Heat capacities of linear aliphatic polyesters

S. Lim and B. Wunderlich
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12181, USA
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Heat capacities of solid polypentadecanolactone, polytridecanolactone, polyundecanolactone, polycaprolactone, polyvalerolactone, polybutyrolactone, polypropiolactone, polyglycolide, poly(ethylene oxalate), poly(butylene adipate) and poly(ethylene sebacate) were analysed using an approximate group vibration spectrum and fitting of the skeletal heat capacity to a Tarasov function. All polyesters have the same Θ_1 (513.6±19 K) and Θ_3 varies less than would be expected with the variations due to crystallinity for polyethylene, and can be represented by a quadratic function of COO/CH_2. An addition scheme is proposed that is capable of predicting heat capacities of the polyesters with a precision close to experimental accuracy.

(Keywords: crystalline; glassy; heat capacity; poly(butylene adipate); polybutyrolactone; polycaprolactone; polyester; poly(ethylene oxalate); poly(ethylene sebacate); polyglycolide; polypentadecanolactone; polypropiolactone; polytridecanolactone; polyundecanolactone; polyvalerolactone; vibration spectrum)

INTRODUCTION

In several prior papers we established in the framework of ATHAS, our advanced thermal analysis system, the connection between measured and calculated heat capacities of a series of solid, linear macromolecules. The prior analysed polymers were polyethylene and linear aliphatic polyoxides[1], polypropylene[2], fluorinated and chlorinated polyethylenes[3-5], polystyrene and poly(*p*-xylene)[6] and the polybutadienes[7]. The calculations are based on an approximate vibrational frequency spectrum synthesized from group and skeletal vibrations. Inversion of the vibrational spectrum to heat capacity is done with the Einstein function using appropriate computer programs[8]. Agreements between calculation and experiments are usually better than ±5%, close to the experimental precision for many experimental data sets. For chemically similar molecules, it has been possible to derive predictions of heat capacities based on the frequency spectrum[1,5].

In this paper we shall extend this analysis to the linear aliphatic condensation polyesters, $(-(CH_2)_n-OCO-(CH_2)-COO-)_x$, polyglycolide and polylactones, $(-(CH_2)_n-COO-)_x$.

First, the calculated heat capacities of polypentadecanolactone, polytridecanolactone, polyundecanolactone, polycaprolactone, polyvalerolactone, polybutyrolactone, polypropiolactone, polyglycolide and poly(ethylene oxalate) are compared with their experimental heat capacities. From these data a prediction scheme is developed and tested on limited experimental data of poly(ethylene sebacate) and poly(butylene adipate).

COMPUTATIONS

The computations follow the procedure established in the previous work[1-7]. The experimental heat capacities are taken from the prior established databank[9] and some updates[10,11]. As in the databank treatment, the new data were fitted to spline functions and listed in the ATHAS standard intervals for analysis. The general basis of this heat-capacity discussion was detailed earlier[12]. First, the contributions of the group vibrations to heat capacity are calculated and subtracted from the experimental heat capacity, which is first converted to constant-volume heat capacity C_v. The remaining skeletal heat capacity is fitted to the Tarasov equation $T(\Theta_1/T, \Theta_3/T)$ to obtain the limiting one- and three-dimensional vibration frequencies Θ_1 and Θ_3.

All frequencies in this discussion are, for convenience, expressed in kelvin ($1\,cm^{-1} = 1.4388\,K$). The detailed computer programs were given in a previous publication[13]. The C_p-to-C_v conversion is done using the Nernst–Lindemann equation, since experimental data for the conversion are never available over the full temperature range:

$$C_p - C_v = C_p^2 A_0 T / T_m^\circ \qquad (1)$$

where A_0, when expressed per mole of heavy atom (C or O in our case), is close to a universal constant 5.11×10^{-3} K mol J^{-1} (ref. 14) and T_m° is the equilibrium melting temperature.

With the approximate vibrational group frequencies and Θ temperatures established, heat capacities are calculated[8] and compared to the experiment. Note that only two fitting parameters (Θ_1 and Θ_3) are extracted from the experimental data; all other information is independent of heat-capacity measurement.

The linear, aliphatic polyester, being of similar chemical composition except for the number of methylene groups per repeat unit, were treated as follows. The group vibrations were separated into two components with contributions from (a) the methylene (CH_2–) unit and (b) the carboxyl (COO–) unit. Each methylene group contributes one CH_2 asymmetric stretching, one CH_2 symmetric stretching, one CH_2 bending, one CH_2 wagging, one CH_2 twisting, one CH_2 rocking, and one stretching vibration between CH_2 and its neighbouring group (i.e. either CH_2– or CO–). This gives a total of seven group vibrations per methylene group. Each carboxylic group, on the other hand, contributes one C=O stretching, one C–O stretching, one O–CH_2 stretching, one in-plane and one out-of-plane C=O

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bending, a total of five group vibrations per COO– unit. Subtracting the number of group vibrations from the total number of degrees of freedom of each component gives the number of skeletal modes. Thus, each methylene group contributes two skeletal (largely bending and torsion-related) vibrations and each carboxylic group gives four skeletal vibrations (similarly approximately related to the two bending and two torsional vibrations of COO–). The results are summarized in *Table 1*.

Very few studies of the vibrational spectra of the aliphatic polyesters have been made and no full dispersion curves have been published. The assignments in *Table 1* are thus justified by the following observations. Holland-Mortiz[20] showed that for condensation polyesters the C–C stretching frequencies increased less than 2% with the number of methylene groups in the acid. In the alcohol portion, on the other hand, it decreases as m was increased from 4 to 6, then increased up to $m=12$. Again, the overall change was less than 2%. The O–CO and CH_2–O stretching vibrations were constant, regardless of the number of methylene groups in either component, whereas the CO–CH_2 stretching vibration decreased from 1360 K for $n=4$ to a constant value of 1327 K for $n \geqslant 6$. Furthermore, Holland-Moritz and Hummel[21] showed that alcohol CH_2 bending vibrations increased in frequency with the number of methylene groups, but the variation was of the order of only 0.5%. The reverse was true with the acidic CH_2 bending vibrations, which also exhibited variations of the same small order of magnitude. Wagging frequencies decreased by about 2% with each addition of a methylene group; rocking vibrations also decreased in frequency, approaching a constant value in the 900 K region. Tadokoro *et al.*[22] analysed the far-infra-red spectrum of polylactones up to polycaprolactone, making possible the assignments of some isolated skeletal vibrations, which are, however, fitted to experimental heat capacities in our treatment. These observations make it likely then that the approximate frequencies in *Table 1* do not change significantly from polyester to polyester.

For the heat-capacity calculations, approximate group vibration spectra were assembled for the various polyesters, as outlined in *Table 2* for polyglycolide and the polylactones and in *Table 3* for the condensation polyesters treated in this publication. These tables can easily be extended to any other linear, aliphatic polyester.

The results from the fit of the skeletal heat capacity to Tarasov functions are given in *Table 4*. First a preliminary fit of the lowest-temperature heat-capacity data (<30 K) was made to a three-dimensional Debye function yielding the parameter Θ_D (THETA 3 program)[13]. With Θ_D established, the Tarasov fit was carried out using the THETA-TAR-EB program[8,13] giving the best Θ_3, Θ_1 pair representing the skeletal heat capacity. Since Θ_3 changes considerably with crystallinity, an extrapolation to complete crystallinity was made assuming Θ_3 of the polyesters changes parallel to the known change in polyethylene. The results of this extrapolation are also

Table 1 Contributions of methylene and carboxyl groups to the vibrations of solid linear aliphatic polyesters

Mode	N	$\nu(K^a)$	Reference
A. Methylene group (–CH_2–A–)			
Group modes			
CH_2 asym. stretch	1	4148.1	Polyethylene[b]
CH_2 sym. stretch	1	4097.7	
CH_2 bend	1	2074.7	
CH_2 wag	0.65	1698.3–1976.6	
	0.35	1976.6	
CH_2 twist and rock	0.48	1689.6–1874.3	
	0.52	1874.3	
CH_2 rock and twist	0.04	1494.1	
	0.59	1038.0–1494.1	
	0.37	1079.1	
CH_2–A stretch			
($A=CH_2$)	0.34	1377.6–1637.5	
	0.35	1377.6–1525.4	
	0.31	1525.4	
(A=COO)	1	1215	Methyl acetate[c]
Skeletal modes	2		
B. Carboxyl group (–Y–COO–X–)			
Group modes			
C=O stretch	1	2530	Methyl acetate[c]
C–O stretch	1	1800	
O–X stretch ($X=CH_2$)	0.22	1385.1	Polyoxymethylene[d]
	0.11	1632.1	
	0.67	1385.1–1632.1	
Y–C stretch (Y=OOC)	1	1170	Oxalic acid[e]
C=O in-plane bend	1	980	Polylactones[f]
C=O out-of-plane bend	1	840	
Skeletal modes	4		

[a] Single frequency modes are converted to heat capacity with the Einstein function $E(\Theta_E/T)=(\Theta_E/T)^2\exp(\Theta_E/T)/[\exp(\Theta_E/T)-1]^2$. Frequency ranges are assumed to be a box distribution, converted to heat capacity using the equation $B(\Theta_L/T,\Theta_U/T)=\Theta_U/(\Theta_U-\Theta_L)[D_1(\Theta_U/T)-(\Theta_L/\Theta_U)D_1(\Theta_L/T)]$ where D_1 is the one-dimensional Debye function, tabulated earlier[15], and Θ_L and Θ_U designate the lower and upper frequency limits

[b] From ref. 1, based on the dispersion curves of ref. 16

[c] Based on the assignment given in ref. 17

[d] See ref. 1, based on the dispersion curves of ref. 18

[e] Approximated by the C–C– stretching vibration in oxalic acid, given in ref. 19 for $Y=CH_2$ (see part A, above)

[f] Averaged values from ref. 22

Table 2 Vibrational frequencies of polylactones

Mode	Number of modes							
	PGL[a]	PPL[b]	PBL[c]	PVL[d]	PCL[e]	PUDL[f]	PTDL[g]	PPDL[h]
A. Contribution from CH_2								
CH_2 asym. stretch	1	2	3	4	5	10	12	14
CH_2 sym. stretch	1	2	3	4	5	10	12	14
CH_2 bend	1	2	3	4	5	10	12	14
CH_2 wag	1	2	3	4	5	10	12	14
CH_2 twist	1	2	3	4	5	10	12	14
CH_2 rock	1	2	3	4	5	10	12	14
CH_2–CH_2 stretch	–	1	2	3	4	9	11	13
CH_2–COO stretch	1	1	1	1	1	1	1	1
B. Contribution from COO								
C=O stretch	1	1	1	1	1	1	1	1
C–O stretch	1	1	1	1	1	1	1	1
O–CH_2 stretch	1	1	1	1	1	1	1	1
C=O in-plane bend	1	1	1	1	1	1	1	1
C=O out-of-plane bend	1	1	1	1	1	1	1	1
C. Skeletal vibrations	6	8	10	12	14	24	28	32
Total	18	27	36	45	54	99	117	135

[a] PGL = polyglycolide, 3 chain atoms
[b] PPL = polypropiolactone, 4 chain atoms
[c] PBL = polybutyrolactone, 5 chain atoms
[d] PVL = polyvalerolactone, 6 chain atoms
[e] PCL = polycaprolactone, 7 chain atoms
[f] PUDL = polyundecanolactone, 12 chain atoms
[g] PTDL = polytridecanolactone, 14 chain atoms
[h] PPDL = polypentadecanolactone, 16 chain atoms

Table 3 Vibrational frequencies of condensation polyesters

Mode	Number of modes		
	PEO[a]	PBA[b]	PES[c]
A. Contribution from CH_2			
CH_2 asym. stretch	2	8	10
CH_2 sym. stretch	2	8	10
CH_2 bend	2	8	10
CH_2 wag	2	8	10
CH_2 twist	2	8	10
CH_2 rock	2	8	10
CH_2–CH_2 stretch	1	6	8
CH_2–COO stretch	–	2	2
B. Contribution from COO			
C=O stretch	2	2	2
C–O stretch	2	2	2
O–CH_2 stretch	2	2	2
OCC–COO stretch	1	–	–
C=O in-plane bend	2	2	2
C=O out-of-plane bend	2	2	2
C. Skeletal vibrations	12	24	28
Total	36	90	108

[a] PEO = poly(ethylene oxalate), 6 chain atoms
[b] PEA = poly(butylene adipate), 12 chain atoms
[c] PES = poly(ethylene sebacate), 14 chain atoms

Table 4 Θ_1 and Θ_3 temperatures of polyethylene and linear aliphatic polyesters

Polymer	w^c	COO/CH_2	Θ_1 (K)	Θ_3 (K)	$\Theta_3(w^c=1)$ (K)
PE	0	0	519	80	158
PPDL	0.75	0.071	525.2±8	113.6±0.8	133.1
PTDL	0.75	0.083	519.4±7	111.8±0.8	131.3
PUDL	0.71	0.10	527.9±11	104.7±1	127.3
PCL	0.63	0.20	490.7±20	101.3±2	130.1
PVL	0.70	0.25	502.4±11	101.1±1	124.5
PBL	0.67	0.33	474.4±19	95.7±2	121.4
PPL	0.79	0.50	522.0±13	84.6±1	100.9
PGL	0.67	1.0	521.3±24	97.6±2	123.3
PEO	0.40	1.0	533.2±22	88.5±2	135.3
PBA	0.84	0.25	–	–	–
PES	–	0.20	–	–	–

shown in *Table 4* ($\Theta_3(w^c=1)$). The value of Θ_1 was shown before to vary only little with crystallinity[13].

All C_p-to-C_v and reverse conversions were carried out using equation (1) with the universal A_0 and published melting temperatures.

Polyethylene (PE)

The heat capacity of polyethylene had been previously matched within experimental accuracy to its vibrational spectrum; this is discussed in greater detail in ref. 1. The Θ_D of crystalline polyethylene was reported to be 235.0 K, whereas that of amorphous polyethylene was 150.0 K; Θ_1 was reported as 519.0 K, and Θ_3 of amorphous and crystalline polyethylene were 80.0 K and 158.0 K, respectively. These are included in *Table 4* and are used as a base to estimate the crystallinity effect of all polyesters.

Polypentadecanolactone (PPDL)

The Debye temperatures of 75% crystalline polypentadecanolactone were averaged between 5 and 20 K to be 189.2 K. Correcting Θ_D to 100% crystallinity, based on the increase of Θ_D in polyethylene, leads to 210.5 K. The Θ_1 value was observed to decrease from 544.7 K at $T=25$ K to a minimum (515.8 K) at 60 K, gradually increasing again to 528.7 K at $T=120$ K, then decreasing to 439.4 K at $T=250$ K. The Θ_1 and Θ_3 values in *Table 4* are averaged over the temperature range from 20 to 160 K. *Figure 1* shows a plot of experimental C_p and calculated C_v, and the deviation of calculated from experimental heat capacity C_p is shown in *Figure 4*. The overall average deviation is $-2.4 \pm 4.0\%$, the relatively large standard deviation being caused by the low-temperature heat capacities (5–15 K).

Polytridecanolactone (PTDL)

The low-temperature heat capacity of 75% crystalline polytridecanolactone from 5 to 20 K gave an average Θ_D of 186.5 K; this may lead to 207.8 K for the crystalline polymer. The value Θ_1 was observed to increase from 480.7 K at $T = 20$ K to 517.3 K at $T = 25$ K, to decrease to 510.3 K at 50 K, and then to increase slowly to a maximum at $T = 120$ K ($\Theta_1 = 529.7$ K), followed by a gradual decrease to 405.0 K at $T = 229$ K. The average was taken from 25 to 160 K and is listed in *Table 4*. The heat capacity is plotted in *Figure 2*, and *Figure 4* shows the deviations between calculated and experimental heat capacity. The average deviation is $-2.4 \pm 3.9\%$, with larger standard deviations again coming from the 5 and 15 K heat capacity.

Polyundecanolactone (PUDL)

Between 5 and 20 K, the Θ_D of 71% crystalline polyundecanolactone was averaged and is reported as 179.5 K; Θ_D corrected for 100% crystallinity is 204.2 K. From a value of 552.5 K at 20 K, Θ_1 decreased to 517.5 K at $T = 50$ K, then increased gradually to 529.6 K at $T = 120$ K, followed by a slow decrease to 430.5 K at 227 K. Both Θ_1 and Θ_3 were averaged over 20 to 160 K and are listed in *Table 4*. These were used in our heat-capacity calculations, whose results are plotted in *Figure 3*. *Figure 4* shows how the calculated C_p deviates from the experimental C_p; the average deviation is $-2.7 \pm 5.7\%$, with good agreement starting at 15 K ($-1.2 \pm 1.9\%$ for data above 15 K).

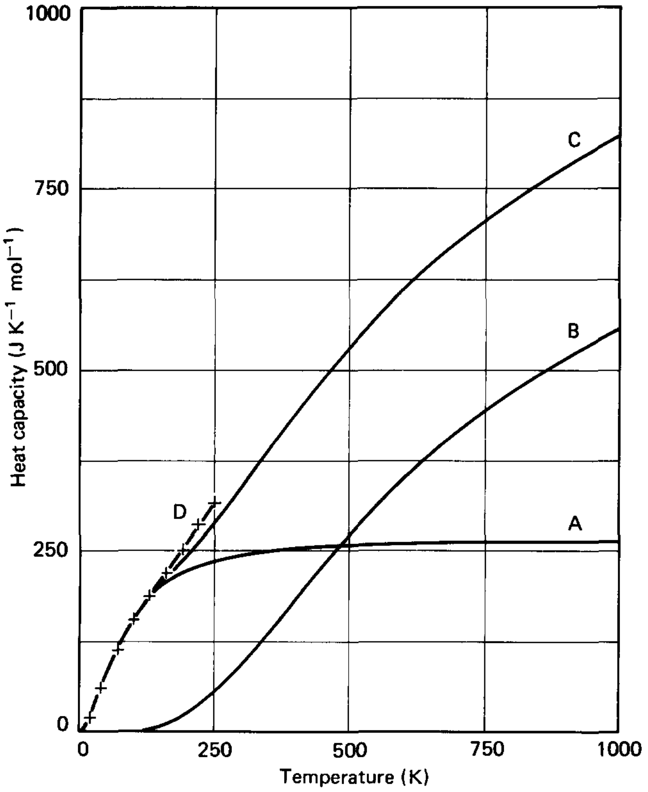

Figure 1 Heat capacity of polypentadecanolactone. Calculated C_V and experimental C_P. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 113.6$ K, $\Theta_1 = 525.2$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

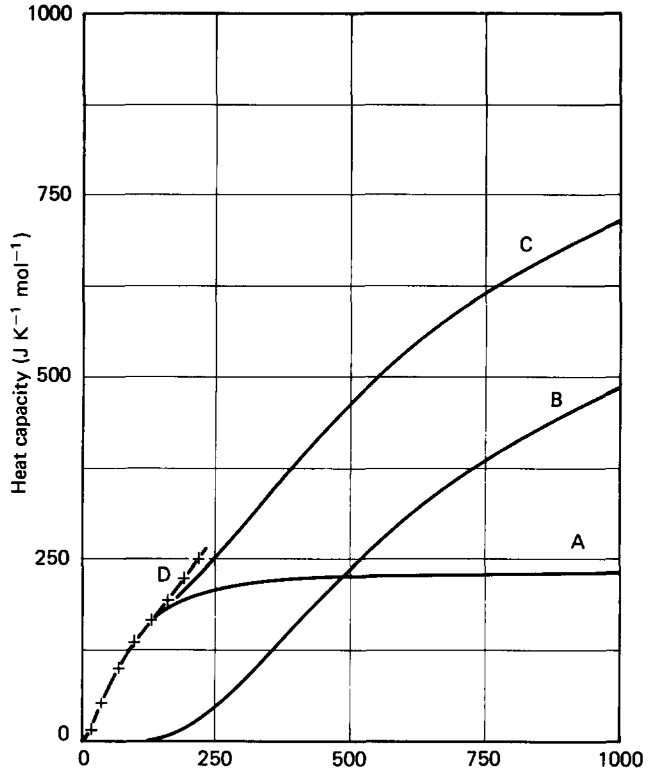

Figure 2 Heat capacity of polytridecanolactone. Calculated C_V and experimental C_P. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 111.8$ K, $\Theta_1 = 519.4$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

Polycaprolactone (PCL)

The skeletal heat capacity of semicrystalline polycaprolactone was analysed previously[13], but without subtraction of the group vibrations and only over the temperature range from 30 to 120 K. The characteristic constants Θ_D, Θ_1 and Θ_3 were reported as 150, 491 and 83 K, respectively, assuming 14 skeletal vibrations per repeating unit.

The 63% crystalline polycaprolactone led to a new Θ_D of 171.3 K when averaged at 10 and 20 K. This may lead to a Θ_D of 202.8 K for the 100% crystalline polymer. The value of Θ_1 increased continuously from 449.5 K at 25 K to a maximum of 512.2 K at $T = 140$ K and then dropped slowly to 466.4 K at 209 K. All data were averaged and led to the results in *Table 4*; the heat capacities are plotted in *Figure 5*. The deviation calculated from the experimental C_p is shown in *Figure 8* and leads to an average of $-2.6 \pm 7.3\%$ with good agreement above 40 K ($0.9 \pm 1.2\%$).

Polyvalerolactone (PVL)

The average value of $\Theta_D = 172.5$ K was calculated from the fitting of heat-capacity data of 70% crystalline polyvalerolactone between 5 and 10 K. This corresponds to 198.0 K for the crystalline polymer. The value of Θ_1 was observed to increase from 510.5 K at $T = 15$ K to

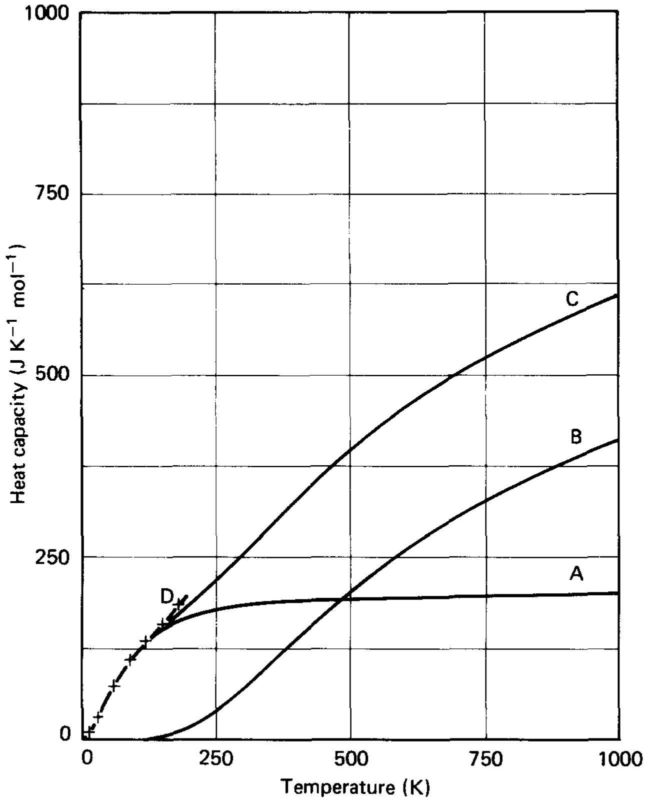

Figure 3 Heat capacity of polyundecanolactone. Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution. Tarasov treatment ($\Theta_3 = 104.7$ K, $\Theta_1 = 527.9$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

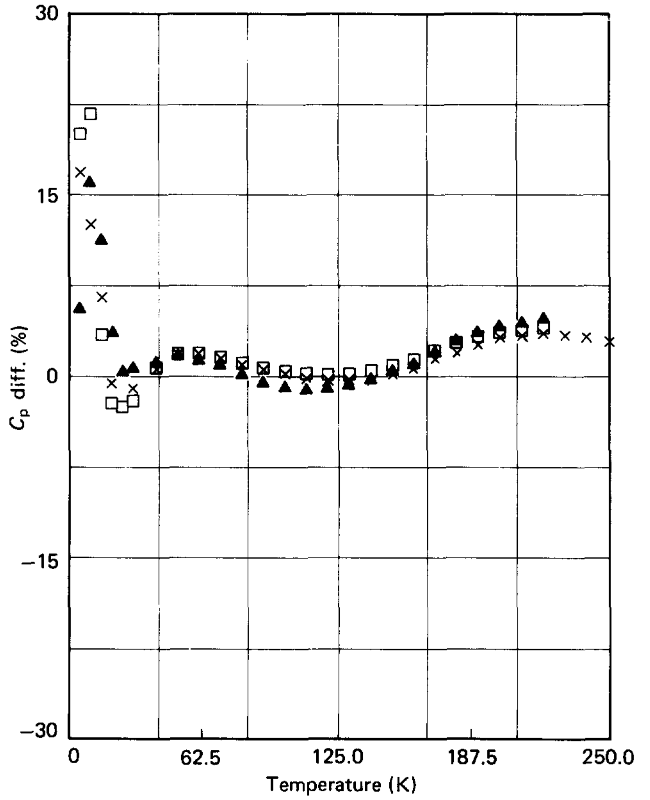

Figure 4 Heat-capacity difference C_p(expt) − C_p(calc) (in %) as a function of temperature: polypentadecanolactone (★), polytridecanolactone (▲) and polyundecanolactone (☐)

530.9 K at $T = 20$ K, followed by a decrease to 485.8 K at 50 K; Θ_1 then increased gradually to 511.8 K at $T = 140$ K, and decreased to a final value of 487.9 K at $T = 207$ K. The reported values of Θ_1 and Θ_3 in *Table 4* are averaged from 15 to 207 K, and the heat capacity is plotted in *Figure 6*. *Figure 8* shows the deviation of calculated C_p from experimental C_p. The average deviation is $-0.3 \pm 1.4\%$.

Polybutyrolactone (PBL)

The Θ_D of 67% crystalline polybutyrolactone was averaged from 5 to 10 K; it is reported as 163.1 K, corresponding to a possible crystalline value of 191.2 K. From a value of 450.6 K at 20 K, Θ_1 increases slowly up to a maximum of 498.5 K at $T = 130$ K, then decreases gradually to 443.8 K at $T = 214$ K. Averages for the temperature range of 20–214 K are listed in *Table 4*, and the heat capacity is plotted in *Figure 7*. The agreement between calculated and experimental C_p is below the 5% experimental error in the whole temperature range except in the region of 15–70 K (*Figure 8*); the average deviation was $-0.4 \pm 2.3\%$.

Polypropiolactone (PPL)

The reported value of Θ_D is 155.1 K and refers to 79% crystalline polypropiolactone. It was calculated from the heat capacity at 10 K. For 100% crystalline polymer this might correspond to 173.0 K. The Θ_1 value decreased from a value of 574.2 K at 15 K to 499.7 K at $T = 40$ K, then increased slowly up to a value of 519.3 K at 245 K. *Table 4* lists the reported values of Θ_1 and Θ_3 averaged in the temperature region 15–245 K, and the heat capacity is

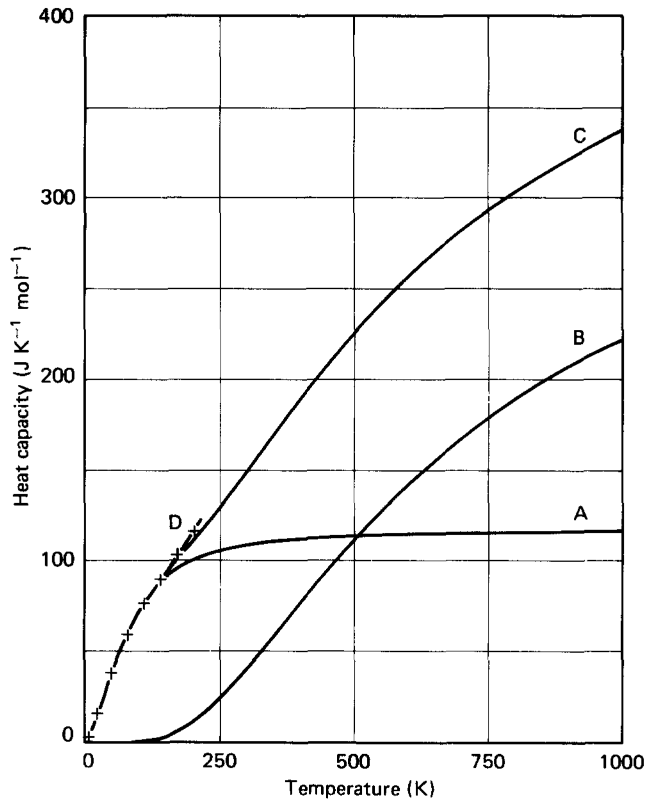

Figure 5 Heat capacity of polycaprolactone. Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 101.3$ K, $\Theta_1 = 490.7$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

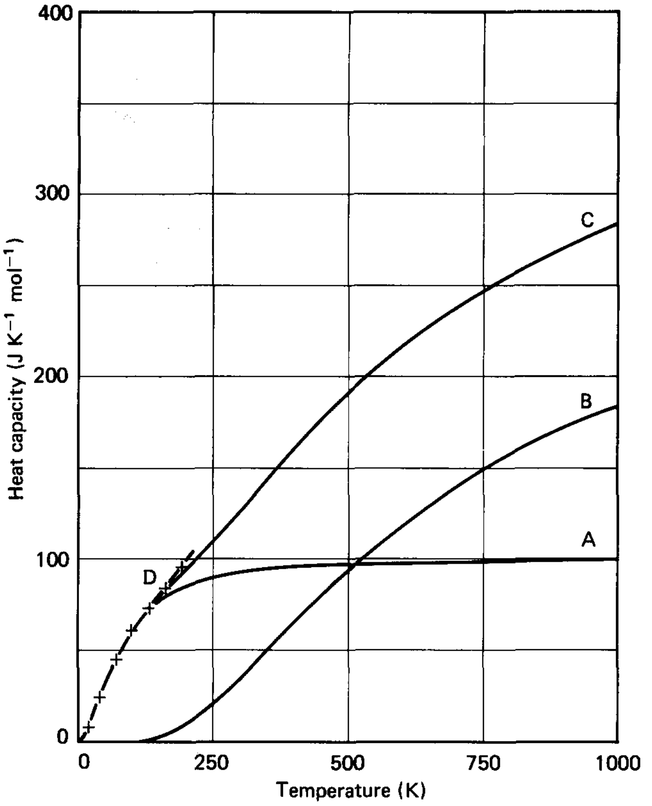

Figure 6 Heat capacity of polyvalerolactone. Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 101.1$ K, $\Theta_1 = 502.4$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

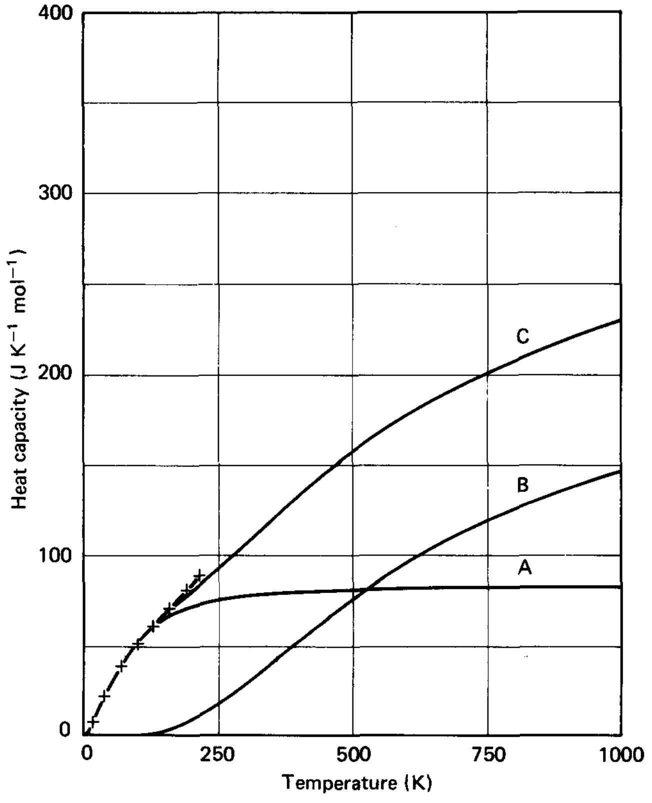

Figure 7 Heat capacity of polybutyrolactone. Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 95.7$ K, $\Theta_1 = 474.4$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

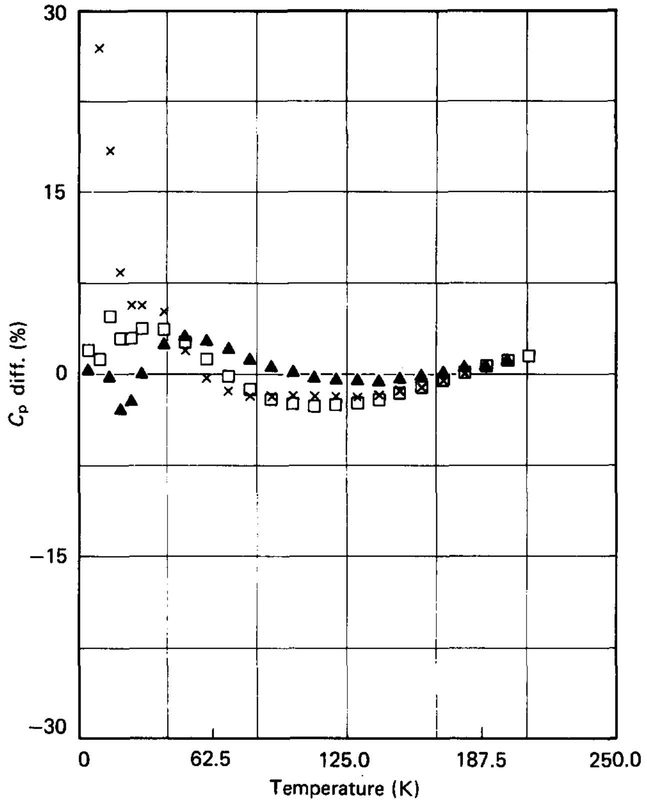

Figure 8 Heat-capacity difference $C_p(\text{expt}) - C_p(\text{calc})$ (in %) as a function of temperature: polycaprolactone (★), polyvalerolactone (▲) and polybutyrolactone (□)

plotted in *Figure 9*. *Figure 12* shows the deviation of the calculated from the experimental heat capacity. The average deviation is $-0.2 \pm 2.8\%$.

Polyglycolide (PGL)

In a previous analysis[13] the 67% crystalline polyglycolide data[9,10] were reported not to fit the vibrational analysis. Similarly, the glycolide uniquely does not fit the thermodynamic discussion of the experimenters[10]. The solution to the problem seems to be that, starting the synthesis with the bimolecular lactide instead of the unstable three-atom lactone, the original data must have referred to (CH_2–COO–CH_2–COO–) and not to half this formula, as erroneously suggested in ref. 10. For the present analysis we thus divided all prior listed heat capacities by 2. With this correction, Θ_D was calculated from the heat capacities between 5 and 10 K to be 170.5 K. For full crystallinity this may have to be corrected to 198.6 K. The trends in Θ_1 are then as follows. From the value of 465.8 K at 10 K, Θ_1 increased to 552.9 K at 20 K, then decreased slowly to a minimum value of 488.9 K at 50 K, followed by a gradual increase up to 871.1 K at 318 K. For our further calculation, we took the average values between 15 and 170 K; these are listed in *Table 4* and the heat capacity is plotted in *Figure 10*. The deviation of the calculated from the experimental C_p is plotted in *Figure 12* and the average is $-0.2 \pm 2.7\%$.

The good fit of the present analysis (and also an improvement in the thermodynamic data of ref. 10) justifies the drastic alteration of the experimental data.

Poly(ethylene oxalate) (PEO)

Poly(ethylene oxalate) is a structural isomer of polyglycolide. The low-temperature heat capacity of 40%

crystalline poly(ethylene oxalate) at 5 and 10 K yielded $\Theta_D = 161.0 \pm$ K, or possibly 212 K for the completely crystalline polymer. From 10 K, where Θ_1 was 408.1 K, Θ_1 increased to 515.3 K at 25 K, followed by a decrease to a minimum of 498.7 K at 50 K; this then increased slowly to 774.9 K at $T = 306$ K. We chose to average the values between 25 and 170 K for the data in *Table 4*. Both polyglycolide and poly(ethylene oxalate) have a ratio $COO/CH_2 = 1.0$ and their heat capacities and vibrational characteristics are similar. *Figure 11* shows the experimental and calculated heat capacity of PEO, and the differences in C_p are shown in *Figure 12*. The average deviation is $-0.6 \pm 2.6\%$.

Poly(butylene adipate) (PBA)

To test the additivity concept suggested in this treatment of polyesters, the Θ_3 value for PBA was obtained from equation (3), developed below, to be 120.2 K. Correction to 84% crystallinity gives 107.7 K, the value then used in the C_v calculation. An average Θ_1 value of 513.6 K was then used together with the Θ_D of 107.7 K for the calculation of the skeletal heat capacity. This was then converted to C_p, using equation (1), and compared to the experimental results, which give C_p data from 80 to 200 K[23]. The average deviation was $-8.3 \pm 2.0\%$. The systematic error may well be of experimental nature rather than a true test of the addition scheme since the experimental data did not quite meet the standards of acceptable data established for the ATHAS databank[9].

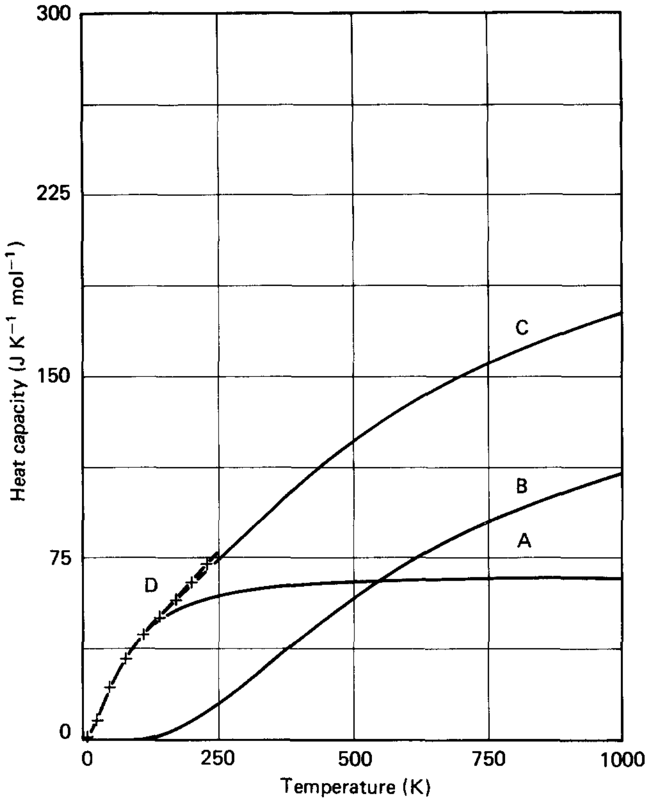

Figure 9 Heat capacity of polypropiolactone. Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 84.6$ K, $\Theta_1 = 522.0$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

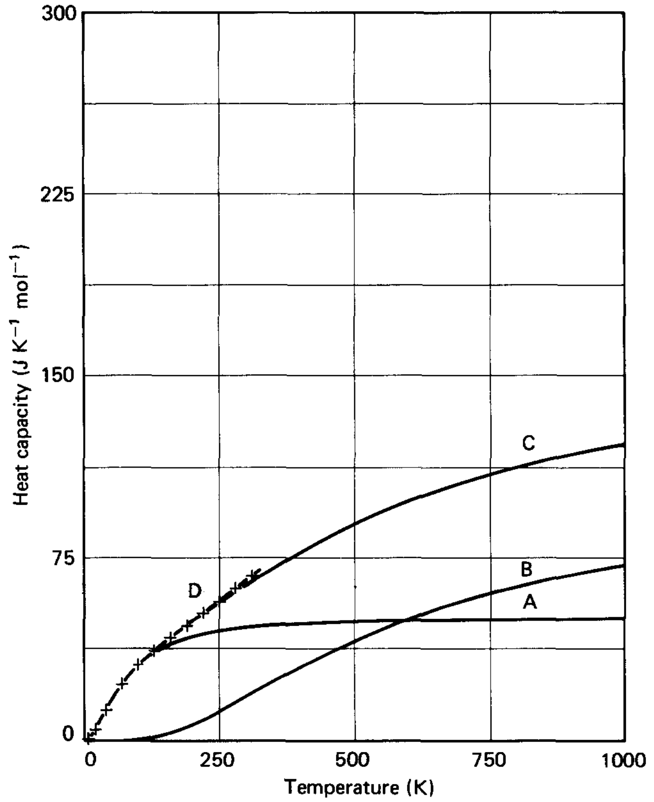

Figure 10 Heat capacity of polyglycolide. Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 97.6$ K, $\Theta_1 = 521.3$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

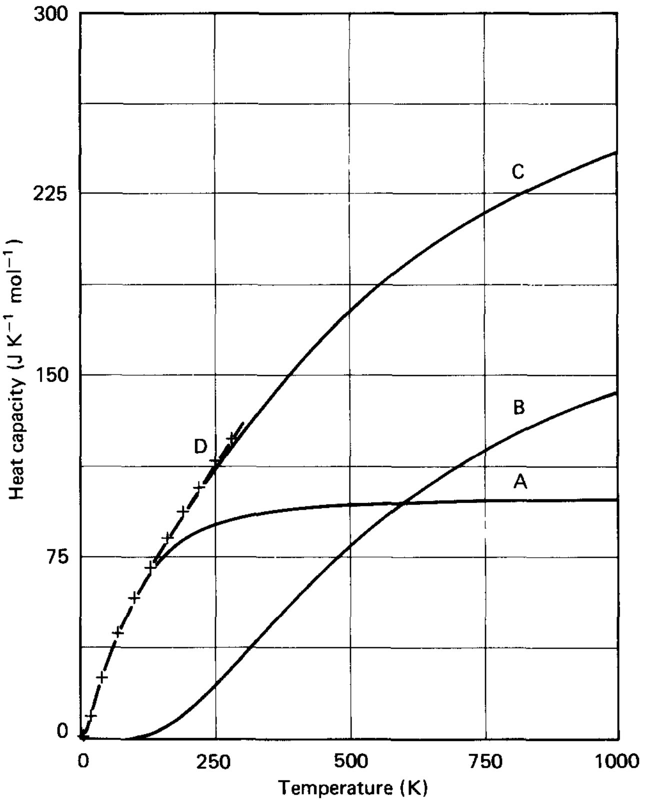

Figure 11 Heat capacity of poly(ethylene oxalate). Calculated C_v and experimental C_p. Curve A: skeletal vibration contribution, Tarasov treatment ($\Theta_3 = 88.5$ K, $\Theta_1 = 533.2$ K). Curve B: group vibration contribution (as given in *Tables 1* and *2*). Curve C: sum of curves A and B. Curve D: experimental data from ref. 10

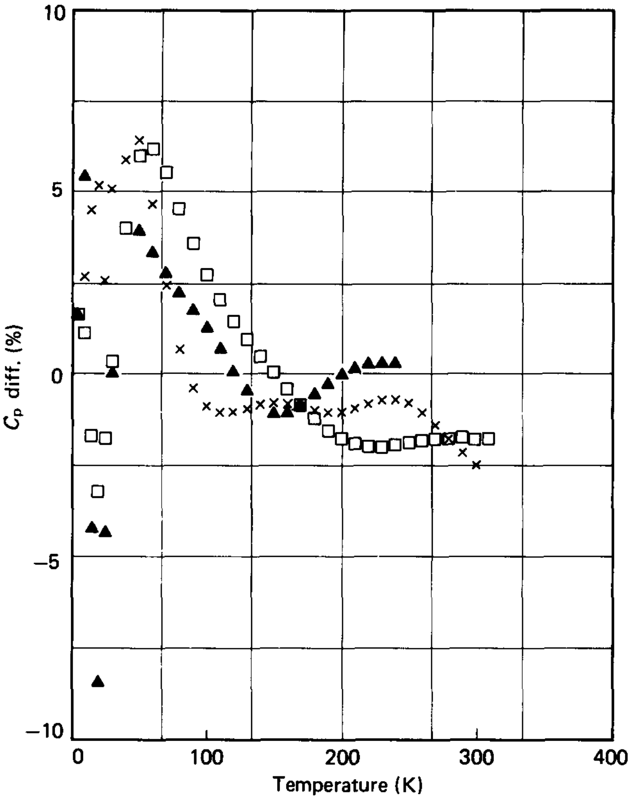

Figure 12 Heat-capacity difference C_p(expt)−C_p(calc) (in %) as a function of temperature: polypropiolactone (★), polyglycolide (□) and poly(ethylene oxalate) (▲)

Poly(ethylene sebacate) (PES)

Similar to the PBA, the PES heat capacity C_v was calculated using a Θ_3 value of 124.6 K (100% crystalline) and $\Theta_1 = 513.6$ K and converted to C_p using equation (1).

Only one heat-capacity investigation[24] had been carried out for poly(ethylene sebacate) and the measurements were done at temperatures above the glass transition temperature (about 245 K). Satisfactory agreement with the calculation presented here can be obtained at 250 K assuming additivity of solid and liquid heat capacities (error 2.6%). Above this temperature, the error increases to above 10%. Since these temperatures are not far from the melting point (356 K), the (positive) deviations of the experimental data may be attributed to the onset of melting. Newly measured heat-capacity data by d.s.c.[25] on a series of five differently crystallized PES samples led to a heat capacity (in J K^{-1} mol^{-1}) of

$$C_p = 52.11 + 0.8269T \qquad (2)$$

in the temperature range of 120 to 220 K. Equation (2) represents the experiments with a standard deviation of ±2% (maximum error 4.7%). The calculated data show an average deviation from equation (2) of +4.4 to +5.5%, i.e. they are close to the experimental precision.

DISCUSSION

The analysis of such an extended series of samples permits a general assessment of the quality of heat-capacity calculations using the simplifications applied here. A comparison of *Figures 4*, *8* and *12* shows similar positive errors at low temperatures (below 25 K). They clearly indicate the limitation of the simplified Tarasov spectrum to represent heat capacities of polymers, especially in the frequency range for the junction of Θ_3 and Θ_1. Comparing the errors to prior analyses in this series of papers[1–7,13], one finds that these limitations become more serious with increasing deviations from linearity of the molecule. Two examples of especially serious difficulties are the polymers with phenylene groups in the chain and alternating heavy and light repeating units. In the present case, the percentage error at low temperature is still tolerable since the absolute magnitude of the heat capacity is low already. Furthermore, the experimental precision at the lower temperatures is also limited, and effects of crystallinity are expected to cause similar deviations in heat capacity. The systematic, small, positive deviation at temperatures above 125 K for the long CH_2– sequence polyesters (*Figures 4* and *8*) may be an indication that the experimental data still contain glass transition effects. Polyethylene[26] is known to extend the influence of its glass transition on the heat capacity from the major increase between 220 and 260 K to about 110 K, and similar increases are expected for the polyesters; indeed, no such effect is seen in *Figure 12*, in which data are collected on polyesters with only single and double CH_2– groups between carboxyl groups.

The Θ_1 temperature, a largely crystallinity-independent parameter, should change mainly with changing intramolecular interactions. For the linear aliphatic polyesters, it is observed to have little variation with composition; the average Θ_1 of all polyesters (513.6 ± 19 K) is very close to the polyethylene value of 519 K and the standard deviation is of the same magnitude as the experimental uncertainty. It has been shown previously that Θ_1 and the mass of a repeating unit are inversely related[12]; thus, the presence of the heavier carboxyl groups is expected to decrease Θ_1. The opposite trend, however, is expected when one considers the nature of the carboxyl groups, which impart some double-bond character on the acyl oxygen. This results in increased stiffness and larger force constants along the chains, and, consequently, a higher Θ_1 is expected[12]. Apparently the two opposing factors cancel, resulting in an approximately constant Θ_1.

The Θ_D and Θ_3 temperatures depend more on the nature of the intermolecular interactions, and are thus crystallinity-dependent. We assumed (arbitrarily) throughout our calculations that the changes in Θ_D with crystallinity known from polyethylene (0.85 K for each 1% crystallinity change) could also be applied to the polyesters, to be able at least to make a comparison between the different polymers with a reduced influence of the crystallinity. *Figure 13* shows such a comparison plot for Θ_3 ($\Theta_D^3 = \Theta_1\Theta_3^2$). Clearly, the overall change is less than that produced by the crystallinity in polyethylene. Still, there seems to be a pronounced minimum at PPL in the plot, which should be related to changes in the crystal structure.

Known crystal parameters of interest are collected in *Table 5*. Most data are available for the ethylene glycol series. PEO and poly(ethylene succinate) have *gauche* conformations in the ethylene portion, shortening the chain substantially and increasing the cross-section needed to pack the chains[27]. Poly(ethylene adipate) to poly(ethylene sebacate) are then more continuously tending towards polyethylene with segments of close-to-planar zig-zag conformation[28]. The PGL is quite

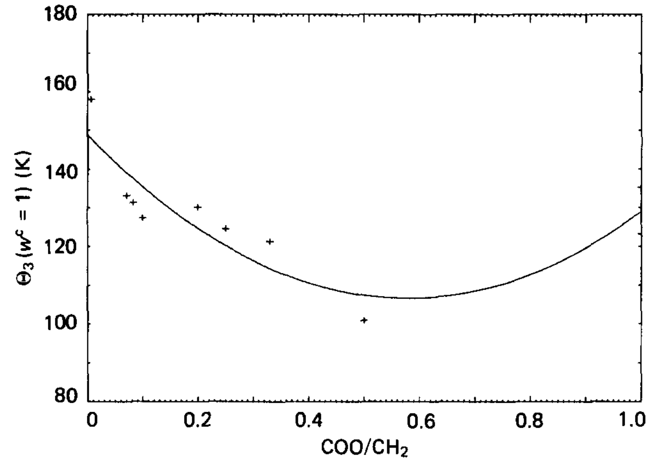

Figure 13 Crystalline Θ_3 for homologous CH_2-based polyesters as a function of carboxyl ratio

Table 5 Crystal properties of polyethylene and linear aliphatic polyesters[a]

Polymer[b]	Space group	c per chain atom (nm)	k^c	Crystal density (g cm^{-3})	Repeat-unit cross-section[d] (nm^2)
PGL	*Pcmn*	0.117	0.81	1.700	0.162
PPL		0.119	0.69	1.33	0.189
PCL	$P2_12_12_1$	0.1218	0.70	1.195	0.186
PEO	*Pbcn*	0.0994	0.77	1.613	0.200
PESuc	*Pbnb*	0.1041	0.73	1.406	0.204
PEA	$P2_1/a$	0.1155	0.75	1.363	0.182
PESub	$P2_1/a$	0.1175	0.74	1.300	0.182
PES	$P2_1/a$	0.1189	0.73	1.247	0.183
PE	*Pnam*	0.1273	0.70	0.997	0.184

[a] For references, see text
[b] PESuc = poly(ethylene succinate)
PEA = poly(ethylene adipate)
PESub = poly(ethylene suberate)
PES = poly(ethylene sebacate)
[c] Packing fraction; calculated from $k = zV_0/V$, where z = no. of repeat unit cell, V_0 = occupied volume, V = van der Waals volume
[d] Calculated from $A = N_cV/C = N_cM/(\rho N_0 C)$ where A = cross-section normal to the chain axis, N_c = number of repeating units along the c-axis, M = MW of repeating unit, C = fibre axis length

different from polyethylene, with a sheet-like arrangement of the chains, a small cross-section, shortened chains and a high packing fraction[29]. Already with PCL the structure is closer to polyethylene[30,31] with longer portions of planar zig-zag conformations. PPL also has a planar zig-zag conformation, but its carboxyl oxygens lie at random levels. Common for all polyesters is an increase in density with increasing oxygen content. One can thus suggest that the slow decrease in Θ_3 from polyethylene with increasing number of carboxyl groups may be caused mainly by the increasing mass of the backbone chain and the difficulties of accommodating carboxyl groups in a largely polyethylene crystal. The possible increase in interaction due to the C=O dipoles is for the lactones seemingly compensated by the increase in repeat-unit cross-section. The first members of the homologous series, PEO and PGL, reverse the trends by quite different crystal structures, based more on carboxyl-group alignment than CH_2– group accommodation. Specially the PGL has a much better packing fraction. Similarly, the data of PPL show the worst packing, in accord with the lowest Θ_3.

ADDITION SCHEME

The discussion of the heat capacities of the solid aliphatic polyesters has shown definite trends, so that one can attempt to develop a prediction scheme based on their composition alone. Similar prediction schemes have been suggested earlier for solid halogenated polyethylene[4] as well as for solid polyoxides[1]. As before, we expect this prediction scheme to hold not only for different polyesters but also for copolyesters and blends. *Table 6* contains the needed heat-capacity contributions of the group vibrations; they correspond to the group vibration contributions as outlined in *Tables 1* to *3* and are plotted in *Figure 14*. The value of Θ_1 is the same for all aliphatic polyesters (513.6 K). The value of Θ_3 in kelvin can be taken from *Figure 13* in which the curve is represented by

$$\Theta_3 = 125.46(COO/CH_2)^2 - 145.06(COO/CH_2) + 148.63 \quad (3)$$

Equation (3) fits the data points of *Figure 13* with a standard deviation of ±7 K. A correction for crystallinity is possible, as outlined in the 'Discussion'. Finally, C_v-to-C_p conversions can be done with the help of equation (1).

An example calculation may be that of polyvalerolactone (PVL). Its group vibration contribution is

$$C_v^{PVL}(g) = 3C_v^{CH_2}(g) + 1C_v^{COO}(g) + 1C_v^{CH_2COO}(g) \quad (4)$$

Some selected values are shown in *Table 7*. Calculating the skeletal vibrations with the proper Θ_3 (101.3 K) and converting to C_p with equation (1) leads to the prior

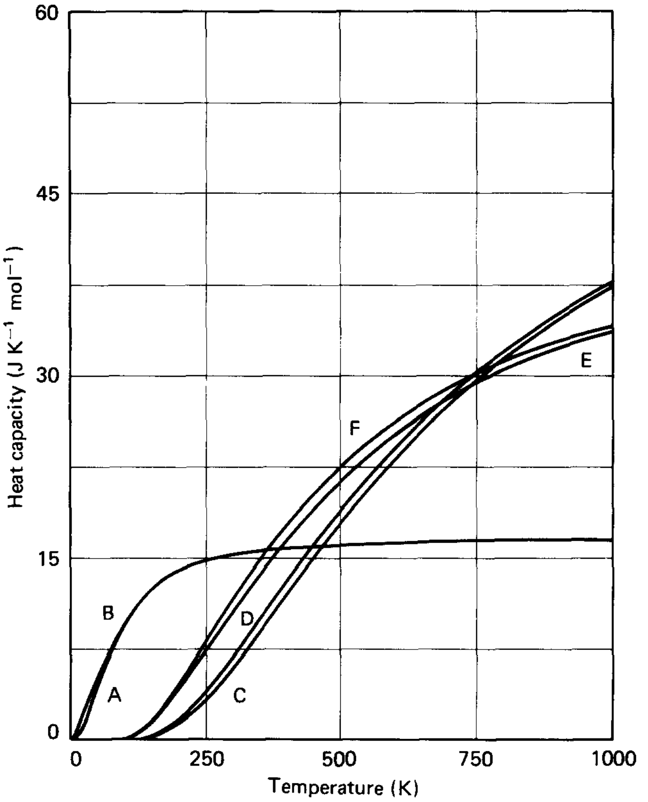

Figure 14 Heat-capacity contribution of CH_2 and COO groups. Curve A: skeletal contribution of crystalline methylene. Curve B: skeletal contribution of amorphous methylene. Curve C: group contribution of methylene attached to methylene. Curve D: group contribution of methylene attached to a carboxyl group. Curve E: group contribution of COO attached to CH_2. Curve F: group contribution of COO attached to another COO

Table 6 Group (g) and skeletal (s) heat-capacity contributions of CH_2– and COO– groups (in J K^{-1} mol^{-1})

Temp. (K)	CH_2 cryst. $C_V(s)$	CH_2 amorph. $C_V(s)$	$CH_2(CH_2)$ $C_V(g)$	$CH_2(COO)$ $C_V(g)$	$COO(CH_2)$ $C_V(g)$	COO(COO) $C_V(g)$
1.0	0	0.0004	0	0	0	0
2.0	0.0008	0.0031	0	0	0	0
3.0	0.0027	0.0105	0	0	0	0
4.0	0.0064	0.0250	0	0	0	0
5.0	0.0125	0.0488	0	0	0	0
10.0	0.1000	0.3630	0	0	0	0
20.0	0.7412	1.5991	0	0	0	0
30.0	1.9122	2.8567	0.9513	0.9864	0.456	0.4565
40.0	3.2230	4.0223	0.4304	0.4797	0.2894	0.2896
50.0	4.4992	5.13	0.6073	0.7444	0.0001	0.0001
60.0	5.700	6.199	0.2254	0.2800	0.0015	0.0015
70.0	6.815	7.211	0.0002	0.0002	0.0087	0.0088
80.0	7.836	8.155	0.0012	0.0017	0.0312	0.0320
90.0	8.758	9.020	0.0044	0.0063	0.0827	0.0856
100.0	9.582	9.800	0.0124	0.0182	0.1771	0.1857
110.0	10.313	10.497	0.0288	0.0429	0.3260	0.3462
120.0	10.958	11.114	0.0580	0.0866	0.5363	0.5764
130.0	11.524	11.659	0.1046	0.1559	0.8103	0.8805
140.0	12.022	12.139	0.1732	0.2564	1.1462	1.2578
150.0	12.458	12.562	0.2682	0.3928	1.5395	1.7038
160.0	12.842	12.933	0.3932	0.5682	1.9841	2.2115
170.0	13.180	13.261	0.5514	0.7845	2.4732	2.7725
180.0	13.479	13.551	0.7449	1.0425	2.9999	3.3779
190.0	13.743	13.808	0.9754	1.3418	3.5576	4.0189
200.0	13.977	14.036	1.2434	1.6812	4.1405	4.6873
210.0	14.186	14.239	1.5491	2.0589	4.7432	5.376
220.0	14.372	14.421	1.8916	2.4728	5.361	6.078
230.0	14.538	14.584	2.2698	2.9203	5.991	6.788
240.0	14.688	14.730	2.6821	3.3986	6.628	7.502
250.0	14.823	14.861	3.1262	3.9047	7.270	8.216
260.0	14.945	14.980	3.5998	4.4357	7.914	8.926
270.0	15.055	15.088	4.1005	4.9886	8.559	9.631
280.0	15.155	15.186	4.6254	5.561	9.203	10.328
290.0	15.247	15.275	5.172	6.149	9.843	11.015
300.0	15.330	15.357	5.737	6.751	10.479	11.692
310.0	15.406	15.431	6.318	7.363	11.110	12.357
320.0	15.476	15.499	6.913	7.985	11.734	13.010
330.0	15.540	15.562	7.519	8.613	12.350	13.650
340.0	15.599	15.620	8.133	9.245	12.959	14.278
350.0	15.653	15.673	8.754	9.880	13.559	14.892
360.0	15.704	15.722	9.380	10.515	14.150	15.493
370.0	15.750	15.768	10.018	11.151	14.731	16.080
380.0	15.794	15.810	10.638	11.784	15.303	16.654
390.0	15.834	15.850	11.268	12.414	15.864	17.215
400.0	18.871	15.886	11.895	13.041	16.415	17.762
410.0	15.906	15.920	12.521	13.662	16.955	18.297
420.0	15.938	15.952	13.142	14.278	17.484	18.818
430.0	15.969	15.982	13.758	14.887	18.003	19.327
440.0	15.997	16.010	14.370	15.490	18.511	19.824
450.0	16.024	16.036	14.975	16.085	19.008	20.308
460.0	16.049	16.061	15.574	16.672	19.494	20.780
470.0	16.073	16.084	16.166	17.252	19.969	21.240
480.0	16.095	16.105	16.751	17.824	20.434	21.689
490.0	16.116	16.126	17.328	18.387	20.888	22.126
500.0	16.135	16.145	17.897	18.942	21.332	22.552
510.0	16.154	16.163	18.458	19.489	21.765	22.968
520.0	16.172	16.181	19.012	20.027	22.188	23.372
530.0	16.188	16.197	19.557	20.557	22.600	23.766
540.0	16.204	16.212	20.094	21.078	23.003	34.150
550.0	16.219	16.227	20.623	21.591	23.396	24.524
560.0	16.233	16.241	21.144	22.096	23.779	24.889
570.0	16.246	16.254	21.658	22.593	24.153	25.244
580.0	16.259	16.266	22.161	23.081	24.518	25.590
590.0	16.271	16.278	22.657	23.562	24.873	25.926
600.0	16.283	16.290	23.146	24.035	25.220	26.254
610.0	16.294	16.300	23.627	24.500	25.558	26.574
620.0	16.304	16.311	24.100	24.958	25.887	26.885
630.0	16.314	16.321	24.566	25.409	26.209	27.188
640.0	16.324	16.330	25.024	25.852	26.522	27.484
650.0	16.333	16.339	25.475	26.288	26.827	27.771
660.0	16.342	16.347	25.918	26.716	27.124	28.051
670.0	16.350	16.356	26.355	27.138	27.414	28.324
680.0	16.358	16.363	26.784	27.553	27.697	28.590
690.0	16.366	16.371	27.207	27.962	27.973	28.849
700.0	16.373	16.378	27.623	28.364	28.241	29.102

Table 7 Calculation of heat capacity of polyvalerolactone using the addition scheme of *Table 6* (in $J K^{-1} mol^{-1}$)

T (K)	$C_V(g)^a$	$C_V(s)^b$	$C_V(tot)^c$	$C_V(calc)^d$	ΔC_V (%)^e	ΔC_p (%)^f
1	0	1.87×10^{-3}	1.87×10^{-3}	1.514×10^{-3}	23.58	–
5	0	0.2338	0.2338	0.1893	27.20	−0.39
10	0	1.752	1.752	1.489	17.66	−1.58
15	negligible	4.673	4.673	4.389	6.47	2.92
20	negligible	8.204	8.204	8.230	−0.32	−3.05
50	1.31×10^{-4}	29.77	29.77	31.07	−4.18	−0.09
100	0.2326	58.45	58.68	60.23	−2.57	−0.81
200	9.550	84.14	93.69	94.53	−0.89	–
300	34.44	92.11	126.55	126.99	−0.35	–
400	65.15	95.31	160.46	160.71	−0.16	–
500	93.97	96.88	190.85	191.00	−0.08	–

[a] Group vibration contribution
[b] Skeletal contribution
[c] Total heat capacity = group + skeletal
[d] Computer-calculated heat capacity, from complete vibrational spectrum
[e] Difference (in %) between C_V(tot) and C_V(calc)
[f] Difference (in %) between computer-calculated and experimental heat capacity

discussed good fit to the experimental data, as shown in the last column. To avoid the cumbersome looking-up of one- and three-dimensional Debye functions for the Tarasov equation (unless one has a computer program as in the ATHAS Computation Center), an acceptable alternative for the computation of the skeletal heat capacities above about 10 K is as follows. The Θ_3 temperature is converted to a corresponding polyethylene crystallinity using the same (arbitrary) adjustment procedure for crystallinity described above: (158.0–101.3)/(158.0–80) = 0.73, i.e. $w^c = 0.27$. Next $C_v(s)$ is calculated from the first two columns of *Table 6* using the equation

$$C_p = w^c C_p^c + (1 - w^c) C_p^a \tag{5}$$

The result is indicated in columns 3 and 4 of *Table 7* and compared to the calculation using the full Tarasov function (column 5 of *Table 7*). The error in column 6 of *Table 7* indicates that although the fit is poor at 1–10 K, it is quite acceptable at higher temperatures. Similar results were obtained with PGL and PPL. *Table 6* can thus be used to approximate heat capacities of polyesters.

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