Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. VIII. Polyesters and Polyamides

Umesh Gaur, Suk-fai Lau, Brent B. Wunderlich, and Bernhard Wunderlich

⊕
View Online

⬆
Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. VIII. Polyesters and Polyamides

Umesh Gaur, Suk-fai Lau, Brent B. Wunderlich, and Bernhard Wunderlich

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Heat capacity of polyglycolide, poly(ϵ-caprolactone), poly(ethylene terephthalate), poly(ethylene sebacate), polyglycine, poly(L-alanine), poly(L-valine),nylon 6, nylon 6.6, and nylon 6.12 is reviewed on the basis of measurements on 35 samples reported in the literature. All heat capacity data are compiled and a set of recommended data have been derived for each polymer. Crystallinity dependence is critically evaluated for poly(ethylene terephthalate). Enthalpy and entropy functions are calculated for amorphous poly-(ethylene terephthalate). This is the eighth paper in a series of publications which will ultimately cover all heat capacity measurements of linear macromolecules.

Key words: amorphous; crystal; enthalpy; entropy; fusion; glass transiton; heat capacity; polyester; polyamide; polypeptide; nylon; thermodynamic properties.

Contents

List of Tables Deposited in PAPS[a]

List of Figures

1. Introduction

This is the eighth paper in a series of discussions on the heat capacity of linear macromolecules. In the earlier papers,[1-7] the heat capacity of selenium, polyethylene, polypropylene, polystyrene and various types of polyoxides, acrylic polymers, and other carbon backbone polymers have been analyzed. In this paper polyesters and polyamides for which heat capacity data are available have been analyzed. These are polyglycolide, poly(ε-caprolactone), poly(ethylene terephthalate), poly(ethylene sebacate), polyglycine, poly(L-alanine), poly(L-valine), nylon 6, nylon 6.6, and nylon 6.12. In the last paper in this series the analysis of heat capacities of aromatic and inorganic polymers will be reported.

2. Heat Capacity of Polyesters

2.1. Introduction

Polyesters derive from all-carbon backbone polymers by occasional substitution of the ester group —COO in the backbone chain. The repeating units, formula weight, crystal structure, density, melting temperature, heat of fusion, and glass transition temperature of all polyesters analyzed in this paper are listed in Table 1.[9,47,48]

The ester group is directional, and successive units can be introduced into the polymer so that all point in one direction or, in alternating directions. The first type of polymer is polar and can be obtained on polymerization of a hydroxy acid or the corresponding lactone. The second polyester is nonpolar and the polymerization can be thought of as involving the reaction of a diacid with a glycol.

The first and the fifth members of the series of polar, unsubstituted aliphatic polyesters are polyglycolide and poly-ε-caprolactone. Chatani et al.[8,47] have reported crystal stuctures of both, polyglycolide and poly-ε-caprolactone. Polyglycolide crystals contain planar zig-zag chains in an arrangement different from all three polyethylene structures.[47] Increasing the number of CH_2 groups per ester

Table 1. Crystal structures and thermal properties of polyesters

Polyester (Formula wt.) Structure of repeat unit	Crystal syst. space group mol. helix	Unit cell axes and angles	No. of units.	ρ_c Mg m^{-3}	Crystal packing density	T_m (K)	ΔH_f kJ mole^{-1}	ρ_a Mg m^{-3}	Amorph. packing density	T_g (K)
poly(ethylene terephthalate) [192.16] -(CH$_2$)$_2$O-CO- C$_6$H$_4$-CO-O-	TRIC PĪ 12*1/1	0.448 0.585 1.075* 99.5 118.4 112.2	2	1.515	0.78	553	26.9	1.336	0.74	342
Poly(ethylene sebacate) [228.28] -(CH$_2$)$_2$O-CO- (CH$_2$)$_8$-CO-O-	MONO P2$_1$/a 14*1/1	0.552 0.730 1.665 β=115.0	2	1.247	0.73	356	32.0	1.085	0.64	
polyglycolide [58.04] -CH$_2$-CO-O-	ORTH Pcmn 3*2/1	0.522 0.619 7.02*	4	1.700	0.81	506	11.1	1.450	0.69	318
poly(ε-caprolactone) [114.15] -(CH$_2$)$_5$-CO-O-	ORTH P2$_1$2$_1$2$_1$ 7*2/1	0.747 0.498 17.05*	4	1.195	0.70	337	16.2	1.096	0.64	209

group must naturally lead to crystal structures similar to polyethylene. Poly-ε-caprolactone already comes close to the polyethylene structure.[8] Equilibrium melting parameters of polyglycolide and poly-ε-caprolactone have been established by Wunderlich.[9] Their crystal structures and related properties are listed in Table 1.

Poly(ethylene terephthalate) is the simplest polyester with a phenylene group within its backbone. Its crystal structure is practically fully extended. The ester groups are tilted about 12° out of the plane of the benzene rings and the CH$_2$–CH$_2$ sequence is rotated about 20° out of the trans-conformation, less than in the aliphatic polyesters of sufficiently long CH$_2$ sequences. Fakirov et al.[10] have recently redetermined the complete unit cell parameters. These are listed in Table 1. Equilibrium melting parameters, recently established in our laboratory from calorimetric data on various semicrystalline samples are also listed in Table 1. The glass transition is reasonably well established at 342 K.[11]

The last polyester for which heat capacity measure-ments have been reported in poly(ethylene sebacate). Its crystal structure and related properties are listed in Table 1.

2.2. Literature Data on Heat Capacity of Polyesters

Twenty investigations have been reported in the literature on the heat capacity of various types of polyesters. Heat capacities of over 40 samples have been measured over wide ranges of temperature.

All investigations were critically evaluated in terms of sample characterization, experimental technique used, error limits, and accuracy of representation of data. It was found that only 9 of the 20 investigations met our standards of acceptable data (discussed in Ref. 1). These investigations are discussed in the following Sec. 2.3. Heat capacity data on 25 samples of four types of polyesters are treated. Eleven investigations which did not contain acceptable data were not included in further analysis. These are listed in Table 2, along with brief commets on the reasons for exclusion from this study.

Table 2. Heat capacity investigations on polyesters
not included in this study.

Reference	Reason(s) for exclusion
Steere (1966) [12]	Heat capacities per unit volume reported for poly(ethylene terephthalate). These values are not directly comparable to the data presented here.
Yoshimoto and Miyagi (1966) [13]	Heat capacity data on poly(ethylene terephthalate) could not be read accurately from too small graphs.
Goetze and Winkler (1967) [14]	Heat capacity data reported for poly-(ethylene terephthalate) fibers in various humidity conditions.
Haly and Snaith (1969) [15]	Heat capacity, data reported from 200 to 400 K for poly(ethylene terephthalate)-water system (water concentration 0.72-2.34 g/100 g of polymer). Heat capacity of poly(ethylene terephthalate) was found to be insensitive to the water content.
Privalko et al. (1970) [16]	Heat capacity reported for filled oligomeric poly(ethylene glycol adipate). $\bar{M}_n$ = 2000 in the crystallization and and melting regions.
Hager (1972) [17]	Heat capacity of poly(ethylene terephthalate) was measured using high speed thin foil calorimetry (Heating rate 30,000 deg/min). The data are associated with large error limits.
Mikhal'chenko et al. (1972) [18]	Heat capacity data reported for a commercial sample of crumbled aluminized poly(ethylene terephthalate).
Philips et al. (1975) [19]	Heat capacities reported for oligomeric poly(hexamethylene sebacate) (DP = 1,2,3).
Yagfarov (1975) [20]	Heat capacity data reported for oligomeric poly(butylene adipate) $\bar{M}_n$ = 1770 in the crystallization and melting regions.
Bair et al. (1976) [21]	Heat capacity reported for poly(butylene terephthalate) semicrystalline (w^c = 0.31) from 290 to 515 K in the glass transition and melting regions.
Ito et al. (1978) [22]	Heat capacity reported for amorphous poly(ethylene terephthalate) at 320 K as a function of annealing below the glass transition temperature.

2.3. Recommended Data on Heat Capacity and Thermodynamic Functions of Polyesters

2.3.1. Polyglycolide

Only one investigation[23,24] has been reported in the literature which deals with the heat capacity of polyglycolide. Details of this investigation are given in Table 3. The heat capacity of this sample has been measured over the temperature range from 13 to 550 K. The data are given in Table A1. Table A1 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Ph s. Since only one set of heat capacity data for a sample with crystallinity 0.67 is available, only the recommended data for the heat capacity of semicrystalline polyglycolide (w^c = 0.67) from 0 K to the glass transition temperature (318 K) and of molten polyglycolide from 318 to 550 K have been derived.

To determine the recommended data for semicrystalline polyglycolide (w^c = 0.67) from 0 to 250 K, the authors' data were interpolated using the spline function technique to obtain heat capacity values are every 10° interval. These rec-

Table 3. Heat capacity measurements of Polyglycolide

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lebedev et al. (1978) [23, 24]	16. $\bar{M}_v$=38,000 ΔH_f=15.7 kJ mol^{-1} w^c=0.67	13-550	Adiabatic (1%)	5-10K: Equation[a] 20-550K: Table[b]

[a]c_p = 2.46 D_3(100/T)

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

Table 4. Recommended heat capacity data for semicrystalline (w^c = 0.67) polyglycolide[a]

T(K)	C_p (J mol^{-1}K^{-1})
0.0	0.0
5.0	0.1990
10.0	1.547
15.0	4.368
20.0	7.973
25.0	11.92
30.0	16.00
40.0	24.22
50.0	32.07
60.0	39.12
70.0	45.39
80.0	51.02
90.0	56.16
100.0	60.94
110.0	65.48
120.0	69.80
130.0	73.90
140.0	77.78
150.0	81.44
160.0	84.88
170.0	88.10
180.0	91.10
190.0	93.87
200.0	96.43
210.0	98.78
220.0	101.1
230.0	103.5
240.0	106.3
250.0	109.5
260.0	111.6
270.0	114.2
273.15	115.0
280.0	116.7
290.0	119.3
298.15	121.4
300.0	121.9
310.0	124.4
318.0(T_g)	126.5

[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.

ommended data are listed in Table 4.

The measured heat capacity values from 260 to 300 K are somewhat higher, because they are associated with the beginning of the glass transition. The data from 260 K up to T_g (318 K) were determined by linearly extrapolating the data below 250 K. The heat capacity values from 200 to 250 K were curve fitted into the equation

$$C_p = 0.2570 \, T + 44.78 \ \text{J mol}^{-1} \text{K}^{-1}. \tag{1}$$

Table 5. Recommended heat capacity data for molten polyglycolide[a]

T(K)	C_p (J mol^{-1}K^{-1})
318.0(T_g)	226.5
320.0	226.6
330.0	227.4
340.0	228.1
350.0	228.8
360.0	229.6
370.0	230.3
380.0	231.0
390.0	231.7
400.0	232.5
410.0	233.2
420.0	233.9
430.0	234.7
440.0	235.4
450.0	236.1
460.0	236.9
470.0	237.6
480.0	238.3
490.0	239.1
500.0	239.8
510.0	240.5
520.0	241.3
530.0	242.0
540.0	242.7
550.0	243.4

[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.

The rms deviation was 0.3%. Equation (1) was used to evaluate the recommended heat capacity of semicrystalline polyglycolide from 260 to 318 K. These values are listed in Table 4 and plotted in Fig. 1.

The recommended data on the heat capacity of molten polyglycolide were determined by curve fitting the data on sample 26 at 501 and 550 K into the equation

$$C_p = 0.07315 \, T + 203.2 \ \text{J mol}^{-1} \text{K}^{-1}. \tag{2}$$
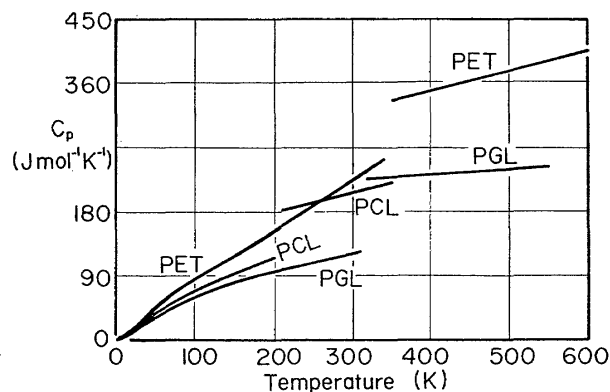
FIG. 1. Recommended heat capacity data for polyglycolide (PGL), poly-ϵ-caprolactone (PCL), and poly(ethylene terephthalate) (PET).

Equation (2) was used to evaluate the heat capacity of molten polyglycolide from 318 to 550 K. These values are listed in Table 5 and plotted in Fig. 1.

2.3.2. Poly(ε-caprolactone)

Only one investigation[25] has been reported in the literature which deals with the heat capacity of poly(ε-caprolactone). Details of this investigation are given in Table 6. The heat capacity of one sample has been measured over the temperature range from 10 to 350 K. The data on this sample are given in Table A2. Table A2 has been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. Since only one set of heat capacity data of poly(ε-caprolactone) with crystallinity of 0.76 is available, only the recommended data for the heat capacity of semicrystalline poly(ε-caprolactone) $(w^c = 0.76)$ from 10 K to the glass transition temperature (209 K) and of molten poly(ε-caprolactone) from 209 to 350 K have been derived.

To determine the recommended data for semicrystalline poly(ε-caprolactone) $(w^c = 0.76)$ from 0 to 200 K, the authors' data were interpolated using the spline function technique to obtain heat capacity values at every 10° interval. These recommended data are listed in Table 7 and are plotted in Fig. 1.

The recommended data on the heat capacity of semicrystalline poly(ε-caprolactone) at the glass transition temperature were determined by curve fitting the data on sample 27 from 150 to 200 K into the equation

$$C_p = 0.4533\, T + 26.11 \text{ J mol}^{-1}\text{ K}^{-1}. \tag{3}$$

The rms deviation was 0.1%. Equation (3) was used to evaluate the heat capacity of semicrystalline poly(ε-caprolactone) at 209 K. This value is listed in Table 7.

The recommended data on the heat capacity of molten poly(ε-caprolactone) were determined by curve fitting the data on sample 27 at 342 and 350 K into the equation

Table 6. Heat capacity measurements of poly(ε-caprolactone)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Lebedev et al. (1974) [25]	27. Melt Crystallized $\bar{M}_w = 29,000$ $\Delta H_f = 12.27$ kJ mol^{-1} $w^c = 0.76$	10-350	Adiabatic (1%)	Table

Table 7. Recommended heat capacity data for semicrystalline $(w^c = 0.76)$ poly(ε-caprolactone)[a]

T (K)	C_p (J mol^{-1}K^{-1})
0.0	0.0
10.0	2.42
20.0	10.72
30.0	20.66
40.0	30.17
50.0	38.36
60.0	45.74
70.0	52.88
80.0	59.61
90.0	65.67
100.0	71.18
110.0	76.14
120.0	80.92
130.0	85.43
140.0	89.82
150.0	94.19
160.0	98.62
170.0	103.1
180.0	107.7
190.0	112.2
200.0	116.8
209.0 (T_g)	120.9

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

Table 8. Recommended heat capacity data for molten
poly(ε-caprolactone)[a]

T(K)	C_p (J mol^{-1}K^{-1})
209.0(T$_g$)	181.1
210.0	181.4
220.0	184.2
230.0	187.1
240.0	190.0
250.0	192.9
260.0	195.7
270.0	198.6
273.15	199.5
280.0	201.5
290.0	204.4
298.15	206.7
300.0	207.2
310.0	210.1
320.0	213.0
330.0	215.9
340.0	218.7
350.0	221.6

[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

$$C_p = 0.2875\ T + 121.0\ \text{J mol}^{-1}\text{K}^{-1}. \qquad (4)$$

Equation (4) was used to evaluate the heat capacity of molten poly(ε-caprolactone) from 209 to 350 K. These values are listed in Table 8 and are plotted in Fig. 1.

2.3.3. Poly(ethylene terephthalate)

Six acceptable investigations[26–31] have been reported in the literature which deal with the heat capacity of poly(ethylene terephthalate). Details of these investigations are given in Table 9. The heat capacities of 25 samples have been measured over the temperature range from 1.2 to 590 K. The data on these samples are given in Tables A3 to A6. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. The heat capacity of various poly(ethylene terephthalate) samples at temperatures below 10 K are given in Table A3. The data on samples below and above the glass transition are given in Tables A4 and A5, respectively. Finally, the data on molten poly(ethylene terephthalate) are given in Table A6. All measurements are either on semicrystalline samples with low crystallinity (samples 1, 2, 10–14, 16–22, and 24) or completely amorphous samples (samples 6, 8, 9, 15, 23, and 25). Thus, the calculation of the heat capacity of completely crystalline poly(ethylene terephthalate) from crystallinity extrapolations using the two phase model cannot be made safely.

The heat capacity of three drawn poly(ethylene terephthalate) (samples 3, 4, and 5) have also been reported by Smith et al.[26] These samples give higher heat capacity values than those that have not been under any strain. Therefore, these three samples are not included in the analysis of the heat capacity data for poly(ethylene terephthalate).

To determine the recommended values of heat capacity of amorphous poly(ethylene terephthalate) below 10 K, the data on samples 8, 9, and 15 were averaged at each temperature and curve fitted into the equation

$$C_p = \exp[-0.112238(\ln T)^3 + 0.458274(\ln T)^2$$
$$+ 2.51758(\ln T) - 4.33633]\ \text{J mol}^{-1}\text{K}^{-1}. \qquad (5)$$

The rms deviation was 2.0%. Equation (5) was used to calculate the recommended values of heat capacity of amorphous poly(ethylene terephthalate) from 1.2 to 10 K. These values are listed in Table 10.

An attempt was made to calculate the heat capacity of crystalline poly(ethylene terephthalate) below 10 K by extrapolating the data in Table A3 with respect to crystallinity. It was found that the heat capacity of semicrystalline samples does not vary linearly with crystallinity. This situation seems to indicate that heat capacity of semicrystalline poly(ethylene terephthalate) does not depend only on the crystallinity.

Only two samples (sample 23 and 24) were available to give the heat capacity data between 12 to 25 K. Since these reported data had to be retrieved from too small graph, they are not very reliable.

From 30 to 120 K, Roinishvili's data[27] on amorphous sample were used as recommended data for this region because no other data were available.

To determine the heat capacity of completely amorphous poly(ethylene terephthalate) above 130 K and up to T_g (342 K) the data at each temperature from 240 to 330 K from samples 1, 2, 6, 19–25 were plotted as a function of crystallinity. Plots of w^c vs C_p at several temperatures are

GAUR ET AL.

Table 9. Heat capacity measurements of poly(ethylene terephthalate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[a]
Smith and Dole (1956) [26]	1. Melt annealed[b] ρ =1.423 Mg m^{-3} ΔH_f=17.21 kJ mol^{-1} w^c= 0.52	270-470	Adiabatic (1%)	270-320K: Equation 1 380-470K: Equation 2
	2. Premelt annealed fiber[b] ρ = 1.404 Mg m^{-3} ΔH_f=14.39 kJ mol^{-1} w^c=0.41	260-470	Adiabatic (1%)	260-350K: Equation 3 370-470K: Equation 4
	3. Flake[b] ρ =1.341 Mg m^{-3} ΔH_f=14.23 kJ mol^{-1} w^c=0.03	250-330	Adiabatic (1%)	Equation 5
	4. Drawn[b] ρ =1.374 Mg m^{-3} ΔH_f=14.39 kJ mol^{-1} w^c=0.23	260-330	Adiabatic (1%)	Equation 6
	5. Cold-drawn[b] ρ =1.349 Mg m^{-3} ΔH_f=13.91 kJ mol^{-1} w^c=0.08	270-310	Adiabatic (1%)	Equation 7
	6. Undrawn[b] ρ =1.338 Mg m^{-3} ΔH_f=12.70 kJ mol^{-1} w^c=0.01	270-330	Adiabatic (1%)	Equation 8
	7. Melt[b]	540-560	Adiabatic (1%)	Equation 9
Rainishvili, et al. (1967) [27]	23. Amorphous ρ =1.338 Mg m^{-3} w^c=0.01	11-280	Adiabatic (unreported)	Graph
	24. Semicrystalline ρ =1.401 Mg m^{-3} w^c=0.39	11-280	Adiabatic (unreported)	Graph
Assfalg (1975) [28]	8. Amorphous[c] ρ =1.335 Mg m^{-3} w^c=0.0	1.2-10	Transient Method (15%)	Equation 10
	9. Annealed[c] 393 K. 10 min ρ =1.338 Mg m^{-3} w^c=0.013	1.2-10	Transient Method (15%)	Equation 11
	10. Annealed[c] 393 K, 15 min ρ =1.349 Mg m^{-3} w^c=0.082	1.2-10	Transient Method (15%)	Equation 12

Table 9. Heat capacity measurements of poly(ethylene terephthalate)--Continued

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[a]
	11. Annealed[c] 393 K, 30 min ρ =1.362 Mg m^{-3} w^c=0.16	1.2-10	Transient Method (15%)	Equation 13
	12. Annealed[c] 493 K, 30 min ρ =1.382 Mg m^{-3} w^c=0.28	1.2-10	Transient Method (15%)	Equation 14
	13. Annealed[c] 533 K, 3 h ρ =1.405 Mg m^{-3} w^c=0.42	1.2-10	Transient Method (15%)	Equation 15
	14. Annealed[c] 533 K, 24 h ρ =1.421 Mg m^{-3} w^c=0.51	1.2-10	Transient Method (15%)	Equation 16
Choy et al. (1975) [29]	15. Quenched ρ =1.337 Mg m^{-3} w^c=0.00	1.2-4.2	Heat pulse (10%)	Graph
	16. Annealed 373 K, 70 min ρ =1.354 Mg m^{-3} w^c=0.11	1.2-4.2	Heat pulse (10%)	Graph
	17. Annealed 403 K, 30 min ρ =1.382 Mg m^{-3} w^c=0.28	1.2-4.2	Heat pulse (10%)	Graph
	18. Annealed 483 K, 20 h ρ =1.403 Mg m^{-3} w^c=0.40	1.2-4.2	Heat pulse (10%)	Graph
Dröscher (1979) [30]	19. Annealed 527 K, 10 min ΔH_f=9.68 kJ mol^{-1} w^c=0.36	280-520	DSC (Unreported)	Table
	20. Annealed 527 K, 46 min ΔH_f=12.53 kJ mol^{-1} w^c=0.47	280-520	DSC (Unreported)	Table
	21. Annealed 527 K, 260 min ΔH_f=12.49 kJ mol^{-1} w^c=0.46	280-560	DSC (Unreported)	Table
	22. Annealed 527 K, 886 min ΔH_f=12.91 kJ mol^{-1} w^c=0.48	280-570	DSC (Unreported)	Table
Menczel and Wunderlich (1980) [31]	25. Amorphous w^c=0.0	240-590	DSC (1%)	Table

[a] Equations cited as sources of data are tabulated separately in table 9a.

[b] Commercial sample: Dacron (DuPont). $\overline{M}_w$ = 23,000, $\overline{M}_n$ = 15,400

[c] $\overline{M}_n$ = 22,100

Table 9a. Source of data[a]

Eq. 1	$C_p = 0.2399 + 9.22 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.60%)
Eq. 2	$C_p = 0.2628 + 8.62 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.20%)
Eq. 3	$C_p = 0.2431 + 9.23 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.15%)
Eq. 4	$C_p = 0.2502 + 9.31 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.06%)
Eq. 5	$C_p = 0.2502 + 9.40 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.32%)
Eq. 6	$C_p = 0.2482 + 9.89 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.20%)
Eq. 7	$C_p = 0.2525 + 9.42 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.26%)
Eq. 8	$C_p = 0.2469 + 1.007 \times 10^{-3}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.47%)
Eq. 9	$C_p = 0.3243 + 5.65 \times 10^{-4}$ (T-273) cal $g^{-1}K^{-1}$ (Av. Dev.=0.7%)
Eq. 10	$C_p = 6.26 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$
Eq. 11	$C_p = 6.82 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$
Eq. 12	$C_p = 5.80 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$
Eq. 13	$C_p = 5.39 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$
Eq. 14	$C_p = 3.76 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$
Eq. 15	$C_p = 0.05 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$
Eq. 16	$C_p = 7.84 \times 10^{-5} T^3$ J $g^{-1}K^{-1}$

[a]Equation numbers correspond to the equations in table 9.

given in Fig. 2. The results of the crystallinity extrapolations to obtain heat capacity of amorphous poly(ethylene terephthalate) are given in Table 11. The heat capacity of amorphous poly(ethylene terephthalate) from 240 to 330 K, obtained from crystallinity extrapolation, and the heat capacity data on sample 23 from 130 to 230 K were then further smoothed by curve fitted into the following equation:

$$C_p = 6.6153 \cdot 10^4 T^{-2} + 0.72042 T + 8.3776 \text{ J mol}^{-1} \text{K}^{-1}. \quad (6)$$

The rms deviation was 0.5%. Equation (6) was used to evaluate the heat capacity of amorphous poly(ethylene terephthalate) from 130 to 340 K. These recommended values are listed in Table 10 and plotted in Fig. 1.

The recommended data on the heat capacity of molten poly(ethylene terephthalate) above T_g (342 K) were determined by curve fitting the data on sample 7 from 540 to 560 K, on samples 21 and 22 from 550 to 570 K, and on sample 25 from 360 to 400 K and from 540 to 590 K into the equation

$$C_p = 0.282 \, T + 236.95 \text{ J mol}^{-1} \text{K}^{-1}. \quad (7)$$

The rms deviation was 0.9%. Equation (7) was used to evaluate the heat capacity of molten poly(ethylene terephthalate) from 350 to 590 K. These values are listed in Table 10 and plotted in Fig. 1.

Enthalpy and entropy of amorphous poly(ethylene terephthalate) were calculated by numerically integrating the heat capacity data. These thermodynamic functions are listed in Table 10.

2.3.4. Poly(ethylene sebacate)

Only one investigation[32] has been reported in the literature which deals with the heat capacity of poly(ethylene sebacate). Details of this investigation are given in Table 12. The heat capacity of one semicrystalline sample has been measured over the temperature range of 250 to 410 K. The data on this sample are given in Table 13.

Since only one set of heat capacity data are available over a limited temperature, no further analysis of heat capacity data were made.

Table 10. Recommended thermodynamic data for amorphous
poly(ethylene terephthalate)[a]

T(K)	C_p (J mol^{-1}K^{-1})	H_T-H_o (J mol^{-1})	S_T-S_o (J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
1.2	0.02101	0.0126	0.0105
1.4	0.03201	0.0179	0.0145
1.6	0.04672	0.0258	0.0197
1.8	0.06581	0.0370	0.0263
2.0	0.08995	0.0526	0.0345
3.0	0.3115	0.2533	0.1089
4.0	0.7676	0.7929	0.2567
5.0	1.545	1.949	0.5072
6.0	2.719	4.081	0.8883
7.0	4.353	7.617	1.426
8.0	6.496	13.04	2.143
9.0	9.182	20.88	3.059
10.0	12.43	31.69	4.190
30.0	22.91	385.1	24.26
40.0	36.18	680.5	32.60
50.0	48.24	1103	41.94
60.0	56.68	1627	51.49
70.0	63.92	2230	60.78
80.0	69.95	2900	69.72
90.0	77.18	3635	78.38
100.0	84.42	4443	86.89
110.0	91.70	5321	95.28
120.0	100.1	6283	103.6
130.0	105.9	7313	111.9
140.0	112.6	8405	120.0
150.0	119.4	9565	128.0
160.0	126.2	10793	135.9
170.0	133.1	12009	143.7
180.0	140.1	13455	151.5
190.0	147.1	14891	159.3
200.0	154.1	16397	167.0
210.0	161.2	17974	174.7
220.0	168.2	19621	182.4
230.0	175.3	21338	190.0
240.0	182.4	23127	197.6
250.0	189.5	24986	205.2
260.0	196.7	26917	212.8
270.0	203.8	28920	220.3
273.15	206.1	29576	222.8
280.0	210.9	30994	227.9
290.0	218.1	33139	235.4
298.15	223.8	34950	241.6
300.0	225.2	35354	242.9
310.0	232.4	37642	250.4
320.0	239.6	40002	257.9
330.0	246.7	42434	265.4
340.0	253.9	44937	272.9
342.0(T$_g$)	255.6	45446	274.4
342.0(T$_g$)	333.4	45446	274.4
350.0	335.7	48123	282.1
360.0	338.5	51494	291.6
370.0	341.3	54893	300.9
380.0	344.1	58320	310.1
390.0	346.9	61775	319.0

Table 10. Recommended thermodynamic data for amorphous
poly(ethylene terephthalate)[a]--Continued

T(K)	C_p (J mol^{-1}K^{-1})	H_T-H_o (J mol^{-1})	S_T-S_o (J mol^{-1}K^{-1})
400.0	349.8	65258	327.8
410.0	352.6	68770	336.5
420.0	355.4	72310	345.0
430.0	358.2	75878	353.4
440.0	361.0	79474	361.7
450.0	363.9	83099	369.9
460.0	366.7	86752	377.9
470.0	369.5	90433	385.8
480.0	372.3	94142	393.6
490.0	375.1	97879	401.3
500.0	378.0	101644	408.9
510.0	380.8	105438	416.4
520.0	383.6	109260	423.9
530.0	386.4	113110	431.2
540.0	389.2	116988	438.4
550.0	392.1	120895	445.6
560.0	394.9	124830	452.7
570.0	397.7	128793	459.7
580.0	400.5	132784	466.7
590.0	403.3	136803	473.5

[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.
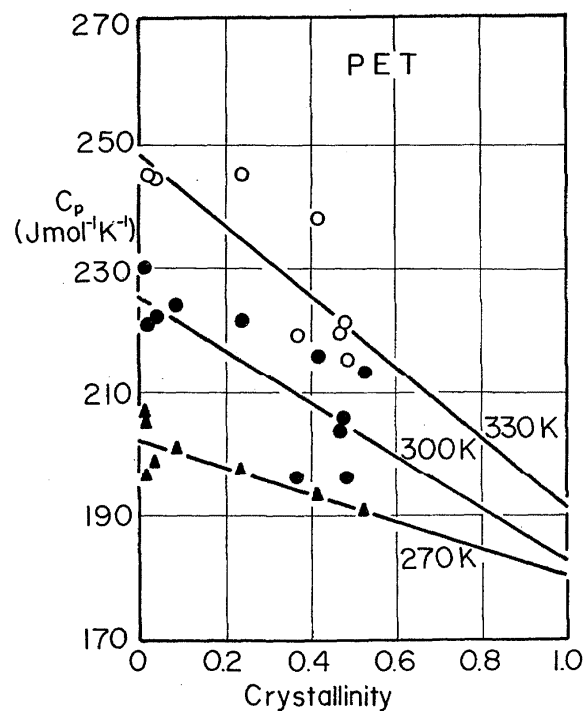
FIG. 2. Heat capacity of poly(ethylene terephthalate) as a function of crystallinity at various temperatures.

GAUR ET AL.

Table 11. Heat capacity vs. crystallinity: Results of curve

fitting data into the equation $C_p = w^c C_p^c + (1-w^c) C_p^a$

T(K)	C_p (amorphous) (J mol^{-1}K^{-1})	RMS deviation (%)
240	183.6	
250	188.5	
260	196.5	1.2
270	202.2	1.5
280	209.6	3.0
290	218.3	3.4
300	225.2	3.3
310	233.3	3.5
320	238.4	3.7
330	248.2	3.0

Table 12. Heat capacity measurements of poly(ethylene sebacate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Wunderlich and Dole (1958) [32]	28. Semicrystalline $\rho = 1.167$ Mg m^{-3} $\Delta H_f = 17.4$ cal/g $w^c = 0.54$	250-410	Adiabatic (1%)	250-310K: Equation[a] 350-410K: Equation[b]

[a]$C_p = 0.159 + 1.26 \times 10^{-8} T^3$ cal g^{-1}C^{-1}. (Authors' curve-fitted equation)

[b]$C_p = 0.444 + 5.81 \times 10^{-4} T$ cal g^{-1}C^{-1}. (Authors' curve-fitted equation)

Table 13. Heat capacity data for poly(ethylene sebacate)

in J mol^{-1}K^{-1}

T(K)	28[a]
250	340.2
260	363.7
270	389.0
280	416.4
290	445.7
300	477.2
310	510.0
320	546.7
melting	
350	467.1
360	472.7
370	478.2
380	483.9
390	489.4
400	494.9
410	500.5

[a]Sample number corresponds to the sample described in table 12.

3. Heat Capacity of Polyamides

3.1. Introduction

Polyamides derive from all-carbon backbone polymers by occasional substitution of the amide group NHCO into the backbone chains. The polyamides derived from the first member of the series, having the general formula CHR–NHCO–, are referred to as polypeptides. Higher members of the series are referred to as nylons

$$\text{Nylon a} \qquad (CH_2-)_{a-1} \overset{\displaystyle O}{\overset{\|}{C}}-NH-$$

$$\text{Nylon a.b} \qquad NH-(CH_2-)_a NH-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2-)_{b-2}\overset{\displaystyle O}{\overset{\|}{C}}-$$
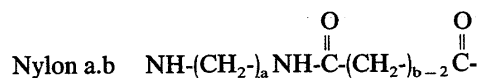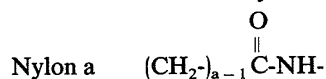
Two other related types of polymers are polyurethanes and polyureas. Both derive from polycarbonates by substitution of one or both of the ester oxygen atom by NH groups, respectively.

Heat capacity data have been reported for a number of polypeptides and nylons over a wide range of temperature. However, the heat capacity measurements on polyurethanes and polyureas have been on poorly characterized samples over only limited temperature ranges.[33-46]

The repeating units, formula weight, and crystal structure of polyglycine and poly-(L-alanine) are listed in Table 14.[47] Reliable crystal structure data on poly(L-valine) are not available. Also, reliable melting and glass transition data are not available for any of the polypeptides. The crystal structures of simple polypeptides are characterized by the α-helix and the pleated sheet (with parallel or antiparallel chains). Polyglycine I is a β structure or pleated structure and the crystal form II is 3*3/1 helix with intermolecular hydrogen bonds. α-poly-(L-alanine) is made up of a statistical distribution of right-handed helices pointing up and down, and the β-crystal form consists of sheets of almost planar zig-zag molecules. The sheets are parallel to the ac plane with hydrogen bonds along the a-axis.

The crystal structure of all the nylons contains two-dimensional layers of fully or almost fully extended polymers linked together by hydrogen bonds as in the pleated sheet structures. Crystal structures for all the nylons for which heat capacity measurements have been reported are listed in Table 15. Also listed in the table are equilibrium melting data for nylon 6 and nylon 6.6 [9] and nonequilibrium melting data for nylon 6.12.[9] Glass transition temperatures for nylons are not well established. Preferred values taken from Ref. 48 are listed in Table 15.

Table 14.   Crystal structures of polypeptides

Polypeptide (formula wt.) structure of repeat unit	Crystal syst. space group mol. helix	Unit Cell axes (nm) and angles	No. of units	ρ_c Mgm^{-3}	Crystal packing density
Polyglycine I (57.05) CH$_2$-CO-NH-		0.477 0.477 0.70 γ=66	2	1.30	
Polyglycine II (57.05) CH$_2$-CO-NH-	TRIG P3$_1$(P3$_2$) 3*3/1	0.48 0.48 0.93	3	1.53	0.79
α-Poly(L-alanine) (71.08) CHCH$_3$-CO-NH-	TRIG (P3$_1$) 3*47/13	0.855 0.855 7.03	47	1.246	0.69
β-Poly(L-alanine) (71.08) CHCH$_3$-CO-NH-	ORTH (C222$_1$) 3*2/1	0.4734 1.0535 0.689	4	1.374	0.76

Table 15.   Crystal structures and thermal properties of nylons

Nylon (Formula wt.) Structure of repeat unit	Crystal syst. space group Mol. helix	Unit cell axes (nm) and angles	No. of units	ρ_c (Mg m^{-3})	Crystal packing density	T_m(K)	ΔH_f (kJ mol^{-1})	(Mg m^{-3})	Amorp. packing density	T_g(K)
Nylon 6, α (113.16) (CH$_2$-)$_5$CO-NH-	MONO P2$_1$ 7*2/1	0.956 1.724 0.801 β=67.5	8	1.235	0.75	543	26.0	1.090	0.66	313-360
Nylon 6,γ (113.16) (CH$_2$-)$_5$CO-NH-	MONO P2$_1$/a 7*2/1	0.933 1.688 0.478 β=121	4	1.163	0.71					
Nylon 6.6,α (226.31) (CH$_2$-)$_6$NH-CO- (CH$_2$-)$_4$CO-NH	TRIC P1 14*1/1	0.49 0.54 1.7? 48.5 77 65.5	1	1.24	0.75	553	67.9	1.091	0.66	∿323
Nylon 6.12 (310.5) (CH$_2$-)$_6$NHCO- (CH$_2$-)$_{10}$CO-NH-										319

GAUR ET AL.

Table 16. Heat capacity measurements of polyglycine

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Fanconi and Finegold (1975) [49, 50]	10. Polyglycine II	2.0-20	Adiabatic (Unreported)	Equation[a]
Finegold and Kumar [51]	11. Polyglycine I	150-375	DSC (8%)	Equation[b]
	12. Polyglygine II	150-375	DSC (8%)	Equation[c]

$$^aC_p = (exp[-0.218472(lnT)^3 + 0.993217(lnT)^2 - 1.33988(lnT + 3.13432)])T^3 \ \mu J \ g^{-1}$$

(authors' tabulated data curve fitted into the equation)

$$^bC_p = 7.592 + 0.401T - 2.505 \cdot 10^{-4}T^2 \ J \ mol^{-1}K^{-1}$$ (authors' curve fitted equation)

$$^cC_p = 34.19 + 0.177T + 8.927 \cdot 10^{-5}T^2 \ J \ mol^{-1}K^{-1}$$ (authors' curve fitted equation)

Table 17. Heat capacity of polyglycine I[a] in J mol^{-1}K^{-1}

T(K)	11
150	62.11
160	65.34
170	68.52
180	71.66
190	74.74
200	77.77
210	80.75
220	83.69
230	86.57
240	89.40
250	92.19
260	94.92
270	97.60
280	100.2
290	102.8
300	105.4
310	107.8
320	110.3
330	112.6
340	115.0
350	117.3
360	119.5
370	121.7

[a] Description of sample 11 is given in table 16.

3.2. Heat Capacity of Polypeptides

Nine investigations[49-57] have been reported in the literature which deal with the heat capacity of various types of polypeptides. Heat capacity data have been reported for various crystal forms of polyglycine, poly(L-alanine), and poly(L-valine). The heat capacities of 10 samples have been measured over a wide temperature range. Details of these investigations are given in Tables 16, 19, and 23. All the measurements meet our standards of acceptable data[b] (discussed in Ref. 1).

Since all the measurements were made on polypeptides of different crystal forms and their mixtures, and only a few measurements are available, no recommendations are made for the heat capacity of polypeptides. Acceptable data on various types of polypeptides are presented in Tables 17, 18, 20–22, and 24. The acceptable data are summarized in Fig. 3.

[b] The data on polyglycine (samples 11 and 12) are associated with large error limits (claimed uncertainty 8%). Since there are the only data available for polyglycine, these measurements were included in the discussion, but should be considered preliminary.

Table 18. Heat capacity of polyglycine II[a] in J mol^{-1}K^{-1}

T(K)	10	12
1.4	0.002542	
1.6	0.003482	
1.8	0.004688	
2.0	0.006207	
3.0	0.02015	
4.0	0.04933	
5.0	0.09991	
6.0	0.1771	
7.0	0.2849	
8.0	0.4253	
9.0	0.599	
10	0.8056	
12	1.308	
14	1.907	
16	2.570	
18	3.265	
20	3.959	
150		62.75
160		64.80
170		66.86
180		68.94
190		71.04
200		73.16
210		75.30
220		77.45
230		79.62
240		81.81
250		84.02
260		86.24
270		88.49
280		90.75
290		93.03
300		95.32
310		97.64
320		99.97
330		102.3
340		104.7
350		107.1
360		109.5
370		111.9

[a]Sample numbers correspond to the samples described in table 16.

GAUR ET AL.

Table 19. Heat capacity measurements of poly(L-alanine)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Finegolad and Cude (1972) [52,53,54]	1. Random form; $M_w = 19,000$	1.5-10	Heat pulse (Unreported)	Graph
	7. α-helix; $M_w = 106,000$	1.5-20	Heat pulse (Unreported)	Equation[a]
	8. β-sheet; $M_w = 5,650$	1.5-20	Heat pulse (unreported)	Equation[b]
Delhaes et al. (1972) [55]	4. Mixture of α-helix (85%) and β-sheet (15%) $M_v = 35,000$	1.5-4.0	Adiabatic (3%)	Graph
Daurel et al. (1975) [56]	5. α-helix (85%)	2.0-300	Adiabatic (3%)	Graph[c]
	6. β-sheet (85%)	2.0-300	Adiabatic (3%)	Graph[c]

[a]Authors' tabulated data curve fitted into the equation

$$C_p = \exp[-0.0434849(\ln T)^3 - 0.0728239(\ln T)^2 + 3.09478(\ln T) - 3.11191] \text{ mJ g}^{-1}\text{K}^{-1}$$

(RMS deviation 1.4%)

[b]Authors' tabulated data curve fitted into the equation

$$C_p = \exp[-0.0897401(\ln T)^3 + 0.198371(\ln T)^2 + 2.78085(\ln T) - 3.32327] \text{ mJ g}^{-1}\text{K}^{-1}$$

(RMS deviation 1.4%)

[c]Heat capacity data presented on a logarithmic plot. Retrieving data from a logarithmic plot increases the error by 2-5%.

Table 20. Heat capacity of random poly(L-alanine)[a] in J mol^{-1}K^{-1}

T(K)	1
1.8	0.01700
2.0	0.02337
3.0	0.07811
4.0	0.1733
5.0	0.3119
6.0	0.4836
7.0	0.6948
8.0	0.9426
9.0	1.218
10	1.521

[a]Sample number corresponds to the sample described in table 19.

Table 21. Heat capacity of alpha poly(L-alanine)[a] in J mol^{-1}K^{-1}

T(K)	4	5	7
1.6	0.007573		0.01328
1.8	0.01270		0.01886
2.0	0.01507	0.01841	0.02573
3.0	0.05806	0.05945	0.08194
4.0	0.1460	0 1397	0.1788
5.0		0.2577	0.3182
6.0		0.4084	0.4992
7.0		0.5598	0.7192
8.0		0.7351	0.9737
9.0		0.9770	1.260
10		1.025	1.573
12		1.548	2.264
14		2.200	3.019
16		2.620	3.811
18		3.724	4.621
20		4.439	5.433
30		8.004	
40		12.53	
50		16.96	
60		21.48	
70		25.46	
80		30.34	
90		34.26	
100		36.84	
110		40.48	
120		44.48	
130		48.99	
140		53.35	
150		57.10	
160		61.30	
170		66.98	
180		73.51	
190		79.98	
200		86.02	
210		91.71	
220		98.32	
230		106.9	
240		116.5	
250		126.0	
260		135.6	
270		146.1	
280		158.7	
290		174.2	
300		191.5	

[a]Sample numbers correspond to the samples described in Table 19.

Table 22. Heat capacity of beta poly(L-alanine)[a] in J mol^{-1}K^{-1}

T(K)	6	8
1.6		0.009793
1.8		0.01381
2.0	0.01260	0.01879
3.0	0.03729	0.06131
4.0	0.09033	0.1394
5.0	0.1780	0.2587
6.0	0.2891	0.4215
7.0	0.4184	0.6274
8.0	0.6280	0.8749
9.0	0.8657	1.160
10	1.096	1.480
12	1.682	2.205
14	2.322	3.015
16	3.033	3.877
18	3.757	4.762
20	4.912	5.646
30	8.920	
40	13.31	
50	17.80	
60	21.48	
70	25.92	
80	31.10	
90	37.07	
100	41.84	
110	46.85	
120	52.34	
130	58.71	
140	65.90	
150	73.62	
160	81.00	
170	87.40	
180	93.68	
190	100.8	
200	108.3	
210	116.0	
220	125.3	
230	137.3	
240	149.4	
250	159.1	
260	168.6	
270	179.8	
280	190.3	
290	197.4	
300	202.2	

[a]Sample numbers correspond to the samples described in table 19.

Table 23. Heat capacity measurements of poly(L-valine)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Daurel et al. (1976) [57]	9. Beta sheet	2.0-300	Adiabatic (3%)	Graph[a]

[a]Heat capacity data presented on a logarithmic plot. Retrieving data from a logarithmic plot increased the error by 2-5%.

Table 24. Heat capacity of poly(L-valine)[a]
in J mol^{-1}K^{-1}.

T(K)	y
2.0	0.02727
3.0	0.08688
4.0	0.2157
5.0	0.4296
6.0	0.6671
7.0	0.9348
8.0	1.349
9.0	1.680
10	2.082
12	2.875
14	3.965
16	5.254
18	6.642
20	8.327
30	13.90
40	21.57
50	32.04
60	37.65
70	47.61
80	57.61
90	65.75
100	78.40
110	89.46
130	115.2
140	131.0
150	145.5
160	160.9
170	180.0
180	200.3
190	220.6
200	239.0
210	255.1
220	272.7
230	295.3
240	320.4
250	345.1
260	371.0
270	399.1
280	423.5
290	439.1
300	449.1

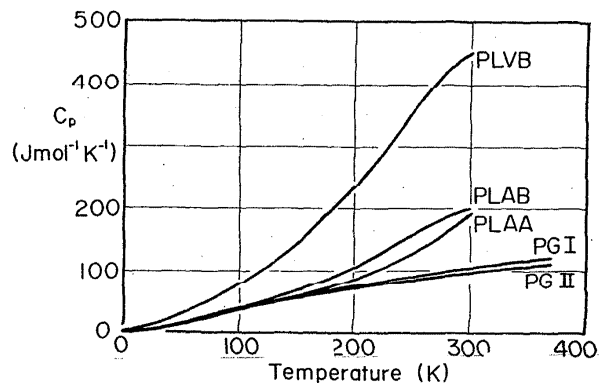[a]Sample number corresponds to the sample described in table 23.

FIG. 3. Heat capacity of polyglycine I (PGI), polyglycine II (PGII), α-poly(L-alanine) (PLAA), β-poly(L-alanine) (PLAB), and β-poly(L-valine) (PLVB).

Table 25. Heat capacity investigations on nylons
not included in this study

Reference	Reason(s) for exclusion
Allen (1952) [58]	Indirect measurement of heat capacity of nylon 6 and nylon 6.6. Data associated with large error limits.
Wilhoit and Dole (1952) [59]	Heat capacity data reported for nylon 6.10. Very limited number of data points to establish heat capacity variation below the glass transition and in the molten state (acceptable data).
Hellwege et al. (1959) [60]	Nylon, type not reported
Mikhailov et al. (1959) [61]	Heat capacity data on various nylons, could not be read accurately from too small graphs.
Kolesov et al. (1962) [62]	Heat capacity data reported for nylon 6 and 7. Based upon additivity of heat capacity, values on nylon 7 are large. Since no characterization of nylon 7 is reported, the sample characterization is questionable.
Tautz et al. (1963, 1964) [63, 64]	Data could not be read accurately from too small graphs.
Jones and Porter (1965) [65]	Heat capacity data reported for nylon 6.6 yarn containing moisture.
Reese and Tucker (1905) [66]	Nylon, type not reported
Yoshimoto and Miyagi (1966) [13]	Heat capacity data on nylon 6, could not be read accurately from too small graphs.
Egorov and Kilesov (1970) [68]	Indirect measurement of heat capacity from thermal diffusivity: Sample characterization not reported for nylon 6.
Neduzhit et al. (1971) [69]	Heat capacity data reported for nylon 6 fibers with various degrees of drawing.
Pilvalko et al. (1979) [70]	Heat capacity data reported for filled nylon 6 over the glass transition and melting regions only.

3.3. Heat Capacity of Nylons

3.3.1. Literature Data on Heat Capacity of Nylons

Nineteen investigations have been reported in the literature on the heat capacity measurements of various types of nylons. Heat capacities of 26 samples have been measured over wide ranges of temperature.

All investigations were critically evaluated in terms of sample characterization, experimental technique used, error limits, and accuracy of representation of data. It was found that only 7 of the 19 investigations met our standards of acceptable data (discussed in Ref. 1). The investigations are listed in Sec. 3.3.2 which contains heat capacity data on 10 samples of three types of nylons. Fourteen investigations which did not contain acceptable data were not included in further analyses. These are listed in Table 25, along with brief comments on the reasons for exclusion for this study.

3.3.2. Recommended Data on Heat Capacity of Nylons

Nylon 6

Four investigations[62,71–73] have been reported in the literature which deal with the heat capacity of nylon 6. Details of these investigations are given in Table 26. The heat capacity of six semicrystalline samples has been measured over the temperature range from 70 to 600 K. The data on these samples are given in Table A7 to A9. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. The heat capacities of various nylon 6 samples below and above the glass transition are given in Tables A7 and A8, respectively. The data on molten nylon 6 are given in Table A9.

The heat capacity data on various semicrystalline samples from 180 K to the glass transition show little or no dependence on the crystallinity (Table A7). Thus crystallinity independent data cannot be derived for nylon 6 below the glass transition.

The recommended data on the heat capacity of nylon 6 below the transition was determined by curve fitting the data on samples 1, 2, 3, 4, 5, and 13 from 70 to 300 K into the equation

$$C_p = \exp[0.174083(\ln T)^3 - 2.56412(\ln T)^2 + 13.3387(\ln T) - 19.8298] \text{ J mol}^{-1}\text{K}^{-1}. \quad (8)$$

The rms deviation was 1.3%. Equation (8) was used to evaluate the heat capacity of nylon 6 from 70 to 313 K. These values are listed in Table 27 and plotted in Fig. 4.

The recommended data on the heat capacity of molten nylon 6 were determined by curve fitting the data on samples 4, 5, and 13 from 500 to 600 K into the equation and plotted

Table 26. Heat capacity measurements of nylon 6

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Marx et al. (1955) [71]	1. Undrawn (melt annealed) DuPont (1050 denier, 34 filament) M_w = 18,500 w^c = 0.67[a]	270-430	Adiabatic (0.5%)	Graph
	2. Drawn DuPont (210 denier, 34 filament) M_w = 18,500 w^c = 0.45[a]	270-450	Adiabatic (0.5%)	Graph
Kolesov et al. (1962) [62]	3. Highly crystalline[b]	70-360	Vacuum Adiabatic (1%)	Table
Gee and Melia (1970) [72]	4. Film form sample ρ = 1.125 Mg m^{-3} M_v = 46,000 w^c = 0.27	180-560	DSC (2%)	180-310 K: Equation[d] 500-560 K: Equation[e]
	5. Film (0.5 mm thick) ρ = 1.125 Mg m^{-3} M_v = 46,000 w^c = 0.27 The film has been irradiated with Co^{60} γ-radiation at 298 K, total dose 600 Megrad before DSC analysis.	180-560	DSC (2%)	180-310 K: Equation[d] 500-560 K: Equation[f]
Gaur and Wunderlich (1979) [73]	13. Zytel 211; DuPont ρ = 1.130 Mg m^{-3} w^c = 0.30[c]	230-600	DSC (1%)	Table

[a]Enthalpy measurements

[b]Crystallinity unreported

[c]From density measurements

[d]C_p = 0.179 + 4.27·10^{-3} J K^{-1}g^{-1}

[e]C_p = 1.331 + 2.73·10^{-3} J K^{-1}g^{-1}

[f]C_p = 1.236 + 2.73·10^{-3}T J K^{-1}g^{-1}

Table 27. Recommended heat capacity data for nylon 6 below the glass transition[a]

T(K)	Heat Capacity $(J\ mol^{-1}K^{-1})$
70.0	49.78
80.0	56.40
90.0	62.45
100.0	68.06
110.0	73.34
120.0	78.38
130.0	83.26
140.0	88.01
150.0	92.70
160.0	97.35
170.0	102.0
180.0	106.7
190.0	111.4
200.0	116.2
210.0	121.0
220.0	126.0
230.0	131.0
240.0	136.2
250.0	141.4
260.0	146.9
270.0	152.4
273.15	154.1
280.0	158.1
290.0	164.0
298.15	168.8
300.0	170.0
310.0	176.2
313.0(T_g)	178.1

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

FIG. 4. Recommended heat capacity data for nylon 6, nylon 6.6, and nylon 6.12.

Table 28. Recommended heat capacity data for molten nylon 6[a]

T(K)	Heat Capacity $(J\ mol^{-1}K^{-1})$
313.0(T_g)	271.7
320.0	272.6
330.0	274.3
340.0	275.8
350.0	277.4
360.0	278.9
370.0	280.4
380.0	281.9
390.0	283.5
400.0	285.0
410.0	286.5
420.0	288.0
430.0	289.6
440.0	291.1
450.0	292.6
460.0	294.1
470.0	295.7
480.0	297.2
490.0	298.7
500.0	300.2
510.0	301.8
520.0	303.3
530.0	304.8
540.0	306.3
550.0	307.9
560.0	309.4
570.0	310.9
580.0	312.4
590.0	314.0
600.0	315.5

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

in Fig. 4:

$$C_p = 0.1526\ T + 223.95\ \mathrm{J\ mol^{-1}\ K^{-1}}. \tag{9}$$

The rms deviation was 2.2%. Equation (9) was used to evaluate the heat capacity of molten nylon 6 from 313 to 600 K. These values are listed in Table 28 and plotted in Fig. 4.

Nylon 6.6

Four investigations[59,73–75] have been reported in the literature which deal with the heat capacity of nylon 6.6. Details of these investigations are given in Table 29. Heat capacity of five semicrystalline samples have been measured over the temperature range of 0.3 to 600 K. The data on these samples are given in Tables A10 to A13. These tables have been deposited with the Physics Auxiliary Publication Ser-
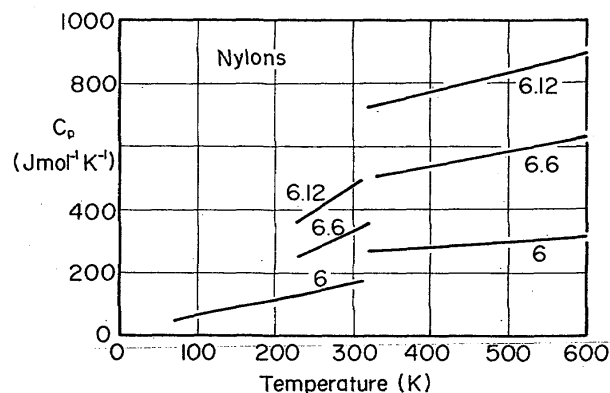
vice of the American Institute of Physics. Table A10 contains heat capacity data on nylon 6.6 at low temperatures. Tables A11 and A12 contain data on semicrystalline nylon 6.6 below and above the glass transition, respectively. Heat capacity data on molten nylon 6.6 are listed in Table A13.

At low temperatures (below 5 K) the heat capacity of linear macromolecules shows a large dependence upon crystallinity. It is necessary to extrapolate the heat capacity with

respect to crystallinity using the two phase model (discussed in Ref. 2). Since heat capacity data below 5 K are available only for two samples ($w^c = 0.36$) and these data are in good agreement, the recommended heat capacity below 5 K have been derived only for semicrystalline nylon 6.6 ($w^c = 0.36$).

The recommended data on the heat capacity of semicrystalline nylon 6.6 ($w^c = 0.36$) were determined by curve fitting the data on samples 9 and 10 from 0.3 to 4.0 K into the

Table 29. Heat capacity measurements of nylon 6.6

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Wilhoit and Dole (1953) [59]	6. Annealed $M_n = 11,000$ $w^c = 0.70$ (enthalpy)	280-510	Adiabatic (2%)	Table[a]
	7. Hot drawn (80 denier; tensile strength = 6.5g/denier elongation at break = 14.3%) $M_n = 11,000$ $w^c = 0.58$ (enthalpy)	280-510	Adiabatic (2%)	Table[a]
Brewer et al. (1966) [74]	9. Commercial sample $\rho = 1.140$ Mg m^{-3} $w^c = 0.36$	1.0-4.0	Heat pulsed (3%)	Graph
Scott et al. (1973) [75]	10. Commercial sample $\rho = 1.140$ Mg m^{-3} $w^c = 0.36$	0.3-1.6	Heat pulsed (Unreported)	Graph
Gaur and Wunderlich (1979) [73]	14. Zytel 101; duPont $\rho = 1.140$ Mg m^{-3} $\overline{M}_n = 11,000$ $w^c = 0.36$	230-600	DSC (1%)	Equation

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

[b]Author's curve fitted equation: Below T_g 230-520K: $C_p = 1.138T - 8.10$ J mol^{-1}K^{-1}
                                                              (RMS dev = 0.4%)

                                      Above T_g 550-600K: $C_p = 0.4683T + 351.14$
                                                              (RMS dev. = 0.3%)

Table 30. Recommended heat capacity data for semicrystalline nylon 6.6 ($w^c = 0.36$)[a]

T(K)	Heat Capacity (mJ mol^{-1}K^{-1})
0.3	0.2308
0.4	0.3951
0.5	0.6426
0.6	0.9946
0.7	1.474
0.8	2.107
0.9	2.919
1.0	3.939
1.2	6.714
1.4	10.67
1.6	16.06
1.8	23.13
2.0	32.13
3.0	114.6
4.0	279.6

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

GAUR ET AL.

Table 31. Recommended heat capacity data for nylon 6.6
below the glass transition temperature

T(K)	Heat Capacity $(J\ mol^{-1}K^{-1})$
230.0	252.1
240.0	263.4
250.0	274.7
260.0	286.0
270.0	297.3
273.15	300.9
280.0	308.6
290.0	320.0
298.15	329.2
300.0	331.3
310.0	342.6
320.0	354.0
323.0(T_g)	357.4

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

Table 32. Recommended heat capacity data for molten nylon 6.6[a]

T(K)	Heat Capacity $(J\ mol^{-1}K^{-1})$
323.0(T_g)	502.4
330.0	505.7
340.0	510.4
350.0	515.0
360.0	519.7
370.0	524.4
380.0	529.1
390.0	533.8
400.0	538.5
410.0	543.1
420.0	547.8
430.0	552.5
440.0	557.2
450.0	561.9
460.0	566.5
470.0	571.2
480.0	575.9
490.0	580.6
500.0	585.3
510.0	590.0
520.0	594.6
530.0	599.3
540.0	604.0
550.0	608.7
560.0	613.4
570.0	618.1
580.0	622.7
590.0	627.4
600.0	632.1

[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.

equation

$$C_p = \exp[-0.110533(\ln T)^3 + 0.297475(\ln T)^2$$
$$+ 2.87493(\ln T) + 1.37083]\ \mathrm{mJ\ mol^{-1}K^{-1}}. \quad (10)$$

The rms deviation was 3.1%. Equation (10) was used to evaluate the recommended data from 0.3 to 4.0 K. These values are listed in Table 30.

The heat capacity data on various semicrystalline samples from 230 to the glass transition temperature show little or no dependence on crystallinity (Table A11). Thus, crystallinity independent data can be derived for nylon 6.6 below the glass transition.

The recommended data on the heat capacity of nylon 6.6 below the glass transition were determined by curve fitting the data on samples 6, 7, and 14 from 230 to 310 K into the equation

$$C_p = 1.132T - 8.28\ \mathrm{J\ mol^{-1}K^{-1}}. \quad (11)$$

The rms deviation was 1.4%. Equation (11) was used to evaluate the heat capacity of nylon 6.6 from 230 to 323 K. These values are listed in Table 31 and are plotted in Fig. 4.

Recommended data on the heat capacity of molten ny-

lon 6.6 were obtained from authors' curve fitted equation on sample 14. These data from 323 to 600 K are listed in Table 32 and are plotted in Fig. 4.

Nylon 6.12

Only one investigation[73] has been reported in the literature which deals with the heat capacity of nylon 6.12. Details of this investigation are given in Table 33. The heat capacity of a semicrystalline sample has been measured over the temperature range from 230 to 600 K.

The heat capacity of nylons shows little or no dependence upon crystallinity from about 100 K to the glass transition (see preceding sections). Thus, crystallinity independent, recommended data can be derived for nylon 6.12 below the glass transition.

Recommended data for nylon 6.12 below the glass transition and for molten nylon were obtained from the author's curve fitted equations for heat capacity of sample 15. These data are listed in Tables 34 and 35 and plotted in Fig. 4.

Table 33. Heat capacity measurements of nylon 6.12

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Gaur and Wunderlich (1979) [73]	15. Zytel 151L: duPont ρ=1.07 Mg m^{-3}	230-600	DSC (1%)	Equation[a]

[a]Author's curve fitted equation

Below T_g 230-310 K: 1.628T - 11.96 J mol^{-1}K^{-1} (RMS dev. 1.1%)

Above T_m 510-600 K: 0.6038T + 529.81 J mol^{-1}K^{-1} (RMS dev. 0.2%)

Table 34. Recommended heat capacity data for nylon 6.12 below the glass transition[a]

T(K)	Heat Capacity (J mol^{-1}K^{-1})
230.0	362.4
240.0	378.7
250.0	395.0
260.0	411.2
270.0	427.5
273.15	432.7
280.0	443.8
290.0	460.1
298.15	473.4
300.0	476.3
310.0	492.6
319.0(T_g)	507.3

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

Table 35. Recommended heat capacity data for
molten nylon 6.12[a]

T(K)	Heat Capacity ($J\ mol^{-1}K^{-1}$)
319.0(T_g)	722.1
320.0	723.0
330.0	729.1
340.0	735.1
350.0	741.1
360.0	747.2
370.0	753.2
380.0	759.3
390.0	765.3
400.0	771.3
410.0	777.4
420.0	783.4
430.0	789.5
440.0	795.5
450.0	801.5
460.0	807.6
470.0	831.6
480.0	819.6
490.0	825.7
500.0	831.7
510.0	837.8
520.0	843.8
530.0	849.8
540.0	855.9
550.0	861.9
560.0	867.9
570.0	874.0
580.0	880.0
590.0	886.1
600.0	892.1

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

4. Conclusions

The heat capacities of polyglycolide, poly(ε-caprolactone), poly(ethylene terephthalate), poly(ethylene sebacate), polyglycine, poly(L-alanine), poly(L-valine), nylon 6, nylon 6.6, and nylon 6.12 are reviewed on the basis of 35 measurements in the literature. A set of recommended data is derived for each polymer. Crystallinity dependence is critically evaluated for poly(ethylene terephthalate) and enthalpy and entropy functions are calculated for amorphous poly(ethylene terephthalate).

Recommended 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.[74-76] 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

Table 36. Heat capacity change at the glass transition

Polymer	T_g(K)	ΔC_p ($J\ mol^{-1}\ K^{-1}$)
Polyglycine	318.0	100.0
Poly(ε-caprolactone)	209.0	60.2
Poly(ethylene terephthalate)	342.0	77.8
Nylon 6	313.0	93.6
Nylon 6.6	323.0	145.0
Nylon 6.12	319.0	214.0

capacity data are available in their glassy and molten states are listed in Table 36. These ΔC_p (T_g) data are being analyzed, along with ΔC_p (T_g) data for other linear macromolecules in terms of the hole theory of the glass transition.[67,75] The results of this analysis will also be reported at a later date.

Acknowledgment

References

[1]U. Gaur, H.-C. Shu, A. Mehta, and B. Wunderlich, J. Phys. Chem. Ref. Data 10, 89 (1981).

[2]U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data 10, 119 (1981).

[3]U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data 10, 1001 (1981

[4]U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data 10, 1051 (1981).

[5]U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data 11, 313 (1982).

[6]U. Gaur, S.-F. Lau, B. B. Wunderlich, and B. Wunderlich, J. Phys. Chem. Ref. Data 11, 1065 (1982).

[7]U. Gaur, B. B. Wunderlich, and B. Wunderlich, "Heat capacity and other thermodynamic properties of linear macromolecules. VII. Other carbon backbone polymers," J. Phys. Chem. Ref. Data (to be published).

[8]Y. Chatani, Y. Okita, H. Tadokoro, and Y. Yamashita, Polymer J. 1, 55 (1970).

[9]B. Wunderlich, Macromolecular Physics. Vol. III. Crystal Melting (Academic, New York, 1980).

[10]S. Fakirov, E. W. Fischer, and G. F. Schmidt, Makromol. Chem. 176, 2459 (1975).

[11]Y. Chatani, K. Suehiro, Y. Okita, H. Tadokoro, and K. Chujo, Makromol. Chem. 113, 215 (1968).

[12]R. C. Steere, J. Appl. Polymer Sci. 10, 1673 (1966).

[13]T. Yoshimoto and A. Miyagi, Kogyo Kagaku Zasshi 69, 1767 (1966).

[14]W. Goetze and F. Winkler, Faserforsch. Textiltech. 18, 385 (1967).

[15]A. R. Haly and J. W. Snaith, Text. Res. J. 39, 906 (1969).

[16]V. P. Privalko, Yu. S. Lipatov, and Yu. Yu. Kercha, "Calorimetric study of the phase boundary effect on oligoethylene glycol adipate," Vysokomol. Soedin., Ser. A. 12, 1340 (1970).

[17]N. E. Hager, Rev. Sci. Instrum. 43, 1116 (1972).

[18]R. S. Mikhal'chenko, N. P. Pershin, A. G. Gerzhin, and E. I. Shchirov, "Temperature dependence of thermal conductivity, specific heat, and thermal diffusivity of laminated vacuum insulators at low temperatures," Teplo-Massoperenos, Dokl. Vses, Soveshch., 4th 7, 454 (1972).

[19]J. C. Phillips, L. A. Wall, and M. H. Aldridge, Polym. End. Sci. 15, 73 (1975).

[20]M. S. Yagfarov, "Recrystallization of poly(butylene adipate)," Vysokomol. Soedin. Ser. A. 17, 2148 (1975).

[21]H. E. Bair, G. H. Beddington, and P. G. Kelleher, J. Polym. Sci. Polym. Phys. Ed. 14, 2113 (1976).

[22]E. Ito, K. Yamamoto, Y. Kobayashi, and T. Hatakeyama, Polymer 1, 39 (1978).

[23]B. V. Lebedev, A. A. Evstropov, E. G. Kiparisova, E. G. Lyudvig, and G. S. Sanina, Dokl. Akad. Nauk. SSSR 236, 669 (1977).

[24]B. V. Lebedev, A. A. Evstropov, E. G. Kiparisova, and V. I. Belov, "Thermodynamics of the glycolide, and glycolide polymerization process in the 0-550 K," Vysokomol. Soedin. Ser. A. 20, 29 (1978).

[25]B. V. Lebedev, A. A. Evstropov, N. K. Lededev, E. A. Karpova, E. B.

Lyudvig, and B. G. Belen'kaya, "Thermodynamics of ε-caprolactone, poly-ε-caprolactone and the ε-caprolactone polymerization process in the region 0–350 K," Vysokomol. Soedin. Ser. A. **20**, 1974 (1978).

[26]C. W. Smith and M. Dole, J. Polym. Sci. **20**, 37 (1956).

[27]E. Yu. Roinishvili, N. N. Tavkhelidzem, and V. B. Akopyan, "Heat capacity of amorphous and crystalline poly(ethylene terephthalate) at low temperature," Vysokomol. Soedin. Ser. B. **9**, 254 (1967).

[28]A. Assfalg, J. Phys. Chem. Solids **36**, 1389 (1975).

[29]C. L. Choy, M. Huq, D. E. Moody, Phys. Lett. A **54A**, 375 (1975).

[30]M. Droescher, Makromol. Chem. **180**, 2783 (1979).

[31]J. Menczel and B. Wunderlich (unpublished results).

[32]B. Wunderlich and M. Dole, J. Polym. Sci. **32**, 125 (1958).

[33]Yu. K. Godovskii and Yu. S. Lipatov, "Heat capacity of linear polyurethanes," Vysokomol. Soedin. Ser. A. **10**, 32 (1968).

[34]V. V. Vasc'ev, G. M. Palyutkin, A. A. Zaplazin, O. G. Tarakanov, A. P. Kafengavz, and F. K. Samigulia, "Effect of the concentration of urethane groups on the heat capacity of polyester urethanes," Sin. Frz,-Khim. Polim. **12**, 103 (1973).

[35]Y. Y. Keroha, Y. S. Lipatov,'S. S. Krafchik, and V. P. Privalko, "Calorimetric study of linear polyurethanes with different distribution of urethane groups," Vysokomol. Soedin. Ser. A. **15**, 1297 (1973).

[36]V. P. Privalko, Yu. S. Lipatov, Yu. Yu. Kercha, and L. V. Mozzhukhina, "Calorimetric investigation of filled linear polyurethanes," Vysokomol. Soedin., Ser. A. **13**, 103 (1971).

[37]Y. S. Lipatov, V. P. Privalko, Y. Y. Kercha, and B. E. Myuller, "Calorimetric studies of linear and cross linked polyurethanes. V. Specific heat of oligotetramethylene glycols and synthesized linear and crosslinked polyurethanes based on them," Sin. Fiz.-Khim. Polim. **6**, 98 (1970).

[38]T. A. Agfarova, L. A. Cherkasova, N. P. Aputhtina, M. S. Yagfarov, and B. Y. Teitel'baum, "Effect of composition on the thermophysical properties of block-polyester urethanes from hexamethylene diisocyanate," Vysokomol. Soedin. Ser. A. **16**, 407 (1974).

[39]M. Sh. Yagfarov and E. F. Gubanov, "Thermal behavior and phase state of some polyester-urethane block copolymer," Vysokomol. Soedin. Ser. A. **12**, 1155 (1970).

[40]S. D. Lipshitz and C. W. Macosko, J. Appl. Polym. Sci. **21**, 2029 (1977).

[41]R. Becker and G. Neumann, "Precalculation of glass temperature of polyurethanes," Plast. Kaut. **20**, 809 (1973).

[42]E. F. Gubanov, M. S. Yagfarov, N. V. Ranova, and R. A. Shlyakhter, "Effect of the polydispersity of oligomeric blocks on the properties of urethane polymers and blocks copolymers formed by them," Sin. Fiz.-Khim. Polum. **12**, 80 (1973).

[43]T. A. Yagfarova, B. Y. Teitel'baum, M. S. Yagfarov, and L. A. Cherkasova, "Effect of the composition on phase states of urethane thermoplastic elastomers based on 4, 4'-diphenylmethane diisocyanate," Vysokomol. Soedin. Ser. A. **19**, 990 (1977).

[44]V. P. Rivalko and Yu. S. Lipatov, "Influence of methane groups on the thermodynamic and kinetic properties of polyurethanes," Vysokomol. Soedin. Ser. A. **14**, 2000 (1972).

[45]V. P. Privalki, Yu. S. Lipatov, and Yu. Yu. Kercha, "Calorimetric study of oligo(ethylene adipates) and linear and crosslinked polyurethanes prepared from them," Vysokomol. Soedin. Ser. A. **11**, 273 (1969).

[46]Yu. K. Godovskii and Yu. S. Lipatov, "Heat capacity of linear polyurethanes based on hexamethylenediisocyanate and triethylene glycol," Vysokomol. Soedin. Ser. B. **10**, 323 (1968).

[47]B. Wunderlich, *Macromolecular Physics. Vol. I. Crystal Structure, Morphology, Defects* (Academic, New York, 1973).

[48]J. Brandup and E. H. Immergut, *Polymer Handbook*, 2nd ed. (Wiley, New York, 1975).

[49]B. Fanconi and L. Finegold, Science **190**, 458 (1975).

[50]L. Finegold and B. Fanconi, "Vibrational states of a biopolymer (polyglycine II)—theory and experiment," Conf. Int. Thermodyn. Chim., (C.C.R.), 4th, **2**, 117 (1975).

[51]L. Finegold and P. K. Kumar, "Specific Heat of Polyglycine I and II in the temperature interval 150–375 K (to be published).

[52]L. Finegold and J. L. Cude, Biopolymers **11**, 683 (1972).

[53]L. Finegold and J. L. Cude, Nature (London) **237**, 334 (1972).

[54]L. Finegold and J. L. Cude, Biopolymers **11**, 2483 (1972).

[55]P. Delhaes, M. Daurel, and E. Dupart, C. R. Acad. Sci. Ser. B. **274**, 308 (1972).

[56]M. Daurel, P. Delhaes, and E. Dupart, "Variations thermiques, Entre 1 et 300 °K de la Chaleur Specifique de la L-Alanine, Tri(L-Alanine), et de la Poly(L-Alanine) sous Formes α et β," Biopolymers **14**, 801 (1975).

[57]M. Daurel, P. Delhaes, and E. Dupart, Biopolymers **15**, 415 (1976).

[58]P. W. Allen, Research **5**, 492 (1952).

[59]R. C. Wilhoit and M. Dole, J. Phys. Chem. **57**, 14 (1953).

[60]K. H. Hellwege, W. Knappe, and V. Semjonow, Z. Angew. Phys. **11**, 285 (1959).

[61]N. V. Mikhailov, E. Z. Fainberg, and V. O. Gorbacheva, "Molecular structure of synthetic polyamide fibers. XV Thermochemical properties of poycapramide-polyundecan-amide polymers of the polyamide series, Vysokomol. Soedin. Vsesoyuz. Khim. Obshchestvo im D. I. Mendeleeva **1**, 201 (1959) II.

[62]V. P. Kolesov, I. E. Paylov, and S. M. Skuratov, "Free energy in the polymerization of lactams under standard condition (low temperature heat capacities of lactams and of potassium chloride)," Zh. Fiz. Khim. **36**, 770 (1962).

[63]H. Tautz, M. Glück, G. Hartmann, and R. Leuteritz, "Die spezifische Warme von Hochpolymeren in Temperaturbereich von — 150 bis + 180 °C," Plaste Kautschuk **10**, 648 (1963).

[64]H. Tautz, M. Glück, G. Hartmann, and R. Leuteritz, "Die spezifische Warme von Hochpolymeren in Abhängigkeit von der Vorgeschichte des Materials," Paste Kautschuk **11**, 657 (1964).

[65]C. R. Jones and J. Porter, J. Textile Inst. Trans. **56**, T498 (1965).

[66]W. Reese and J. E. Tucker, J. Chem. Phys. **43**, 105 (1965).

[67]B. Wunderlich, J. Phys. Chem. **64**, 1052 (1960).

[68]B. N. Egorov and V. S. Kilesov, "Actual specific heat and temperature conductivity of polymers studied by a pulsed-adiabatic method," Plast. Massy **1970**, 72 (1970).

[69]I. A. Neduzhit, S. D. Labinov, T. Y. Shimchuk, and S. A. Vishenskii, "Specific heat capacity and thermal conductivity of polycaprolactam fibers with various degrees of drawing," Sin. Fin.-Khim. Polim. **9**, 73 (1971).

[70]V. P. Privalko, T. Kawai, Yu. S. Liptov, Polym. J. **11**, 699 (1979).

[71]P. Marx, C. W. Smith, A. E. Worthington, and M. Dole, J. Phys. Chem. **59**, 1015 (1955).

[72]T. P. Melia and D. R. Gee, Polymer **11**, 192 (1970).

[73]U. Gaur and B. Wunderlich, "Additivity of the heat capacities of linear macromolecules in the molten state," Polym. Preprints **20**, 429 (1979).

[74]D. F. Brewer, D. O. Edwards, D. R. Howe, and T. E. Whall, Cryogenics **6**, 49 (1966).

[75]T. A. Scott, J. de Bruin, M. M. Giles, and C. Terry, J. Appl. Phys. **44**, 1212 (1973).

[76]B. Wunderlich and L. D. Jones, J. Macromol. Sci.-Phys. **B3**, 67 (1969).

[77]U. Gaur and B. Wunderlich, "Additivity of the heat capacities of linear macromolecules in the molten state," Polymers Division American Chemical Society Preprints **20**, 429 (1979).

[78]B. Wunderlich and U. Gaur, "Addition scheme of heat capacities of linear macromolecule," in *Thermal Analysis, ICTA 80*, edited by W. Hemminger (Birkhaeuser, Basel 1980).