.7	14136	108.6
260.0	120.9	15334	113.2
270.0	123.2	16554	117.9
273.15	123.9	16943	119.3
280.0	125.4	17797	122.4
290.0	127.8	19063	126.8
298.15	129.7	20119	130.4
300.0	130.2	20353	131.2
310.0	132.6	21667	135.5
320.0	135.0	23005	139.7
330.0	137.5	24367	143.9
340.0	139.9	25754	148.1
350.0	142.4	27166	152.2
360.0	144.8	28602	156.2

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

[b] Data at the glass transition temperature were obtained by linearly extrapolating the heat capacity values above and below the glass transition temperature.

The heat capacity of the quenched *cis*-1, 4-poly(2-methylbutadiene) is higher than that of the annealed sample. The difference is about 2% below 15 K; it decreases to 0.1% between 35 to 100 K and then increases to 1% at 190 K. The lower heat capacity of the annealed sample can be attributed to a small amount of crystallinity. Data on quenched samples are recommended for the heat capacity of amorphous *cis*-1, 4-poly(2-methylbutadiene). These values are listed in Table 17 and plotted in Fig. 2.

Using Chang and Bestul's data on sample 27, the enthalpy and entropy of amorphous *cis*-1, 4-poly(2-methylbutadiene) were calculated from 0 to 360 K. These thermodynamic functions are listed in Table 17.

2.2.8. Polycyclopentene

Only one investigation[34] has been reported in the literature which deals with the heat capacity of polycyclopentene. Heat capacity of an amorphous sample consisting of 78% *trans* and 22% *cis* bonds ($T_g = 173$ K) has been measured over the temperature range of 10 to 320 K using an adiabatic calorimeter (claimed uncertainty 0.3%). The investigation meets our standards of acceptable data (discussed in Ref. 1).

Recommended data for amorphous polycyclopentene below the glass transition were determined by interpolating the authors' tabulated data using the spline function technique. These data are listed in Table 18 and plotted in Fig. 2.

Recommended data for molten polycyclopentene were determined by curve fitting the authors' tabulated data into the equation

$$C_p = 0.2412\,T + 60.38 \text{ J mol}^{-1}\text{ K}^{-1}.$$

Table 18. Recommended heat capacity data for amorphous polycyclopentene below the glass transition[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
0.0	0.0
10.0	0.5821
20.0	3.453
30.0	9.132
40.0	16.38
50.0	23.62
60.0	29.59
70.0	34.33
80.0	38.23
90.0	41.64
100.0	44.96
110.0	48.47
120.0	52.20
130.0	56.07
140.0	60.03
150.0	64.00
160.0	67.94
170.0	71.85
173.0(T_g)	73.20

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

Table 19. Recommended heat capacity data for molten polycyclopentene[a]

T(K)	Heat capacity (J mol^{-1}K^{-1})
173.0(T_g)	102.1
180.0	103.8
190.0	106.2
200.0	108.6
210.0	111.0
220.0	113.4
230.0	115.9
240.0	118.3
250.0	120.7
260.0	123.1
270.0	125.5
273.15	126.3
280.0	127.9
290.0	130.3
298.15	132.3
300.0	132.7
310.0	135.2
320.0	137.6

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

The rms deviation was 0.2%. These data are listed in Table 19 and plotted in Fig. 2.

2.2.9. Poly(vinyl fluoride)

Only one investigation[35] has been reported in the literature which deals with the heat capacity of poly(vinyl fluoride). The investigation meets our standards of acceptable data (discussed in Ref. 1). Details of this investigation are given in Table 20. Heat capacity of a semicrystalline sample of unknown crystallinity has been measured from 80 to 340 K. The heat capacity data are given in Table A13. Table A13 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

Below 80 K, the heat capacity has been established by summing the group contribution calculated from vibrational frequencies and skeletal contributions calculated from the Tarasov equation[35]

$$C_p/6R = D_1\left(\frac{430}{T}\right) - 0.183\left[D_1\left(\frac{79}{T}\right) - D_3\left(\frac{79}{T}\right)\right]. \quad (11)$$

These are taken as preliminary recommended data below 80 K. They are entered in parentheses in Table 21.

The recommended data from 80 K to the glass transition temperature (314 K) were obtained by curve fitting the data of sample 23 from 80 to 300 K into the equation

$$C_p = \exp[0.181972(\ln T)^3 - 2.60825(\ln T)^2 + 13.1636(\ln T) - 19.9019] \text{ J mol}^{-1}\text{ K}^{-1}. \quad (12)$$

The rms deviation was 0.3%. Recommended data from 10 to 70 K from Eq. (11) and from 80 to 314 K from Eq. (12) are listed in Table 21 and plotted in Fig. 3.

Table 20. Heat capacity measurements of poly(vinyl fluoride)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lee and Choy [35]	23. Powder (Cellomer Associates, Inc.)	80-340	Adiabatic (0.3%)	Table

Table 21. Recommended heat capacity data for poly(vinyl fluoride) below the glass transition[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
0.0	(0.0)
10.0	(0.47)
20.0	(2.8)
30.0	(5.7)
40.0	(8.5)
50.0	(11.8)
60.0	(14.5)
70.0	(17.1)
80.0	20.27
90.0	22.18
100.0	23.96
110.0	25.64
120.0	27.25
130.0	28.83
140.0	30.39
150.0	31.95
160.0	33.51
170.0	35.09
180.0	36.70
190.0	38.34
200.0	40.02
210.0	41.75
220.0	43.52
230.0	45.34
240.0	47.23
250.0	49.17
260.0	51.18
270.0	53.25
273.15	53.92
280.0	55.40
290.0	57.62
298.15	59.48
300.0	59.91
310.0	62.29
314.0(T_g)	63.27

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

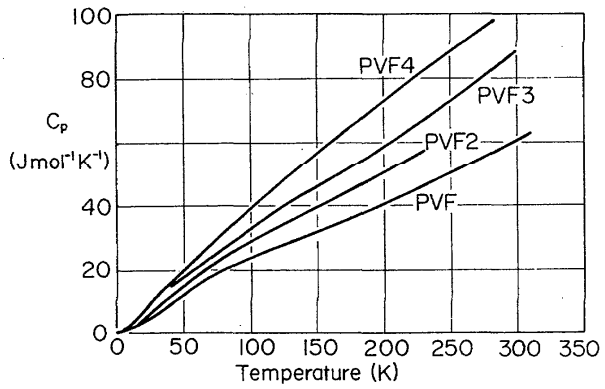

FIG. 3. Recommended heat capacity data for poly(vinyl fluoride) (PVF), poly(vinylidene fluoride) (PVF_2), polytrifluoroethylene (PVF_3), and polytetrafluoroethylene (PVF_4). The data for polytetrafluoroethylene are for two repeat units.

2.2.10. Poly(vinylidene fluoride)

Only one investigation[35,36] has been reported in the literature which deals with the heat capacity of poly(vinylidene fluoride). The investigation meets our standards of acceptable data (discussed in Ref. 1). Details of the investigation are given in Table 22. The heat capacity of a semicrystalline sample ($w^c = 0.53$) has been measured over the temperature range of 5 to 340 K. The data on this sample are given in Table A14. Table A14 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

The heat capacity data on sample 22 are taken as recommended data from 5 to 210 K. The heat capacity values from 220 to 230 are somewhat higher, because they are associated with the beginning of the glass transition. The recommended data from 210 to the glass transition temperature (233 K) were determined by linearly extrapolating the data below 220 K. The heat capacity values from 180 to 210 K were curve fitted into the equation

$$C_p = 0.221\ T + 6.28\ \text{J mol}^{-1}\,\text{K}^{-1}. \quad (13)$$

The rms deviation was 0.2%. The recommended values for the heat capacity of poly(vinylidene fluoride) below the glass transition are listed in Table 23 and plotted in Fig. 3. Above T_g the heat capacity should be strongly crystallinity dependent.

Table 22. Heat capacity measurements of poly(vinylidene fluoride)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Choy et al. (1975, 1979) [35, 36]	22. Powder (Cellomer Associates, Inc.) ρ = 1.770 Mg m^{-3} w^c = 0.53	5-340	Adiabatic (5% below 15 K 1% above 15 K)	5-18 K: Equation[a] 20-340: Table[b]

[a] Tabulated data from 5 to 30 K were curve fitted into the equation $C_p = \exp[-0.105192\ (\ln T)^3 + 0.289748\ (\ln T)^2 + 2.73071\ (\ln T) - 6.29655]$ J mol^{-1}K^{-1} (RMS dev. = 1.5%).

[b] Authors tabulated data were interpolated using the spline function technique to determine heat capacity values at every ten degree interval.

Table 23. Recommended heat capacity data for poly(vinylidene fluoride) below the glass transition.

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
5.0	0.204
6.0	0.340
7.0	0.517
8.0	0.733
9.0	0.987
10.0	1.28
12.0	1.94
14.0	2.70
16.0	3.53
18.0	4.38
20.0	5.25
25.0	7.20
30.0	9.10
40.0	12.2
50.0	15.0
60.0	17.9
70.0	20.9
80.0	23.8
90.0	26.1
100.0	28.4
110.0	30.9
120.0	33.0
130.0	35.2
140.0	37.5
150.0	39.6
160.0	41.8
170.0	44.0
180.0	46.1
190.0	48.3
200.0	50.3
210.0	52.8
220.0	54.9
230.0	57.1
233.0(T_g)	57.8

2.2.11. Polytrifluoroethylene

Two investigations[35,37] have been reported in the literature which deal with the heat capacity of polytrifluoroethylene. Details of these investigations, which meet our standards of acceptable data (discussed in Ref. 1), are given in Table 24. Heat capacity of two samples have been measured over the temperature range of 23 to 340 K. The data on these samples are given in Table A15. Table A15 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

The heat capacity data from the two measurements

Table 24. Heat capacity measurements of polytrifluoroethylene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of Data
Sochava (1960) [37]	24. [a]	23-120	Adiabatic (Unreported)	Table
Lee and Choy (1975) [35]	25. Mildly crosslinked	80-340	Adiabatic (0.3%)	Table

[a]No sample characterization reported.

Table 25. Recommended heat capacity data for polytrifluoroethylene below the glass transition[a]

T(K)	Heat capacity ($J\ mol^{-1} K^{-1}$)
25.0	10.02
30.0	12.49
40.0	15.24
50.0	17.61
60.0	20.28
70.0	23.65
80.0	26.43
90.0	29.99
100.0	33.21
110.0	36.15
120.0	38.89
130.0	41.48
140.0	43.97
150.0	46.39
160.0	48.78
170.0	51.16
180.0	53.56
190.0	55.99
200.0	58.46
210.0	61.00
220.0	63.61
230.0	66.31
240.0	69.11
250.0	72.01
260.0	75.02
270.0	78.16
273.15	79.18
280.0	81.43
290.0	84.84
298.15	87.73
300.0	88.40
304.0(T_g)	89.87

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

overlap the temperature range from 80 to 120 K. The data are in good agreement from 80 to 90 K, however, from 100 to 120 K the data of Sochava on sample 24 are somewhat lower (3%–5%). Similar deviations in Sochava's data above 100 K have been observed for other polymers.[6] Thus, data on sample 24 above 80 K were discarded.

From 25 to 70 K the data on sample 24 are taken as recommended data. To determine the recommended heat capacity data for polytrifluoroethylene from 80 to the glass transition temperature (304 K), the data on sample 25 from 80 to 290 K were curve fitted into the equation

$$C_p = \exp[0.31096(\ln T)^3 - 4.66766(\ln T)^2 + 24.1307(\ln T) - 39.0029]\ \mathrm{J\ mol^{-1}\ K^{-1}}. \quad (14)$$

The rms deviation was 0.4%. Recommended data from 25 to 70 K from sample 24 and from 80 to 304 K from Eq. (14) are listed in Table 25 and plotted in Fig. 3.

2.2.12. Polytetrafluoroethylene

Six investigations[36,38–42] have been reported in the literature which deal with the heat capacity of polytetrafluoroethylene. Details of these investigations, which meet our standards of acceptable data (discussed in Ref. 1), are given in Table 26. The heat capacity of nine samples has been measured from 0.3 to 720 K. The data on these samples are given in Tables 27 and 28. Somewhat less accurate measurements have been reported by Steere,[61] Karasev,[84] Luikov *et al.*,[85] Hager,[56,57] and Martin and Müller.[55]

Heat capacity data are reported for presumably highly

Table 26. Heat capacity measurements of polytetrafluorethylene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Furukawa et al. (1952) [38]	90. Teflon[a] Powder ΔH_f=1.90 kJ mol^{-1}	5-365	Adiabatic	Table
	91. Teflon[a] Average data for molded and quenched samples Molded: ΔH_f=1.744 kJ mol^{-1} Quenched: ΔH_f=1.82 kJ mol^{-1}	5-365	Adiabatic	Table
	92. Teflon[a] Annealed	5-365	Adiabatic	Table
Noer et al. (1959) [39]	93. Teflon[a]	1.4-4.2	Heat pulse (5%)	Equation[b]
Reese and Tucker (1965) [40]	95. Teflon[a] ρ = 2.160 Mg m^{-3}	1.0-4.5	Transient (10%)	Equation[c]
Douglas and Harman (1965) [41]	94. Teflon[a] Powder w^c=0.95	340-560	Drop Calorimeter (5%)	Equation[d]
	96. Teflon[a] Quenched	330-720	Drop Calorimeter (5%)	330-560 K: Equation[e] 660-720 K: Equation[f]
Choy et al. (1979) [36]	99. Teflon[a] w^c=0.9	5-100	Adiabatic (2%)	Table
Salinger and Cieloszyk (unpublished) [42]	98. Teflon[a]	0.3-4.4	Heat pulse (2%)	Equation[g]

[a]Teflon is the trade name for polytetrafluoroethylene manufactured by E.I. DuPont De Nemours Co., Inc.

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

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

[d]$C_p = 0.54268 + 1.345 \cdot 10^{-3}\ T + 208/(603.4 - T)^2$ J g^{-1}K^{-1}

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

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

[g]$C_p = \exp[-0.174744(\ln T)^3 + 0.128498(\ln T)^2 + 3.13958(\ln T) + 5.85181]$ erg g^{-1}K^{-1}

Table 27. Heat capacity of various polytetrafluoroethylenes[a] at low temperatures in mJ mol^{-1}K^{-1}

T(K)	93	95	98
0.3			0.06491
0.4			0.1249
0.5			0.2226
0.6			0.3704
0.7			0.5816
0.8			0.8707
0.9			1.252
1.0		2.274	1.740
1.2		3.929	3.094
1.4	5.741	6.239	5.041
1.6	8.570	9.313	7.687
1.8	12.20	13.26	11.11
2.0	16.73	18.19	15.38
3.0	56.50	61.39	50.71
4.0	133.9	145.5	108.6

[a]Sample numbers correspond to the samples described in table 41.

Table 28. Heat capacity of various polytetrafluoroethylenes in J $mol^{-1}K^{-1}$[a]

T(K)	90	91	92	94	96	99
5	0.1200	0.1200	0.1200			0.2284
10	0.8950	0.9102	0.9102			1.228
15	2.360	2.386	2.416			2.565
20	3.836	3.821	3.796			3.915
25	5.166	5.081	5.061			5.155
30	6.356	6.236	6.221			6.245
40	8.482	8.257	8.212			8.400
50	10.27	10.09	10.10			10.35
60	12.29	11.90	11.89			12.25
70	14.18	13.73	13.72			14.16
80	16.03	15.60	15.60			16.00
90	17.81	17.50	17.50			17.68
100	19.49	19.29	19.29			19.25
110	21.20	21.06	21.08			
120	22.90	22.84	22.83			
130	24.53	24.56	24.56			
140	26.13	26.26	26.26			
150	27.65	28.00	27.94			
160	29.13	29.88	29.86			
170	30.62	31.93	31.76			
180	32.06	33.87	33.53			
190	33.45	35.52	35.10			
200	34.76	37.05	36.54			
210	36.09	38.51	37.92			
220	37.47	39.92	39.28			
230	38.86	41.29	40.58			
240	40.32	42.67	41.87			
250	41.97	44.10	43.20			
260	43.98	45.68	44.60			
270	46.80	47.64	46.29			
280	51.81	50.61	48.82			
290		Transition[b]				
300						
310	49.81	51.06	51.16			
320	49.67	51.36	51.16			
330	49.91	51.91	51.56		51.69	
340	50.31	52.46	52.10	50.12	52.43	
350	50.71	53.06	52.61	50.81	53.18	
360	51.11	53.71	53.41	51.49	53.93	
370				52.18	54.69	

Table 28. Heat capacity of various polytetrafluoroethylenes in J $mol^{-1}K^{-1}$--Continued[a]

T(K)	90	91	92	94	96	99
380				52.87	55.45	
390				53.56	56.21	
400				54.26	56.98	
410				54.95	57.75	
420				55.66	58.54	
430				56.37	59.33	
440				57.08	60.13	
450				57.80	60.96	
460				58.54	61.80	
470				59.29	62.66	
480				60.06	63.56	
490				60.86	64.51	
500				61.69	65.52	
510				62.58	66.63	
520				63.56	67.87	
530				64.67	69.32	
540				66.00	71.11	
550				67.73	73.50	
560				70.27	77.03	
570						
580				Melting		
590						
600					66.38	
610					67.17	
620					67.77	
630					68.37	
640					68.97	
650					69.56	
660					70.16	
670					70.76	
680					71.35	
690					71.95	
700					72.55	
710					73.15	
720					73.74	

[a]Sample numbers correspond to the samples described in table 41.

[b]1*13/6 helix to 1*15/7 transition (endothermic).

crystalline samples. However, their crystallinities are not well established due to the lack of equilibrium melting parameters and crystallinity-density correlations. Thus, the crystallinity extrapolations using the two phase to determine the heat capacity of completely crystalline and amorphous polytetrafluoroethylene is not possible at present. Moreover, the analysis of the heat capacity is further complicated by the controversy in the literature on the glass transition temperature and the room temperature transition of polytetrafluoroethylene. Investigations are currently underway in our laboratory to establish these thermodynamic quantities. At present, we recommend the data on sample 98 (0.3 to 4.4 K), sample 92 (5 to 300 K), and sample 99 (600 to 720 K). Heat capacity data from 320 to 560 K are not recommended since they might be associated with crystallization and premelting. The data on sample 92 are plotted in Fig. 3.

2.2.13. Poly(vinyl chloride)

Poly(vinyl chloride) PVC is an important and widely used polymer. Of all thermoplastics, its production is second only to that of polyethylene. Thirty investigations of the heat capacity of poly(vinyl chloride) have been reported in the literature. Heat capacity of over 40 samples have been measured over wide ranges of temperature.

All investigations were critically evaluated in terms of

Table 29. Heat capacity measurements of poly(vinyl chloride)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lebedev et al. (1967) [43]	110 Suspension-polymerized $\bar{M}_w$ = 130,000 w^c = 0.2 (x rays)	60-300 K	Adiabatic (0.5%)	Table[a]
Chang (1977) [44]	112 Suspension-polymerized Geon 103EP (B.F. Goodrich Corp.) $\bar{M}_n$ = 64,300 $\bar{M}_w$ = 142,000 Pelletized at 500 MPa contains 0.03% poly-(vinyl alcohol)	250-370	Adiabatic (0.1%)	Table[a]
	113 Quenched sample 112	8-370	Adiabatic (0.1%)	8-25 K: Equation[b] 30-370 K: Table[a]
	114 Annealed sample 112	310-370	Adiabatic (0.1%)	Table[a]
	115 Bulk-polymerized	300-340	Adiabatic (0.1%)	Table[a]
	116 Geon 80X5 (B.F. Goodrich Corp.)	310-340	Adiabatic (0.1%)	Table[a]
	117 Pelletized sample 115 at 140 MPa.	310-360	Adiabatic (0.1%)	Table[a]
	118 Quenched sample 117	280-370	Adiabatic (0.1%)	Table[a]
	119 Annealed sample 117	6-380	Adiabatic (0.1%)	6-25 K: Equation[c] 30-380 K: Table
	120 Quenched sample 117	7-360	Adiabatic (0.1%)	7-25 K: Equation[d] 30-360 K: Table[a]

[a] Data were interpolated using the spline function technique to give heat capacities at every ten degree interval.

[b] The authors' tabulated data from 8 to 32.1 K were curve fitted into the equation

$$C_p = \exp[-0.0156374(\ln T)^3 - 0.253526(\ln T)^2 + 3.38239(\ln T) - 5.6602] \text{ J mol}^{-1}\text{K}^{-1}$$

(RMS deviation = 0.1%)

[c] Authors' tabulated data from 6.2 to 31.8 K were curve fitted into the equation

$$C_p = \exp[0.0036811(\ln T)^3 - 0.415076(\ln T)^2 + 3.82721(\ln T) - 6.06208] \text{ J mol}^{-1}\text{K}^{-1}$$ (RMS deviation = 0.4%)

[d] Authors' tabulated data from 6.9 to 31 K were curve fitted into the equation

$$C_p = \exp[-0.0103775(\ln T)^3 - 0.297456(\ln T)^2 + 3.50496(\ln T) - 5.77448] \text{ J mol}^{-1}\text{K}^{-1}$$

(RMS deviation = 0.2%)

sample characterization, experimental technique used, error limits, and accuracy of representation of the data. Most of the measurements have been made on chemically impure samples (commercial samples with additives) and their data span often a somewhat limited temperature range in the vicinity of the glass transition interval. Moreover, most of the results have been reported in graphical form only. It was found that only 2 of the 30 investigations met our standards of acceptable data (discussed in Ref. 1). These contain heat capacity data on 10 largely amorphous bulk and suspension polymerized samples of various thermal histories. Details of these investigations are listed in Table 29. Twenty-eight investigations which did not contain acceptable data were not included in further analysis. These are listed Table 30, along with brief comments on the reasons for exclusion from this study.

The heat capacity data retrieved from the literature are given in Table A16. Table A16 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. Chang's heat capacity data on samples 112–120 are in very good agreement (better than 0.5%) from 6 to 300 K. The data show somewhat larger deviations above 310

Table 30. Heat capacity investigations on poly(vinyl chloride) not included in this study.

Reference	Reason(s) for exclusion
Vieweg and Gottwald (1940) [45]	Data associated with large error limits.
Heuse (1949) [46]	Data associated with large error limits.
Badoche and Li (1950, 1951) [47,48]	Data reported for three samples $\bar{M}_w$ = 23,000; 70,000; 125,000 over a limited temperature range (350-380 K). Heat capacity decreases somewhat with increasing molecular weight.
Gast (1953) [49]	Heat capacity data reported only in the glass transition temperature region.
Alford and Dole (1955) [50]	Heat capacity data reported for an annealed sample in the glass transition temperature range.
Hellwege et al. (1959) [29]	Sample characterization not reported.
Hellwege et al. (1962) [51]	Heat capacity data reported from 300 to 450 K. The data below the glass transition temperature are in good agreement with the values reported here. However, the data above T_g are higher (~8%).
Tautz et al. (1962, 1963, 1964) [52-54]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Martin and Müller (1963) [55]	Data could not be read accurately from too small graphs; large error limits.
Hager (1964, 1972) [56,57]	Data could not be read accurately from too small graphs. Measurements made using thin foil calorimeters are associated with large error limits.
Dunlap (1966, 1972) [58,59]	Heat capacity reported for various plasticized PVC compositions.
Mishchenko et al. (1966) [60]	Heat capacity measurements reported for PVC with 30-35% fillers. Data could not be read accurately from too small graphs.
Steere (1966) [61]	Heat capacities per unit volume have been reported. These values are not directly comparable to the data presented here.
Wilski and Grewer (1966, 1968, 1970) [62-64]	Heat capacity data has been reported on eight commercial samples (emulsion and suspension polymerized). The graphical data covers a limited temperature range (300-400 K) in the region of the glass transition. Most of the samples contain 1-4% additives.
Götze and Winkler (1967) [65]	Heat capacity data reported for PVC fibers in humid conditions from 230 to 310 K.
Chernobyl'skii et al. (1969) [66]	Heat capacity measured at 1-65 bar pressure.
Knappe et al. (1970, 1977) [68,69]	Data only in the glass transition region.
Kartalov et al. (1971) [67]	Heat capacity measured for blends of PVC and polyethylene. The heat capacity decreases with increasing content of PVC.
Ceccorulli et al. (1977) [70]	Data reported in the glass transition region for various samples of different degrees of syndiotacticity and crystallinity.
Dushchenko et al. (1977) [71]	Heat capacity in the glass transition region reported as a function of thermal history.

Table 31. Recommended thermodynamic data for amorphous poly(vinyl chloride)[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a - H^a$ (J mol^{-1})	$S_T^a - S_o^a$ (J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
5.0	0.3820	0.5130	0.1370
6.0	0.5969	0.9988	0.2250
7.0	0.8528	1.720	0.3357
8.0	1.144	2.716	0.4683
9.0	1.466	4.019	0.6213
10.0	1.812	5.656	0.7935
12.0	2.564	10.02	1.189
14.0	3.370	15.95	1.645
16.0	4.208	23.52	2.149
18.0	5.059	32.79	2.694
20.0	5.913	43.76	3.271
25.0	7.999	78.58	4.816
30.0	9.950	123.5	6.445
40.0	13.38	240.1	9.776
50.0	16.28	388.4	13.08
60.0	18.77	563.7	16.27
70.0	20.99	762.5	19.33
80.0	23.05	982.7	22.27
90.0	24.98	1222	25.10
100.0	26.82	1481	27.83
110.0	28.59	1758	30.47
120.0	30.29	2053	33.03
130.0	31.94	2364	35.52
140.0	33.56	2691	37.95
150.0	35.15	3035	40.32
160.0	36.73	3394	42.64
170.0	38.31	3770	44.91
180.0	39.88	4161	47.15
190.0	41.45	4567	49.35
200.0	43.03	4990	51.51
210.0	44.61	5428	53.65
220.0	46.21	5882	55.76
230.0	47.79	6352	57.85
240.0	49.37	6838	59.92
250.0	50.99	7339	61.97
260.0	52.63	7858	64.00
270.0	54.29	8392	66.02
273.15	54.81	8564	66.65
280.0	55.95	8943	68.02
290.0	57.64	9511	70.01
298.15	59.03	9987	71.63
300.0	59.35	10096	72.00
310.0	61.11	10699	73.97
320.0	62.94	11319	75.94
330.0	64.88	11958	77.91
340.0	66.96	12617	79.88
350.0	68.85	13296	81.84
354.0(T_g)	69.62	13573	82.63
354.0	88.99	13573	82.63
360.0	91.08	14113	84.14
370.0	94.56	15041	86.69
380.0	98.05	16005	89.25

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

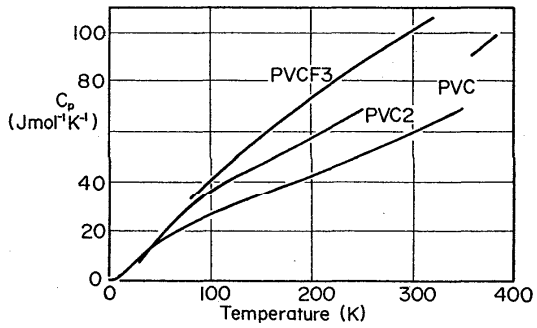

FIG. 4. Recommended heat capacity data for poly(vinyl chloride) (PVC), poly(vinylidene chloride) (PVC2), and polychlorotrifluoroethylene (PVCF3).

K as the glass transition temperature is approached. The data of Lebedev on sample 110 agree with the data of Chang within 2%.

Based upon our prior experience, we feel that the heat capacity data of Chang is more accurate than Lebedev's data.

Of nine measurements (all in good agreement), reported by Chang, only three (samples 113, 119, and 120) cover the entire temperature range. Out of these, two measurements (113 and 120) are on quenched samples and the third one is on an annealed sample 119. The data on the annealed sample were taken as taken as the recommended heat capacity data. These values are listed in Table 31 and plotted in Fig. 4. The heat capacity data for glassy PVC were extrapolated from 340 to 354 K to conform to the widely accepted glass transition temperature of 354 K.

Enthalpy and entropy of amorphous poly(vinyl chloride) were calculated from 0 to 380 K by numerically integrating the heat capacity data. These thermodynamic functions are listed in Table 31.

2.2.14. Poly(vinylidene chloride)

Two investigations[43,72] have been reported in the literature which deal with the heat capacity of poly(vinylidene chloride). Details of these investigations, which meet our standards of acceptable data (discussed in Ref. 1) are given in Table 32. Heat capacity of two semicrystalline samples have been measured over the temperature range of 60 to 300 K. The data on these samples are given in Table A17. Table A17 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

The data of Sochava on sample 28 and the data of Lebedev *et al.* on sample 29 are in good agreement from 60 to 110 K. However, the data of Sochava are higher above 120 K by as much as 20% at 200 K. Similar deviations have been observed for Sochava's data on other polymers above 100 K.[6] Thus the data on sample 28 were discarded over the entire temperature range. The recommended data on the heat capacity of poly(vinylidene chloride) from 60 K to the glass

Table 32. Heat capacity measurements of poly(vinylidene chloride)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Sochava (1964) [72]	28. a	50-200	Adiabatic (unreported)	Table
Lebedev et al. (1967) [43]	29. w^c = 0.40	60-300	Adiabatic vacuum (0.5%)	Table

[a]No characterization reported.

Table 33. Recommended heat capacity data for poly(vinylidene chloride) below the glass transition[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
50.0	(7.316)
40.0	(12.53)
50.0	(17.38)
60.0	21.49
70.0	26.08
80.0	30.01
90.0	33.38
100.0	36.31
110.0	38.91
120.0	41.26
130.0	43.45
140.0	45.53
150.0	47.53
160.0	49.50
170.0	51.46
180.0	53.44
190.0	55.45
200.0	57.51
210.0	59.64
220.0	61.84
230.0	64.12
240.0	66.50
250.0	68.98
255.0(T_g)	70.26

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

Table 34. Heat capacity measurements of polychlorotrifluoroethylene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Hoffmann (1952) [73]	34. Powdered Kel-F[b] quenched	270-510	Differential adiabatic (0.8%)	Table
	35. Powdered Kel-F[b] slow cooled	270-510	Differential adiabatic (0.8%)	Table
Reese and Tucker (1965) [40]	36. Kel-F[b]	1.0-4.5	Heat Pulse (10%)	Equation[a]
Lee et al. (1974) [74]	37. Kel-F[b] Average data of two samples slow cooled (w^c = 0.65) and quenched (w^c = 0.46)	80-340	Adiabatic (0.3%)	Table

[a]$C_p = 1260\ T^3$ erg $K^{-1}g^{-1}$

[b]Kel-F is the trade name of polychlorotrifluoroethylene made by 3M Company.

transition temperature (225 K) was obtained by curve fitting the data on sample 29 from 60 to 250 K into the equation

$$C_p = \exp[0.32494(\ln T)^3 - 4.87152(\ln T)^2 + 24.8528(\ln T) - 39.4329] \text{ J mol}^{-1}\text{ K}^{-1}. \quad (15)$$

The rms deviation was 0.8%. Equation (15) was used to calculate recommended values from 60 to 255 K.

From 30 to 50 K, preliminary recommended data were calculated from the Tarasov equation as reported by Lebedev *et al.*[43]:

$$C_p = 6R\left[D_1\left(\frac{402}{T}\right) - \frac{161}{402} \times\left[D_1\left(\frac{161}{T}\right) - D_3\left(\frac{161}{T}\right)\right]\right]. \quad (16)$$

The recommended data for the heat capacity of poly(vinylidene chloride) below the glass transition are listed in Table 33 and plotted in Fig. 4. Above the glass transition the heat capacity is strongly crystallinity dependent.

2.2.15. Polychlorotrifluoroethylene

Three investigations[40,73,74] have been reported in the literature which deal with the heat capacity of polychlorotrifluoroethylene. All the measurements which meet our standards of acceptable data (discussed in Ref. 1) have been made on commercial semicrystalline samples of Kel-F (trade name of 3 M Co.). Details of these investigations are given in Table 34. Heat capacities have been measured at low temperatures (1.0 to 4.5 K) and at high temperatures (80 to 510 K). The high temperature data on these samples are given in Table A18. Table A18 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

At low temperatures, the data of Reese on sample 36 are taken as the recommended data. At high temperatures, the data of Hoffmann on samples 34 and 35 are not in agreement with more reliable data of Lee *et al.* on sample 37. The data of Lee *et al.* on samples of different crystallinities are in agreement with one another, but agree with Hoffmann's data on slow cooled sample only (sample 35) over a limited temperature range (300 to 340 K). Above 350 K Hoffmann's data are associated with melting of the sample. Thus Hoffmann's data on both the samples were discarded over the entire temperature range. To determine the recommended data on polychlorotrifluoroethylene from 80 K to the glass transition temperature (325 K), the data on sample 37 from 80 to 300 K were curve fitted into the equation

$$C_p = \exp[0.120366(\ln T)^3 - 1.92703(\ln T)^2 + 11.0523(\ln T) - 18.0763] \text{ J mol}^{-1}\text{ K}^{-1}. \quad (17)$$

The rms deviation was 0.2%. Recommended data obtained from sample 36 from 1.0 to 4.0 K and from 80 to 325 K from Eq. (17) are listed in Table 35 and plotted in Fig. 4. No high temperature data are recommended since no crystallinity extrapolations are possible.

Table 35. Recommended heat capacity data for polychlorotrifluoroethylene below the glass transition[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
1.0	0.006942
1.2	0.01200
1.4	0.01905
1.6	0.02843
1.8	0.04049
2.0	0.05554
3.0	0.1874
4.0	0.4445
80.0	52.46
90.0	56.77
100.0	60.81
110.0	64.63
120.0	68.24
130.0	71.69
140.0	75.00
150.0	78.18
160.0	81.26
170.0	84.26
180.0	87.18
190.0	90.05
200.0	92.87
210.0	95.66
220.0	98.41
230.0	101.15
240.0	103.87
250.0	106.57
260.0	109.27
270.0	111.98
273.15	112.84
280.0	114.68
290.0	117.39
298.15	119.64
300.0	120.1
310.0	122.9
320.0	125.6
325.0(T_g)	127.0

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

2.2.16. Poly(vinyl alcohol)

Two investigations[75,76] have been reported in the literature which deal with the heat capacity of poly(vinyl alcohol). Details of these investigations, which meet our standards of acceptable data (discussed in Ref. 1), are given in Table 36. Heat capacity of two samples of unknown characterization have been measured over the temperature range of 60 to 300 K. The data on these samples are given in Table A19. Table

A19 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

The data of Sochava and Trapeznikova on sample 41 are somewhat lower than the data of Lebedev and Rabinovich on sample 42, especially above 100 K. Similar deviations have been observed for the data of Sochava and Trapeznikova above 100 K for other polymers.[6] Thus the data on sample 41 were discarded over the entire temperature range. The recommended data on the heat capacity of poly(vinyl alcohol) from 60 to 300 K were obtained by curve fitting the

Table 36. Heat capacity measurements of poly(vinyl alcohol)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Sochava and Trapeznikova (1957) [75]	41. [a]	60-240	Adiabatic (Unreported)	Table
Lebedev and Rabinovich (1967) [76]	42. [a]	60-300	Adiabatic Vacuum (0.5%)	Table

[a]No characterization reported

Table 37. Recommended heat capacity data for poly(vinyl alcohol)[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
60.0	11.78
70.0	15.05
80.0	17.94
90.0	20.46
100.0	22.69
110.0	24.69
120.0	26.54
130.0	28.29
140.0	29.98
150.0	31.66
160.0	33.34
170.0	35.06
180.0	36.84
190.0	38.69
200.0	40.64
210.0	42.69
220.0	44.85
230.0	47.16
240.0	49.60
250.0	52.21
260.0	54.99
270.0	57.95
273.15	58.92
280.0	61.12
290.0	64.50
298.15	67.42
300.0	68.11

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

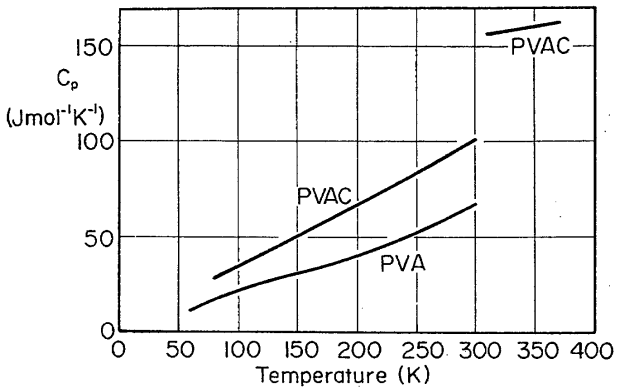

FIG. 5. Recommended heat capacity data for poly(vinyl alcohol) and poly(vinyl acetate).

data on sample 42 into the equation

$$C_p = \exp[0.47262(\ln T)^3 - 6.98249(\ln T)^2 + 35.1696(\ln T) - 56.9169] \text{ J mol}^{-1}\text{ K}^{-1}. \quad (18)$$

The rms deviation was 1.1%. These recommended data from Eq. (18) are given in Table 37 and plotted in Fig. 5.

2.2.17. Poly(vinyl acetate)

Two investigations[77,78] have been reported in the literature which deal with the heat capacity of poly(vinyl acetate). Shieman *et al.*[77] have covered a wide temperature range of 80 to 370 K. Sharanov and Vol'kenshtein[78] have restricted their measurements to the glass transition region (290 to 330 K). Details of the investigation by Shieman *et al.* which meets our standards of acceptable data (discussed in Ref. 1), are given in Table 38. Graphical data from the publication were retrieved and could be curve fitted in linear equations below and above the glass transition temperature (304 K).

Below T_g:

$$C_p = 0.3366\,T + 0.88 \text{ J mol}^{-1}\text{ K}^{-1} \text{ (rms dev. 1.0\%)}. \quad (19)$$

Above T_g:

$$C_p = 0.09786\,T + 127.16 \text{ J mol}^{-1}\text{ K}^{-1} \text{ (rms dev. 0.3\%)}. \quad (20)$$

Data obtained from these equations are recommended and listed in Table 39 and plotted in Fig. 5.

Table 38. Heat capacity measurements of poly(vinyl acetate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Shieman et al. [1972] [77]	102. Amorphous $\rho = 0.9325$ Mg m^{-3}	90-370	Adiabatic (0.7%)	Graph

Table 39. Recommended heat capacity data for amorphous poly(vinyl acetate)[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
80.0	27.81
90.0	31.17
100.0	34.54
110.0	37.90
120.0	41.27
130.0	44.63
140.0	48.00
150.0	51.37
160.0	54.73
170.0	58.10
180.0	61.46
190.0	64.83
200.0	68.19
210.0	71.56
220.0	74.93
230.0	78.29
240.0	81.66
250.0	85.02
260.0	88.39
270.0	91.75
273.15	92.82
280.0	95.12
290.0	98.49
298.15	101.2
300.0	101.9
304.0(T_g)	103.2
304.0(T_g)	156.9
310.0	157.5
320.0	158.5
330.0	159.5
340.0	160.4
350.0	161.4
360.0	162.4
370.0	163.4

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

Table 40. Heat capacity measurements of poly(α-methylstyrene)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lebedev and Rabinovich (1971) [80]	81. Amorphous	60-300	Adiabatic (0.5%)	Table
Zoller et al. (1973) [81]	82. Amorphous	1.6-4.0	Heat pulse (2%)	Equation[a]
Gaur and Wunderlich (1981) [79]	83. Amorphous M_w = 670,000 M_n = 590,000	300-490	DSC (1%)	Table
Gaur and Wunderlich (unpublished) [83]	84. Sample 83	230-290	DSC (1%)	Table[b]

[a]$C_p = 0.429\ T^3 + 1.73(17/T)^2\ \exp(17/T)/[\exp(17/T)-1]^2$ mJ $g^{-1}K^{-1}$

[b]Table of curve fitted data 300-440 K: $C_p = 29.42 + 0.4498\ T - 1.2798 \times 10^6\ T^{-2}$ J $mol^{-1}K^{-1}$

450-490 K: $C_p = 0.5758\ T - 6.43$ J $mol^{-1}K^{-1}$

Table 41. Recommended thermodynamic data for amorphous poly(α-methyl styrene)[a]

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a - H_o^a$ (J mol^{-1})	$S_T^a - S_o^a$ (J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
1.6	.02133	0.01706	0.01067
1.8	0.03101	0.02230	0.01372
2.0	0.04356	0.02976	0.01762
3.0	0.1597	0.1314	0.05513
4.0	0.3787	0.4006	0.1291
10.0	(0.1841)	2.089	0.4683
20.0	(1.473)	10.37	0.9286
30.0	(4.605)	40.76	2.064
40.0	(11.10)	119.3	4.219
50.0	(19.50)	272.3	7.557
60.0	28.97	514.6	11.92
70.0	38.52	852.1	17.09
80.0	45.22	1270	22.66
90.0	51.84	1756	28.37
100.0	55.69	2293	34.04
110.0	61.13	2877	39.60
120.0	66.16	3514	45.13
130.0	70.89	4202	50.64
140.0	75.09	4932	56.05
150.0	79.38	5704	61.37
160.0	83.77	6520	66.64
170.0	88.23	7380	71.85
180.0	92.76	8285	77.02
190.0	97.36	9235	82.16
200.0	102.01	10232	87.27
210.0	106.71	11276	92.36
220.0	111.5	12367	97.4
230.0	116.3	13505	102.5
240.0	121.1	14692	107.5
250.0	126.0	15927	112.6
260.0	130.9	17211	117.6
270.0	135.8	18544	122.7
273.15	137.3	18974	124.2
280.0	140.7	19927	127.7
290.0	145.7	21359	132.7
298.15	149.8	22563	136.8
300.0	150.7	22841	137.7
310.0	155.7	24373	142.8
320.0	160.7	25955	147.8
330.0	165.8	27588	152.8
340.0	170.8	29271	157.8
350.0	175.9	31005	162.8
360.0	181.0	32789	167.9
370.0	186.1	34624	172.9
380.0	191.1	36510	177.9
390.0	196.2	38447	183.0
400.0	201.3	40435	188.0
410.0	206.4	42474	193.0
420.0	211.5	44563	198.1
430.0	216.6	46704	203.1
440.0	221.7	48896	208.1
441.0(T_g)	222.2	49118	208.6
441.0(T_g)	247.5	49118	208.6
450.0	252.7	51368	213.7
460.0	258.4	53924	219.3
470.0	264.2	56537	224.9
480.0	270.0	59208	230.5
490.0	275.7	61936	236.1

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

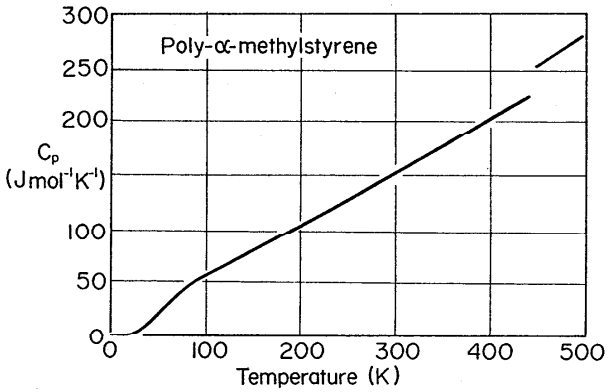

FIG. 6. Recommended heat capacity data for poly(α-methylstyrene).

2.2.18. Poly(α-methylstyrene)

Four investigations[79–81,83] have been reported in the literature which deal with the heat capacity of poly(α-methylstyrene). All the investigations meet our standards of acceptable data (discussed in Ref. 1). Details of these investigations are given in Table 40. The heat capacity data for three amorphous samples have been reported from 1.6 to 490 K. The high temperature data on these samples are given in Table A20. Table A20 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics.

In preliminary analysis, the data on sample 81 and 83 were plotted on a graph. The data on sample 81 and 83 are in good agreement at 300 K, however the data on sample 81 showed an exothermic curvature from 220 to 300 K. These data were then compared with unpublished data from our laboratory on poly(α-methylstyrene) from 230 to 290 K. These data fell on a smooth curve joining the data on sample 81 from 60 to 200 K and the data on sample 83 from 300 to 440 K. Thus for further analysis the data on sample 81 above 200 K were discarded.

The data on sample 82 from 1.6 to 4.0 K and on sample 81 from 60 to 120 K are taken as recommended data. Recommended data from 130 K to the glass transition temperature (441 K) were determined by curve fitting the data on sample 81 from 120 to 200 K, the data on sample 83 from 300 to 400 K and the data on sample 84 from 230 to 290 K into the equation

$$C_p = \exp[-0.068046(\ln T)^3 + 1.22053(\ln T)^2 - 6.28566(\ln T) + 13.7864]\ \text{J mol}^{-1}\,\text{K}^{-1}. \quad (21)$$

The rms deviation was 0.6%. Equation (21) was used to determine recommended data from 130 to 441 K. These data are listed in Table 41.

From 10 to 50 K, the preliminary data were obtained from the Tarasov equation reported by Lebedev and Rabinovich[80]:

$$C_p = 5R\left[D_1\left(\frac{476}{T}\right) - \frac{333}{476} \times \left\{D_1\left(\frac{333}{T}\right) - D_3\left(\frac{333}{T}\right)\right\}\right]. \quad (22)$$

These preliminary data are also listed in Table 41 in parentheses.

The heat capacity data on sample 83 above 441 K are recommended for the heat capacity of molten poly(α-methylstyrene). The data are listed in Table 41 and plotted in Fig. 6.

Enthalpy and entropy of amorphous poly(α-methylstyrene) were calculated by numerically integrating the heat capacity data. These thermodynamic functions are listed in Table 41.

2.2.19. Poly(o-methylstyrene) and Poly(o-chlorostyrene)

Only low temperature heat capacity data (1.6 to 4.0) K have been reported by Zoller *et al.*[81] for amorphous poly(o-methylstyrene) and poly(o-chlorostyrene). Heat capacity measurements which meet our standards of acceptable data (discussed in Ref. 1), were made on commercial samples (Dow Chemicals) by the heat pulse method (claimed uncertainty 2%). Heat capacity of both the samples could be fitted into an equation consisting of Debye and Einstein terms of type

$$C_p = AT^3 + B(\theta_E/T)^2\exp(\theta_E/T)/[\exp(\theta/T) - 1]^2. \quad (23)$$

Heat capacity data from their curve fitted equations are recommended and are listed in Table 42.

Table 42. Recommended heat capacity data for poly(o-methylstyrene) and poly(o-chlorostyrene) in mJ $mol^{-1}K^{-1}$[a]

T(K)	Poly(o-methylstyrene)[b]	Poly(o-chlorostyrene)[c]
1.6	24.81	29.06
1.8	37.40	43.50
2.0	54.07	62.55
3.0	203.3	234.0
4.0	460.8	534.5

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

[b] $C_p = 0.0458\ T^3 + 2.72(14.8/T)^2\exp(14.8/T)/[\exp(14.8/T)-1]^2$ mJ $g^{-1}K^{-1}$

[c] $C_p = 0.0466\ T^3 + 2.52(15/T)^2\ \exp(15/T)/[\exp(15/T)-1]^2$ mJ $g^{-1}K^{-1}$

Table 43. Heat capacity measurements of poly(vinyl benzoate)

Investigator	Sample no., characterization	Temperature range	Experimental technique (claimed uncertainty)	Source of data
Pasquini et al. (1974) [82]	18. Amorphous (X-ray) $\bar{M}_v$ = 133,000 ρ = 1.198 Mg m^{-3} T_g = 347 K	190-500	DSC	190-340: Equation[a] 350-500 Equation[b]

[a] Authors' tabulated data below the glass transition (190 to 300 K) were curve fitted into the equation

$C_p = 0.5178\ T + 8.01$ J $mol^{-1}K^{-1}$ (RMS dev. = 0.2%).

This equation was used to calculate the heat capacity of amorphous, glassy poly(vinyl benzoate) from 190-340 K.

[b] Authors' tabulated data above the glass transition (370 to 500 K) were curve fitted into the equation

$C_p = 0.2878\ T + 157.35$ J $mol^{-1}K^{-1}$ (RMS dev. = 0.1%).

This equation was used to calculate the heat capacity of molten poly(vinyl benzoate) from 350-500 K.

2.2.20. Poly(vinyl benzoate)s

Only one investigation[82] has been reported in the literature which deals with the heat capacity of poly(vinyl benzoate)s. Heat capacities of amorphous poly(vinyl benzoate), poly(vinyl-p-ethylbenzoate), poly(vinyl-p-isopropylbenzoate), and poly(vinyl-p-tert-butylbenzoate) have been measured over the temperature range of 190 to 500 K. The investigation meets our standards of acceptable data (discussed in Ref. 1). Details of these investigations are given in Table 43 to 46.

To determine the recommended values of the heat ca-

Table 44. Heat capacity measurements of poly(vinyl-p-ethylbenzoate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Pasquini et al. (1974) [82]	19. Amorphous (X-ray) $\bar{M}_v$ = 43,600 ρ = 1.145 Mg m^{-3} T_g = 330 K	190-500	DSC (Unreported)	190-330: Equation[a] 330-500: Equation[b]

[a]Authors' tabulated data below the glass transition (190 to 300 K) were curve fitted into the equation

$$C_p = 0.6592\ T + 21.02 \quad J\ mol^{-1}K^{-1} \quad (RMS\ dev. = 0.2\%).$$

This equation was used to calculate the heat capacity of amorphous, glassy poly(vinyl-p-ethylbenzoate) from 190 to 330 K.

[b]Authors' tabulated data above the glass transition (360 to 500 K) were curve fitted into the equation

$$C_p = 0.4461\ T + 148.22 \quad J\ mol^{-1}K^{-1} \quad (RMS\ dev. = 0.1\%).$$

This equation was used to calculate the heat capacity of molten poly(vinyl-p-ethylbenzoate) from 330 to 500 K.

Table 45. Heat capacity measurements of poly(vinyl-p-isopropylbenzoate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Pasquini et al. (1974) [82]	20. Amorphous (X-ray) $\bar{M}_v$ = 43,600 ρ = 1.198 Mg m^{-3} T_g = 335 K	190-500	DSC	190-330: Equation[a] 340-500 Equation[b]

[a]Authors' tabulated data below the glass transition (190-300 K) were curve fitted into the equation

$$C_p = 0.6831\ T + 31.7 \quad J\ mol^{-1}K^{-1} \quad (RMS\ dev = 0.3\%).$$

This equation was used to calculate the heat capacity of amorphous, glassy, poly(vinyl-p-isopropylbenzoate) from 190-330 K.

[b]Authors' tabulated data above the glass transition (350-500 K) were curve fitted into the equation

$$C_p = 0.4775\ T + 167.15 \quad J\ mol^{-1}K^{-1} \quad (RMS\ dev = 0.1\%).$$

This equation was used to calculate the heat capacity of molten poly(vinyl-p-isopropylbenzoate) from 340-500 K.

Table 46. Heat capacity measurements of poly(vinyl-p-tert-butylbenzoate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Pasquini et al. (1979) [82]	21. Amorphous (X-ray) $\bar{M}_v$ = 91,500 ρ = 1.112 Mg m^{-3} T_g = 394 K	190-500	DSC (unreported)	190-390: Equation[a] 400-500 Equation[b]

[a]Authors' tabulated data below the glass transition (190 to 370 K) were curve fitted into the equation

$$C_p = 0.8218\ T + 26.51 \quad J\ mol^{-1}K^{-1} \quad (RMS\ dev = 0.3\%).$$

This equation was used to calculate the heat capacity of amorphous, glassy, poly(vinyl-p-tert-butylbenzoate).

[b]Authors' tabulated data above the glass transition (410 to 500 K) were curve fitted into the equation

$$C_p = 0.6569\ T + 151.88 \quad J\ mol^{-1}K^{-1} \quad (RMS\ dev = 0.1\%).$$

This equation was used to calculate the heat capacity of molten poly(vinyl-p-tert-butylbenzoate) from 400 to 500 K.

Table 47. Recommended heat capacity data for poly(vinyl benzoate)s[a] below the glass transition in J $mol^{-1}K^{-1}$[f]

T(K)	18[b]	19[c]	20[d]	21[e]
190.0	106.4	146.3	161.5	182.7
200.0	111.6	152.9	168.3	190.9
210.0	116.8	159.4	175.2	199.1
220.0	121.9	166.0	182.0	207.3
230.0	127.1	172.6	188.8	215.5
240.0	132.3	179.2	195.7	223.8
250.0	137.5	185.8	202.5	232.0
260.0	142.7	192.4	209.3	240.2
270.0	147.8	199.0	216.2	248.4
280.0	153.0	205.6	223.0	256.6
290.0	158.2	212.2	229.8	264.8
300.0	163.4	218.8	236.7	273.1
310.0	168.6	225.4	243.5	281.3
320.0	173.7	232.0	250.3	289.5
330.0	178.9	238.5	257.1	297.7
340.0	184.1			305.9
350.0				314.2
360.0				322.4
370.0				330.6
380.0				338.8
390.0				347.0

[a]Sample numbers correspond to the samples described in tables 43 to 46.

[b]Poly(vinyl benzoate)

[c]Poly(vinyl-p-ethylbenzoate)

[d]Poly(vinyl-p-isopylbenzoate)

[e]Poly(vinyl-p-tert-butylbenzoate)

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

Table 48. Recommended heat capacity data for molten poly(vinyl benzoate)s in J $mol^{-1}K^{-1}$[f]

T(K)	18[b]	19[c]	20[d]	21[e]
330.0		295.4		
340.0		299.9	329.5	
350.0	258.1	304.3	334.3	
360.0	261.0	308.6	339.1	
370.0	263.9	313.3	343.8	
380.0	266.7	317.7	348.6	
390.0	269.6	322.2	353.4	
400.0	272.5	326.6	358.2	414.6
410.0	275.4	331.1	362.9	421.2
420.0	278.2	335.6	367.7	427.8
430.0	281.1	340.0	372.5	434.3
440.0	284.0	344.5	377.3	440.9
450.0	286.9	348.9	382.0	447.5
460.0	289.8	353.4	386.8	454.1
470.0	292.6	357.9	391.6	460.6
480.0	295.5	362.3	396.4	467.2
490.0	298.4	366.8	401.1	473.8
500.0	301.3	371.3	405.9	480.3

[a]Sample numbers correspond to the samples described in tables 43 to 46.

[b]Poly(vinyl benzoate)

[c]Poly(vinyl-p-ethylbenzoate)

[d]Poly(vinyl-p-isopropylbenzoate)

[e]Poly(vinyl-p-tert-butylbenzoate)

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

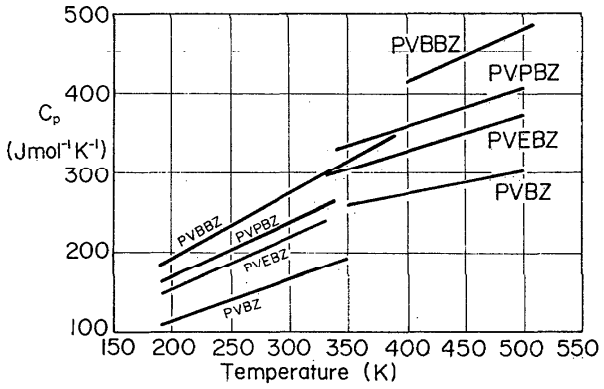

FIG. 7. Recommended heat capacity data for poly(vinyl benzoate) (PVBZ), poly(vinyl-p-ethylbenzoate (PVEBZ), poly(vinyl-p-isopropylbenzoate) (PVPBZ), and poly(vinyl-p-tert-butylbenzoate) (PVBBZ).

pacity of amorphous, glassy and molten poly(vinyl benzoate)s, the data below the start of the glass transition and beyond the end of the glass transition were separately curve fitted into linear functions and extrapolated to the glass transition temperatures. These recommended values are listed in Tables 47 and 48 and plotted in Fig. 7.

3. Conclusions

The heat capacities of poly-1-butene, poly-1-pentene, poly-1-hexene, polyisobutylene, poly(4-methyl-1-pentene), polybutadiene, *cis*-1, 4-poly(2-methylbutadiene), polycyclopentene, poly(vinyl fluoride), poly(vinylidene fluoride), polytrifluoroethylene, polytetrafluoroethylene, poly(vinyl chloride), poly(vinylidene chloride), polychlorotrifluoroethylene, poly(vinyl alcohol), poly(vinyl acetate), poly(α-methylstyrene), poly(o-methylstyrene), poly(o-chlorostyrene), poly(vinyl benzoate), poly(vinyl-p-ethylbenzoate), poly(vinyl-p-isopropylbenzoate), and poly(vinyl-p-tert-butylbenzoate) are reviewed on the basis of 62 measurements reported in the literature. A set of recommended data is derived for each polymer. Entropy and enthalpy functions have been derived

Table 49. Heat capacity change at the glass transition

Polymer	T_g(K)	ΔC_p(J mol^{-1}K^{-1})
Poly-1-butene	249	23.1
Poly-1-pentene	233	27.0
Poly-1-hexene	233	25.1
Polyisobutylene	200	21.3
cis-1,4-Poly(2-methylbutadiene)	200	30.0
Polycyclopentene	173	28.9
Poly(vinyl chloride)	354	19.4
Poly(vinyl acetate)	304	53.7
Poly(α-methylstyrene)	441	25.3
Poly(vinyl benzoate)	347	69.5
Poly(vinyl-p-ethylbenzoate)	330	56.9
Poly(vinyl-p-isopropylbenzoate)	335	66.6
Poly(vinyl-p-tert-butylbenzoate)	394	60.4

for poly-1-hexene, polyisobutylene, *cis*-1, 4-poly(2-methylbutadiene), poly(vinyl chloride), and poly(α-methyl styrene).

Recommended heat capacity data on these polymers are being analyzed in terms of their chemical structure to derive heat capacities of various structural units towards an updated heat capacity addition scheme.[86–88] The results of this analysis will be reported at a later date.

Heat capacity changes at the glass transition, for polymers discussed in this paper, for which recommended heat capacity data are available in their glassy and molten states are listed in Table 49. These $\Delta C_p(T_g)$ data are being analyzed, along with $\Delta C_p(T_g)$ data for other linear macromolecules in terms of the hole theory of the glass transition.[17,87] The results of this analysis will also be discussed at a later date.

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