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AN ADDITION SCHEME OF HEAT CAPACITIES OF LINEAR MACROMOLECULES

Part II: Backbone-Chains that Contain Other than C-Bonds

Robert Y. L. Pan, Miao-Yong Cao and *B. Wunderlich*

DEPARTMENT OF CHEMISTRY RENSSELAER POLYTECHNIC INSTITUTE TROY, NEW YORK 12181, U.S.A.

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The prior developed addition scheme of heat capacities is expanded to macromolecules that contain non-C-bonds in the backbone. Tables for 31 groups are given. 713 data points which have been averaged for group contributions for which more than one measurement was available showed a deviation of 0.1 ± 1.5% (internal consistency). Calculated heat capacities of homopolymers and copolymers for which independent measurements have been made showed average errors of 0.60% and a standard deviation of ± 2.35% (177 data points).

In the first paper [1] we could show that for macromolecules with single-bonded carbon atoms in the backbone there exists additivity in heat capacity almost within the experimental precision. For the solid state this additivity is limited in the low temperature range (below 30–50 K) due to non-additive heat capacity contributions based on intermolecular forces. Outside of this temperature range 155 data points, evaluated both by the addition scheme and by measurement, showed a deviation of $-0.2 \pm 2.5\%$. The sampling included glasses, crystals, semicrystalline and liquid homopolymers as well as copolymers and blends. A total of 42 group contributions were presented.

In the present paper it will be explored in what way inclusion of non-carbon single bonds in a molecule will influence the additivity of heat capacity. It was shown in the general discussion of additivity of heat capacity in the first paper [1] that the group vibration contributions to heat capacity are largely additive. The skeletal vibrations, however, should in the temperature range of θ/T between 1 and 6 only be additive if frequency and number of vibrators do not change for different change for different molecular structures made up of the same base units. θ is the characteristic temperature of a vibration or a specified frequency distribution (expressed in kelvin, 1 K = 2.08×10^{10} Hz, 1 K = 0.695 cm^{-1}). The additivity of

Akadémiai Kiadó, Budapest
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heat capacity of skeletal vibrations of carbon-backbone molecules is thus easy to understand, but problems should arise by interrupting the carbon backbone with hetero atoms like O—, COO—, CONH— groups or non-single bond groups like C=C—, or C_6H_4—. A total of 31 such group contributions are presented and discussed in this paper. General background material and references can be found in the first paper [1].

Tables of group contributions and their justification

The addition scheme is presented in Tables 1 to 4. The data for 17 chemically different groups are presented when measurements are available in the ATHAS data bank [2, 3] for the solid (glassy or crystalline) and the liquid states. Data based on extrapolation, not directly supported by experiment, are placed in parentheses. Effects due to fusion, crystallization, annealing, and broadening of the glass transition are, as much as possible, eliminated. The sources of experimental data and their critical evaluation can be found in the ATHAS data bank [2, 3]. In the course of the work we also developed the needed programming to handle the data bank as well as addition scheme with a personal computer and VisiCalc software (trademark of Visi Corp). The present computer is an Atari 800 computer based on a 6502 microcomputer, 48 K RAM, 1.79 MHz clock rate, DOS 2.5, data stored on 126 kbyte 5¼″ diskettes, data transfer rate 6,000 bits per second. Efforts are underway to upgrade to more commonly available computers and to update and expand the data base by including computed data [4].

Data columns 1 and 2 in Table 1 refer to vinylene groups in the backbone of a macromolecule CH=CH—. The group contribution was derived by subtracting twice the CH_2— contribution [1] from the heat capacity of *cis* and *trans*-1,4-polybutadiene and averaging. When comparing the group contribution heat capacity ($2CH_2$—+CH=CH—) with the experimental data of 1,4-polybutadienes, the average deviation and standard deviation are 0.01% and ±0.80% for the *trans* isomer from 60 to 160 K and $-0.16\pm0.82\%$ for the *cis* isomer from 60 to 180 K. The deviations are somewhat higher below 50 K due to the difference of intermolecular forces between *cis* and *trans* isomers. The reported data for the solid include extrapolations of both *cis* and *trans* to the glass transition region. Extrapolations were also made for the liquid to 600 K and 150 K. All extrapolations are placed in parentheses. Since both isomer melts share the same linear heat capacity function, no standard deviation can be calculated for the liquid.

Heat capacity contributions for $C(CH_3)=CH$— (columns 3 and 4) were calculated from the recommended heat capacity data of *cis*-1,4-poly(2-methylbutadiene) (PMBD). Measured data of PMBD are available in the region of 30–190 K for the solid and 210–360 K for the liquid. Some extrapolation of the

Table 1 [Heat Capacity Contributions C_p in JK^{-1} mole^{-1}]

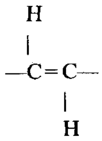
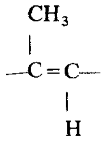
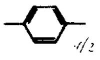
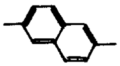
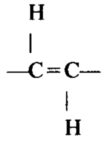
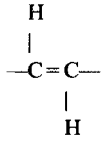
Temperature	 $-\overset{H}{C}=\underset{H}{C}-$		 $-\overset{CH_3}{C}=\underset{H}{C}-$					
(K)	1 Solid	2 Liquid	3 Solid	4 Liquid	5 Solid	6 Liquid	7 Solid	8 Liquid
30	7.07	—	10.56	—	—	—	—	—
40	8.89	—	13.16	—	—	—	—	—
50	10.32	—	15.30	—	—	—	—	—
60	11.39	—	17.35	—	—	—	—	—
70	12.37	—	19.40	—	—	—	—	—
80	13.46	—	21.49	—	28.22	—	—	—
90	14.63	—	23.58	—	30.31	—	—	—
100	15.46	—	25.68	—	32.49	—	—	—
110	17.20	—	27.72	—	34.73	—	—	—
120	18.54	—	29.73	—	37.03	—	—	—
130	19.98	—	31.73	—	39.39	—	—	—
140	21.44	—	33.73	—	41.79	—	—	—
150	23.01	(30.52)	35.74	(47.85)	44.24	—	—	—
160	(24.86)	(31.43)	37.80	(49.24)	46.73	—	—	—
170	(26.12)	(32.35)	39.89	(50.63)	49.26	—	(73.54)	—
180	(27.42)	(33.26)	42.00	(52.03)	51.83	—	(78.31)	—
190	(28.75)	(34.18)	44.75	(53.42)	54.44	—	(83.02)	—
200	(30.14)	(35.09)	(46.89)	(54.81)	57.07	—	(87.87)	—
210	(31.56)	(36.01)	—	(56.20)	59.74	—	(92.67)	—
220	(33.00)	(36.92)	—	(57.59)	62.44	—	(97.62)	—
230	(34.46)	(37.84)	—	(58.99)	65.17	—	102.51	—
240	(35.94)	(38.75)	—	60.38	67.93	—	107.56	—
250	(37.43)	(39.67)	—	61.77	70.72	—	112.55	—
260	(39.01)	(40.58)	—	63.16	73.53	—	117.70	—
270	(40.70)	(41.50	—	(64.56)	76.37	—	122.79	—
280	(42.52)	(42.41)	—	(65.95)	79.24	—	128.04	—
290	—	(43.33)	—	(67.34)	82.12	—	136.93	—
300	—	(44.24)	—	(68.73)	85.04	(119.78)	140.28	(172.25)
310	—	(45.16)	—	(70.12)	—	(120.95)	146.37	(175.10)
320	—	(46.07)	—	(71.52)	—	(122.11)	—	(177.94)
330	—	(46.99)	—	(72.91)	—	(123.28)	—	(180.79)
340	—	(47.90)	—	(74.30)	—	(124.44)	—	(183.63)
350	—	(48.82)	—	(75.69)	—	(125.61)	—	(186.48)
360	—	(49.73)	—	(77.09)	—	(126.67)	—	(189.33)
370	—	(50.65)	—	(78.48)	—	(127.94)	—	(192.17)
380	—	(51.56)	—	(79.87)	—	(129.10)	—	(195.02)
390	—	(52.48)	—	(81.26)	—	130.27	—	(197.86)

Table 1 (continued)

Tem-perature	 $-\overset{H}{C}=\underset{H}{C}-$		 $-\overset{H}{C}=\underset{H}{C}-$					
(K)	1 Solid	2 Liquid	3 Solid	4 Liquid	5 Solid	6 Liquid	7 Solid	8 Liquid
400	—	(53.39)	—	(82.66)	—	131.43	—	(200.71)
410	—	(54.31)	—	(84.05)	—	132.60	—	(203.55)
420	—	(55.22)	—	(85.44)	—	133.76	—	(206.40)
430	—	(56.14)	—	(86.83)	—	134.93	—	(209.25)
440	—	57.05	—	(88.22)	—	136.09	—	(212.09)
450	—	57.97	—	(89.62)	—	137.25	—	(214.94)
460	—	58.88	—	(91.01)	—	138.42	—	(217.78)
470	—	59.80	—	(92.40)	—	139.58	—	(220.63)
480	—	60.71	—	(93.79)	—	140.75	—	(223.48)
490	—	61.63	—	(95.19)	—	141.91	—	(226.32)
500	—	62.54	—	(96.58)	—	143.08	—	229.17
510	—	(63.46)	—	(97.97)	—	144.24	—	232.02
520	—	(64.37)	—	(99.36)	—	145.41	—	234.86
530	—	(65.29)	—	(100.75)	—	146.57	—	237.70
540	—	(66.20)	—	(102.15)	—	147.74	—	240.55
550	—	(67.12)	—	(103.54)	—	(148.90)	—	243.40
560	—	(68.03)	—	(104.93)	—	(150.07)	—	(246.24)
570	—	(68.95)	—	(106.32)	—	(151.23)	—	(249.09)
580	—	(69.86)	—	(107.75)	—	(152.40)	—	(251.93)
590	—	(70.78)	—	(109.14)	—	(153.56)	—	(254.78)
600	—	(71.69)	—	(110.53)	—	(154.72)	—	(257.62)

data of the solid to the glass transition region and of the liquid to 600 and 150 K are included.

The phenylene (Ph) structural group (columns 5 and 6) is found in polyparaphenylene (PPh), polyparaxylene (PPX), poly(oxy-1,4-phenylene) (POPh), poly(p-hydroxybenzoic acid) (PHBA) and poly(ethylene terephthalate) (PET). Recommended data are available for all of these polymers in our ATHAS data bank [2]. Since data of solid PPX, POPh, PHBA were measured only in the vicinity of glass transition region, we did not consider them for the calculation of the solid Ph heat capacity. Since the other polymers except PPh have other hetero atoms in the backbone chain we used the recommended data of solid PPh directly. Data for liquid Ph were evaluated by averaging the phenylene contributions in POPh (by subtracting O contributions of Table 2) and in PET (by subtracting $2CH_2$— [1] and

2COO— contributions of Table 2). Extrapolation to 300 and 600 K are also made for the liquid data from the experimental heat capacities and indicated by parentheses. Standard deviations of the heat capacities generated by the addition scheme of the listed data of Ph are −1.94 ± 1.60% from 220 to 280 K for the solid PPX, 6.50 ± 1.36% from 230 to 300 K for the solid PHBA, −6.61% at 300 K for the solid and −1.27 ± 1.36% from 360 to 600 K for the liquid POPh, and 1.01 ± 3.77% from 130 to 300 K for the solid and 0.49 ± 0.62% from 350 to 590 K for the liquid PET.

Columns 7 and 8 of Table 1 show the heat capacity contribution of a 2,6-naphthylene group derived from poly(2,6-hydroxynaphthoic acid) (PHNA) by subtracting the COO— contribution (see Table 2, below). Since no second source for the group is available, no error discussion can be given.

For the ether-group O— in the backbone chain of columns 1 and 2 of Table 2 many sources are available. We have calculated the heat capacity contributions of O— from the following 7 linear aliphatic polyoxides: polyoxymethylene (POM), polyoxyethylene (POE), poly(oxytrimethylene) (PO3M), poly(oxytetramethylene) (PO4M), poly(oxyoctamethylene) (PO8M), poly(oxymethyleneoxyethylene) (POMOE) and poly(oxymethyleneoxytetramethylene) (POMO4M). To minimize the error introduced by experimental uncertainty, the calculated heat capacity contributions were multiplied with the ratio of O— to CH_2— in the above polymers (for example, 1/2 for POE). We then divided the sum of these statistical weighted O contributions by the sum of O—/CH_2— ratios of all 7 polymers and curve fitted the heat capacity for solid from 90 to 390 K into the equation.

$$C_p = \exp[0.136251(\ln T)^3 - 1.79235(\ln T)^2 + 8.29521 \ln T - 11.462]\ \mathrm{JK^{-1}\ molw^{-1}}\ (\pm 3.4\%) \tag{1}$$

Equation (1) was used to calculate the heat capacity contribution of solid O— from 90 to 390 K. The listed data from 30 to 80 K are the averages without further smoothing. Similarly, data for the liquid O— were obtained by fitting data bank data from 200 to 540 K into the linear equation.

$$C_p = -6.49216 \pm 10^{-3}\,T + 27.5124\ \mathrm{JK^{-1}\ mole^{-1}}\ (\pm 9.2\%) \tag{2}$$

Equation (2) was used to calculate the listed liquid O— contributions from 150 to 600 K. The standard deviations of the addition scheme when one calculates the heat capacities of the above 7 polymers are: POM, 0.67 ± 2.26% from 30 to 390 K for the solid and −2.00 ± 0.02% between 430 and 540 K for the liquid; POE, 0.42 ± 1.35% from 90 to 220 K for the solid and 0.55 ± 0.46% between 330 and 430 K for the liquid; PO3M, 1.83 ± 3.10% from 30 to 180 K for the solid and −1.65 ± 0.87% between 200 and 330 K for the liquid; PO4M, −4.57 ± 1.67%

Table 2 [Heat Capacity Contributions C_p in $JK^{-1} mole^{-1}$]

Temperature, K	$-O-$		$-\overset{\overset{O}{\|}}{C}-O-$		$-\overset{\overset{O}{\|}}{C}-$		$-O-\overset{\overset{O}{\|}}{C}-O-$	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
30	3.94	—	7.80	—	—	—	—	—
40	4.82	—	10.41	—	—	—	—	—
50	5.50	—	12.59	—	—	—	—	—
60	5.92	—	14.53	—	—	—	—	—
70	6.47	—	16.35	—	—	—	—	—
80	7.08	—	18.11	—	—	—	19.10	—
90	7.29	—	19.78	—	—	—	21.04	—
100	7.65	—	21.49	—	—	—	23.13	—
110	7.99	—	22.82	—	—	—	25.32	—
120	8.34	—	24.16	—	—	—	27.59	—
130	8.69	—	25.52	—	15.46	—	29.90	—
140	9.05	—	26.86	—	17.52	—	32.22	—
150	9.42	(26.54)	28.19	—	19.40	—	34.53	—
160	9.80	(26.47)	29.49	—	21.13	—	36.82	—
170	10.19	(26.41)	30.76	—	22.72	—	39.07	—
180	10.60	(26.34)	31.99	—	24.16	—	41.26	—
190	11.02	(26.28)	33.18	—	25.46	—	(43.39)	—
200	11.46	(26.21)	34.33	(62.62)	26.68	—	(45.43)	—
210	11.91	(26.15)	35.43	(63.17)	27.77	—	—	—
220	12.38	(26.08)	36.48	(63.73)	28.74	—	—	—
230	12.87	(26.02)	37.49	(64.29)	29.61	—	—	—
240	13.38	25.95	38.44	64.85	30.36	—	—	—
250	13.91	25.89	39.35	65.40	31.02	—	—	—
260	14.45	25.82	40.20	65.96	31.59	—	—	—
270	15.02	(25.76)	41.01	(66.52)	32.06	—	—	—
280	15.61	(25.69)	41.76	(67.08)	32.42	—	—	—
290	16.22	(25.63)	42.47	(67.64)	32.73	—	—	—
300	16.85	(25.56)	43.12	(68.19)	32.90	(46.33)	—	(92.01)
310	17.51	(25.50)	43.73	(68.75)	—	(47.92)	—	(93.46)
320	18.19	(25.43)	—	(69.31)	—	(49.51)	—	(94.91)
330	18.89	(25.37)	—	(69.87)	—	(51.10)	—	(96.36)
340	19.60	(25.31)	—	(70.42)	—	(52.69)	—	(97.80)
350	20.38	(25.24)	—	(70.98)	—	(54.28)	—	(99.25)
360	21.16	(25.18)	—	(71.54)	—	(55.87)	—	(100.70)
370	21.97	(25.11)	—	(72.10)	—	(57.46)	—	(102.14)
380	22.81	(25.05)	—	(72.66)	—	(59.06)	—	(103.59)
390	(23.68)	24.98	—	73.21	—	(60.65)	—	(105.04)
400	—	24.92	—	73.77	—	(62.24)	—	(106.49)

Table 2 (continued)

Temperature, K	$-O-$		$-\overset{O}{\overset{\mid}{C}}-O-$		$-\overset{O}{\overset{\mid}{C}}-$		$-O-\overset{O}{\overset{\mid}{C}}-O-$	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
410	—	24.85	—	74.33	—	(63.83)	—	(107.93)
420	—	24.79	—	74.89	—	65.42	—	(109.38)
430	—	24.72	—	75.45	—	67.01	—	(110.83)
440	—	24.66	—	76.00	—	68.60	—	(112.27)
450	—	24.59	—	76.56	—	70.19	—	(113.72)
460	—	24.53	—	77.12	—	71.79	—	(115.17)
470	—	24.46	—	77.68	—	73.38	—	(116.62)
480	—	24.40	—	78.23	—	74.97	—	(118.06)
490	—	24.33	—	78.79	—	76.56	—	(119.51)
500	—	24.27	—	79.35	—	78.15	—	(120.96)
510	—	24.20	—	79.91	—	79.74	—	(122.41)
520	—	24.14	—	80.47	—	81.33	—	(123.85)
530	—	24.07	—	81.02	—	82.92	—	(125.30)
540	—	24.01	—	81.58	—	84.52	—	(126.75)
550	—	(23.94)	—	82.14	—	(86.11)	—	(128.19)
560	—	(23.88)	—	(82.70)	—	(87.70)	—	(129.64)
570	—	(23.81)	—	(83.25)	—	(89.29)	—	(131.09)
580	—	(23.75)	—	(83.81)	—	(90.88)	—	(132.54)
590	—	(23.68)	—	(84.37)	—	(92.47)	—	(133.98)
600	—	(23.62)	—	(84.93)	—	(94.06)	—	(135.43)

from 30 to 160 K for the solid and 4.10±0.19% between 280 and 340 K for the liquid; PO8M, −3.99±1.47% from 30 to 230 K for the solid and 2.32±0.27% between 340 and 350 K for the liquid; POMOE, 3.49±2.12% from 100 to 200 K for the solid and 5.68±0.01% between 330 and 390 K for the liquid; and POMO4M, 0.10±2.24% from 100 to 180 K for the solid and 5.85±0.15% between 300 and 360 K for the melt. Despite the somewhat larger error for the O— group contribution, indicating different contributions in different polymers, it is possible to derive reasonable data with the addition scheme since O— is usually a minor component.

Heat capacity data of the ester chemical group (COO—) (columns 3, 4) were derived from the recommended data of 8 polylactones and poly(ethylene oxalate) (PEO) [4]. Similar to the treatment that we have used to derive the heat capacity of the O— group, we multiplied the calculated heat capacity contribution of COO— group by the COO— to CH_2— ratio in each of these polymers (for example, 1/5 for polycaprolactone). After having summed the multiplication product and divided by the sum of all COO— to CH_2— ratios, we further smoothed the results from 100 to 310 K fitting into the following equation:

$$C_p = \exp[-0.181889(\ln T)^3 + 2.73588(\ln T)^2 - \\ -13.0178 \ln T - 22.7591]\ \mathrm{JK^{-1}\ mole^{-1}}\ (\pm 1.1\%) \tag{3}$$

The data below 100 K were not smoothed. The calculated data of liquid COO— were fitted 240 to 550 K to the equation:

$$C_p = 5.57806 \times 10^{-2}\, T + 5.14595\ \mathrm{JK^{-1}\ mole^{-1}}\ (\pm 5.4\%) \tag{4}$$

Equation (4) was used to calculate the listed data of liquid COO— from 200 to 600 K.

When calculating the heat capacities of the polylactones and PEO with the listed data in Table 2 by the addition scheme, one obtains the following deviations: polyglycolide (PGL), 1.70 ± 1.25% from 60 to 310 K for the solid and 0.72 ± 0.79% between 510 and 550 K for the liquid; polypropiolactone (PPL), 0.70 ± 0.95% from 60 to 240 K for the solid and −3.87 ± 0.01% between 370 and 400 K for the liquid; polybutyrolactone (PBL), −3.90 ± 1.21% from 60 to 210 K for the solid and 5.43 ± 0.05% between 340 and 350 K for the liquid; polyvalerolactone (PVL), −2.68 ± 0.80% from 60 to 210 K for the solid and 5.61 ± 0.11% between 340 and 350 K for the liquid; polycaprolactone (PCL), −3.26 ± 1.08% from 60 to 200 K for the solid and 6.70 ± 0.09% between 340 and 350 K for the liquid; polyundecanolactone (PUDL), −2.56 ± 1.57% from 60 to 220 K for the solid and 5.85 ± 0.26% between 370 and 400 K for the liquid; polytridecanolactone (PTDL), −3.04 ± 1.77% from 60 to 220 K for the solid and 3.81 ± 0.16% between 360 and 370 K for the liquid; polypentadecanolactone (PPDL), −3.17 ± 1.70% from 60 to 250 K for the solid and 2.33 ± 0.32% between 360 and 370 K for the liquid; and poly(ethylene oxalate) (PEO), 3.66 ± 2.20% from 60 to 300 K for the solid and 6.28 ± 0.08% between 310 and 360 K for the liquid. All polymers show somewhat larger deviations at temperatures below 50 K.

Columns 5 and 6 of Table 2 show the solid and liquid heat capacity contribution of the carbonyl (CO—) chemical group. It was calculated by subtracting the contributions of O— and Ph— from poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (PEEK). Recommended heat capacity data of PEEK have been reported in the pertaining paper of reference 4.

Columns 7 and 8 of Table 2 display the carbonate (OCOO—) heat capacity contributions. They were derived by subtracting the contributions of 2Ph— (Table 1) and MeCMe— (Ref. 1) from poly(4,4′-isopropylidenephenylene carbonate (PiPdPC). Listed data for the solid, range only from 80 to 200 K due to lack of

Table 3 [Heat Capacity Contributions C_p in JK^{-1} mole^{-1}]

Temperature, K	$-\overset{O}{\overset{\vert}{C}}-NH-$		$-SO_2-$	$-C{\equiv}C-$	$-Si(CH_3)_2-$		$-Si(C_6H_5)_2-$	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
30	—	—	6.89	(0.84)	11.04	—	29.46	—
40	—	—	9.72	(2.20)	16.41	—	40.41	—
50	—	—	12.99	(3.49)	21.73	—	50.24	—
60	—	—	15.69	(4.50)	26.10	—	59.46	—
70	15.63	—	18.42	5.74	31.84	—	68.02	—
80	17.45	—	20.56	6.98	36.34	—	75.83	—
90	19.15	—	22.58	7.79	40.98	—	83.06	—
100	20.81	—	24.50	8.53	45.23	—	90.25	—
110	22.34	—	26.35	9.60	49.29	—	96.30	—
120	23.78	—	28.13	10.49	53.14	—	102.57	—
130	25.26	—	29.86	12.11	56.80	—	108.53	—
140	26.76	—	31.55	13.00	60.30	—	114.46	—
150	28.35	(108.87)	33.21	13.78	—	(73.24)	120.30	(181.38)
160	30.10	(108.59)	34.84	(15.23)	—	(74.52)	(125.94)	(188.47)
170	32.00	(108.30)	36.44	(15.79)	—	(75.80)	(132.18)	(195.55)
180	34.05	(108.02)	38.03	(16.86)	—	(77.08)	(138.69)	(202.64)
190	36.15	(107.74)	39.61	(18.45)	—	(78.36)	(145.45)	(209.72)
200	38.35	(107.45)	41.17	(19.12)	—	(79.64)	(152.47)	(216.81)
210	39.56	(107.17)	42.73	(20.65)	—	(80.92)	(158.45)	(223.89)
220	41.72	(106.88)	44.28	(21.97)	—	(82.20)	(164.81)	(230.98)
230	43.88	(106.60)	45.83	(23.20)	—	(83.48)	(171.25)	(238.06)
240	46.04	(106.32)	47.38	—	—	84.76	(177.57)	(245.15)
250	48.20	(106.03)	48.93	—	—	86.04	(183.97)	(252.23)
260	50.37	(105.75)	50.48	—	—	87.32	—	(259.32)
270	52.53	(105.46)	52.03	—	—	(88.60)	—	(266.40)
280	54.69	(105.18)	53.59	—	—	(89.88)	—	(273.49)
290	56.85	(104.89)	55.15	—	—	(91.16)	—	(280.57)
300	59.02	(104.61)	56.71	—	—	(92.44)	—	(287.66)
310	61.18	(104.33)	—	—	—	(93.72)	—	(294.74)
320	63.34	(104.04)	—	—	—	(95.00)	—	(301.83)
330	—	(103.76)	—	—	—	(96.28)	—	(308.91)
340	—	(103.47)	—	—	—	(97.55)	—	(316.00)
350	—	(103.19)	—	—	—	(98.83)	—	(323.08)
360	—	(102.91)	—	—	—	(100.11)	—	(330.17)
370	—	(102.62)	—	—	—	(101.39)	—	(337.25)
380	—	(102.34)	—	—	—	(102.67)	—	(344.34)
390	—	102.05	—	—	—	(103.95)	—	(351.42)
400	—	101.77	—	—	—	(105.23)	—	(358.51)

Table 3 (continued)

Temperature K	$-\overset{O}{\overset{\|}{C}}-NH-$		$-SO_2-$	$-C{\equiv}C-$	$-Si(CH_3)_2-$		$-Si(C_6H_5)_2-$	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
410	—	101.49	—	—	—	(106.51)	—	(365.59)
420	—	101.20	—	—	—	(107.79)	—	(372.68)
430	—	100.92	—	—	—	(109.07)	—	(379.76)
440	—	100.63	—	—	—	(110.35)	—	(386.85)
450	—	100.35	—	—	—	(111.63)	—	(393.93)
460	—	100.07	—	—	—	(112.91)	—	(401.02)
470	—	99.78	—	—	—	(114.19)	—	(408.10)
480	—	99.50	—	—	—	(115.47)	—	(415.19)
490	—	99.21	—	—	—	(116.75)	—	(422.27)
500	—	98.93	—	—	—	(118.03)	—	(429.36)
510	—	98.65	—	—	—	(119.31)	—	(436.44)
520	—	98.36	—	—	—	(120.59)	—	(443.53)
530	—	98.08	—	—	—	(121.87)	—	(450.61)
540	—	97.79	—	—	—	(123.15)	—	(457.70)
550	—	97.51	—	—	—	(124.43)	—	(464.78)
560	—	97.22	—	—	—	(125.71)	—	(471.87)
570	—	96.94	—	—	—	(126.99)	—	(478.95)
580	—	96.66	—	—	—	(128.27)	—	(486.04)
590	—	96.37	—	—	—	(129.55)	—	(493.12)
600	—	96.09	—	—	—	(130.83)	—	(500.21)

measurements at higher and lower temperatures for polyisobutene. Extrapolation of the data for the melt to the high 600 K and the low 300 K are also included in the table.

Heat capacity group contribution of amide (CONH—) listed in columns 1 and 2 of Table 3 was calculated from the recommended data of nylon 6, nylon 6.6 and nylon 6.12 [2]. Even though heat capacity data of polyglycine are also available in the data bank, we excluded them from consideration due to the unacceptable data uncertainty (>8%) suggested by the author. To minimize the deviation due to experimental error, we multiplied the calculated heat capacity contributions of CONH— with the fraction of the backbone elements C—N— to all backbone elements (for example, 2/7 for nylon 6). The sum of these statistically weighted data was then divided by the sum of all C—N— fractions. The resulting heat capacities cover temperatures from 70 to 320 K for the solid and 390 to 600 for the liquid. Linear extrapolation data to 150 K for the liquid are also included in Table 3. When one use the listed data to calculate the heat capacities of the above three polyamides, one finds the following standard deviations: nylon 6, −0.30±0.45% from 70 to 310 K for the solid and −1.75±1.10% between 320 and 600 K for the liquid; nylon 6.6, 2.05±0.82% from 230 to 320 K for the solid and 2.07±1.40% for the liquid from 330 to 600 K; and nylon 6.12, −0.99±0.89% from 230 to 310 K for the solid and −0.32±0.35% between 320 and 600 K for the liquid.

The second chemical group in Table 3 (column 3) is sulfone, SO_2—. Data for the heat capacity of solid SO_2— could be calculated by subtracting (CH_2—+HCMe—) from poly(propene sulfone) (PPS), (CH_2—+HCEt—) from poly(1-butene sulfone) (PBS) and (CH_2—+HCBu—) from poly(1-hexene sulfone) (PHS). To calculate the listed data, we first multiplied the SO_2— contribution with the fraction of SO_2— to the side chain carbon atoms in the above three polysulfones. After dividing the sum of all statistically weighted SO_2— contributions with the total statistical weights, we further curve smoothed the calculated data into the following equation:

$$C_p = \exp[5.88759\times 10^{-2}(\ln T)^3 - 8.81833\times 10^{-1}(\ln T)^2 + \\ +5.14427\ln T - 7.5401]\ \mathrm{JK^{-1}\ mole^{-1}}\ (\pm 1.4\%) \tag{5}$$

Equation (5) was used to calculate the listed data from 70 to 300 K. No data for the liquid SO_2— are available. Standard deviations of the above three polysulfones calculated by the addition scheme are: PPS, 30–300 K, −1.22±0.71%; PBS, 100–240 K, 2.67±1.31%; and PHS, 30–220 K, 1.52±1.50%.

The heat capacity group contribution of the ethnyl (CC—) group (column 4), which shows a carbon-carbon triple bond C≡C— in the backbone, was calculated by subtracting the contributions of PhSiPh— from poly(diethynyl diphenylsilylene) (PdEdPS), and of PhGePh— from poly(diethnyl diphenylgermylene) (PdEdPG). Reported data were taken as the average of the CC— contributions in these two polymers. Only data for the solid between 30 and 230 K are available. Below 60 K, the recommended data of these two polymers (listed in Table 3) were calculated by a Tarasov function extrapolation. Standard deviations of these two polymers calculated by the addition scheme using the listed data are: −0.30±1.57% for PdEdPS and 0.33±1.70% for PdEdPG between 70 to 230 K.

The heat capacity contribution of dimethylsilylene (MeSiMe—) (columns 5 and 6) was calculated by subtracting contribution of O— (Table 2) from the heat capacity of poly(dimethyl siloxane) PDMSO). Data are available for the solids from 30 to 140 K. Extrapolation was also made for the data of the liquid MeSiMe— to 600 K, because occasionally high temperature data are needed for the addition scheme.

Columns 7 and 8 contain the heat capacity contribution of diphenylsilylene (PhSiPh—). It was calculated by subtracting the contribution of vinylene group

Table 4 [Heat Capacity Contributions C_p in JK^{-1} $mole^{-1}$]

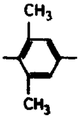
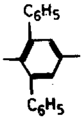
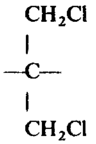
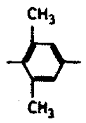
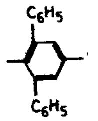
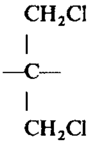
Temperature, K					 $-C(CH_2Cl)_2-$		$-Ge(C_6H_5)_2-$	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
30	—	—	—	—	19.01	—	33.93	—
40	—	—	—	—	24.04	—	45.50	—
50	—	—	—	—	28.18	—	55.71	—
60	—	—	—	—	32.11	—	65.18	—
70	—	—	—	—	35.51	—	73.41	—
80	46.00	—	—	—	38.73	—	80.82	—
90	50.98	—	—	—	42.19	—	88.08	—
100	55.81	—	—	—	45.43	—	95.25	—
110	60.55	—	—	—	48.52	—	101.20	—
120	64.99	—	—	—	51.38	—	107.17	—
130	68.97	—	—	—	54.02	—	113.13	—
140	73.17	—	—	—	56.52	—	118.96	—
150	77.07	—	—	—	58.83	—	125.00	(224.81)
160	80.84	—	—	—	61.23	—	(130.54)	(229.30)
170	84.69	—	—	—	63.51	—	(137.08)	(233.80)
180	88.27	—	170.00	—	66.04	—	(143.59)	(239.29)
190	92.28	—	178.18	—	68.48	—	(150.35)	(242.78)
200	96.14	—	186.74	—	71.20	—	(157.37)	(247.27)
210	99.79	—	195.39	—	73.79	—	(166.25)	(251.76)
220	103.62	—	203.52	—	76.20	—	(174.11)	(256.25)
230	107.03	—	210.23	—	78.73	—	(181.95)	(260.74)
240	110.72	—	216.02	—	80.46	—	—	(265.23)
250	114.39	—	221.99	—	82.39	—	—	(269.72)
260	118.15	—	228.85	—	84.49	—	—	(274.21)
270	121.48	—	236.18	—	86.46	—	—	(278.71)
280	125.09	—	243.69	—	—	(78.05)	—	(283.20)
290	129.48	—	250.78	—	—	(84.95)	—	(287.69)
300	132.85	(183.90)	257.25	(313.23)	—	(90.95)	—	(292.18)
310	136.09	(186.24)	262.99	(320.18)	—	(96.15)	—	(296.67)
320	139.71	(188.58)	268.81	(327.13)	—	(100.75)	—	(301.16)
330	143.21	(190.93)	275.61	(334.08)	—	(104.75)	—	(305.65)
340	146.60	(193.27)	282.90	(341.03)	—	(108.25)	—	(310.14)
350	149.82	(195.61)	289.12	(347.98)	—	(111.35)	—	(314.63)
360	153.34	(197.96)	293.84	(354.94)	—	(113.95)	—	(319.12)
370	156.63	(200.30)	298.23	(361.89)	—	(116.25)	—	(323.62)
380	159.89	(202.65)	303.49	(368.84)	—	(118.25)	—	(328.11)

Table 4 (continued)

Temperature, K					 $-\overset{CH_2Cl}{\underset{CH_2Cl}{C}}-$		$-Ge(C_6H_5)_2-$	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
390	(163.12)	(204.99)	(309.32)	(375.79)	—	119.95	—	(332.60)
400	—	(207.33)	—	(382.74)	—	—	—	(337.09)
410	—	(209.68)	—	(389.70)	—	—	—	(341.58)
420	—	(212.02)	—	(396.65)	—	—	—	(346.07)
430	—	(214.37)	—	(403.60)	—	—	—	(350.56)
440	—	(216.71)	—	(410.55)	—	—	—	(355.05)
450	—	(219.05)	—	(417.50)	—	—	—	(359.54)
460	—	(221.40)	—	(424.46)	—	—	—	(364.03)
470	—	(223.74)	—	(431.41)	—	—	—	(368.53)
480	—	(226.09)	—	(438.36)	—	—	—	(373.02)
490	—	228.43	—	(445.31)	—	—	—	(377.51)
500	—	230.77	—	452.26	—	—	—	(382.00)
510	—	233.12	—	459.32	—	—	—	(386.49)
520	—	235.46	—	466.17	—	—	—	(390.98)
530	—	237.81	—	473.12	—	—	—	(395.47)
540	—	240.15	—	(480.07)	—	—	—	(399.96)
550	—	242.49	—	(487.02)	—	—	—	(404.45)
560	—	(244.84)	—	(493.98)	—	—	—	(408.94)
570	—	(247.18)	—	(500.93)	—	—	—	(413.44)
580	—	(249.53)	—	(507.88)	—	—	—	(417.93)
590	—	(251.87)	—	(514.83)	—	—	—	(422.42)
600	—	(254.21)	—	(521.78)	—	—	—	(426.91)

HC=CH— (Table 1) from the poly(vinylene diphenylsilylene) (PVdPS). Reported data are available from 30 to 250 K for solid PhSiPh. Data at high temperatures were found by linear extrapolations of the data from below to the glass transition regions (210–260 K). Listed data for the liquid include linear extrapolation of the data to 600 K and 150 K.

In the last Table, columns 1 to 4 contain the heat capacity contribution of the structural groups dimethylphenylene (dMePh) and diphenylphenylene (dPhPh). They were calculated by subtracting the heat capacity contribution of the O— group (Table 2) from the poly(oxy-dimethylphenylene) (POdMPh) and poly(oxy-diphenylphenylene) (POdPPh) heat capacities, respectively. The available data for the solids range from 80 to 390 K for dMePh and 180 to 390 K for dPhPh.

Reported data of both groups in the molten state include extrapolations to 600 K and 300 K.

The next group contribution is bis(chloromethyl)methylene (ClMCClM) (columns 5 and 6). It was derived from poly[oxy-2,2′-bis (chloromethyl)trimethylene] (Penton). The listed data of ClMCClM were calculated by subtracting the O— and $2CH_2$— contributions from Penton. Data for the solid are available from 30 to 270 K. For the liquid, data are available from 280 to 390 K.

The last group contribution of Table 4 is that of diphenylgermylene (PhGePh—) (columns 7 and 8). To calculate its contribution was subtracted from the heat capacity of poly(vinylene diphenylgermylene) (PVdPG). Data are available from 30 to 230 K for the solid and 210 to 230 K for the liquid. The latter were extrapolated to 600 and 150 K.

Discussion

Despite some reservations on theoretical grounds, it seems to be possible to extend the empirical addition scheme of heat capacity to macromolecules with other than single bonded carbon backbone atoms. The 713 multiple data points used for the derivation of Tables 1 to 4 show an overall average deviation of +0.1% and the combined standard deviation is ± 1.5%. Values which are not far from the expected experimental accuracy, but show signs of systematic error since the 50 average heat capacity errors shows a larger standard deviation (± 3.5%) than the combined standard deviations.

In addition to the check of internal consistency, one can attempt an analysis of six polymers for which experimental heat capacities are either available and not used in the addition scheme or are of doubtful quality. These experimental heat capacities are compared with heat capacities derived from the addition scheme. Table 5 shows the results.

Experimental heat capacity data of poly(oxypropylene) (POPr) in both solid and liquid states were measured by adiabatic calorimetry [5]. The addition scheme of this polymer is O— + CH_2— + HCMe—. However, note that there are slightly different heat capacity contributions between glassy and crystalline states for HCMe— from 30 to 250 K. The studied polymer POPr was semicrystalline and had a crystallinity 25%. In order to get the best result, we rewrote the above additivity to O— + $0.25(CH_2\text{—} + HCMe\text{—})_{\text{cryst.}} + 0.75(CH_2\text{—} + HCMe\text{—})_{\text{glass}}$ (Part A, Table 6). In the solid state, the addition scheme heat capacity is consistently below the experimental data at the same temperature. Perhaps the measured heat capacity of semicrystalline POPr is complicated by a very broad glass transition region, as in the case of polypropylene. Overall, the standard deviation from the addition scheme is $-5.3\pm0.5\%$ from 80 to 190 K for the solid and $2.7\pm0.9\%$ between 200 and 370 K for the liquid.

In part B of Table 5, the listed experimental heat capacities of solid poly(ethylene sebacate) (PES) are newly measured [6]. Measurements for the liquid were done earlier by adiabatic calorimetry [7]. The additivity of this polymer is expressed by $2COO—+10CH_2—$. The standard deviation from the addition scheme for the solid from 120 to 220 K is $1.80\pm1.10\%$, and for the liquid from 350 to 410 K, $1.04\pm0.08\%$.

The available heat capacity data of solid poly(butylene adipate) (PBA) measured by adiabatic calorimetry was suspected to contain large experimental systematic errors. Indeed, when one compares the addition scheme results with the measured data in Part C of Table 5, one finds considerable deviations (overall standard deviation for the solid between 80 and 190 K is $-9.06\pm0.70\%$, additivity $2COO—+8CH_2—$). The heat capacity of liquid PBA was measured by the same authors by DSC. Our addition scheme results fit these data of the liquid much better. The from 330–440 K is $0.19\pm0.96\%$.

The heat capacity data of poly(ethylene terephthalate) (PET) in the data bank [2] were derived from 6 different measurements. However, there is only one set of measurements at temperatures below 120 K, and there is growing suspicion about the precision of these. In Part D of Table 5, one can see that the deviations of our addition scheme from the reported data below 120 K are about 10% (additivity: $Ph—+2COO—+2CH_2—$). At higher temperature, where there are as many as 5 measurements of the heat capacity the recommended data are close to the addition scheme. The standard deviation of the addition scheme from the recommended data in this region, 130–300 K, is $1.0\pm3.8\%$. Since the heat capacity contribution of Ph in liquid state was derived to equal parts from PET and poly(oxy-phenylene) (POPh), the high precision of prediction is expected. The standard deviation of the addition scheme from the recommended data is only $0.49\pm0.62\%$ for the liquid PET from 350 to 590 K.

Part E of Table 5 contains 3 different compositions of poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) [9]. Structurally, it is the random copolymer of *p*-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid. In Part E1 of Table 5 the composition of this copolymer is 30/70 mole percent, the additivity is thus to be $COO—+0.30Ph—+0.70Na—$. The standard deviation of the addition scheme for the solid is $-1.33\pm1.30\%$ from 230 to 300 K, and for the liquid, $0.11\pm0.50\%$ between 500 and 600 K. In Part E2, where the composition is 58/42 mole percent ($COO—+0.58Ph—+0.42Na—$), the standard deviation of the addition scheme for the solid is $-0.04\pm1.01\%$ from 230 to 300 K and for the liquid $1.96\pm0.01\%$ between 500 and 600 K. In Part E3, the composition changes to 75/25 mole percent

Table 5 Comparison of Calculated Heat Capacities [Heat capacities in JK^{-1} $mole^{-1}$ C_p, Deviations in %]

Temperature, K	Experiment	Calculated	Deviation
A. Polyoxypropylene, Solid, 25% Crystallinity			
80	31.21	29.96	−4.02
90	34.33	32.76	−4.58
100	37.37	35.59	−4.76
110	40.34	38.30	−5.04
120	43.22	40.93	−5.30
130	46.03	43.49	−5.52
140	48.76	45.98	−5.70
150	51.41	48.42	−5.80
160	53.98	50.82	−5.85
170	56.48	53.19	−5.82
180	58.89	55.53	−5.71
190	61.23	58.02	−5.25
Polyoxypropylene, Liquid			
220	95.46	(99.43)	+4.16
210	97.04	(100.88)	+3.96
220	98.61	(102.32)	+3.76
230	100.19	(103.77)	+3.57
240	101.77	(105.22)	+3.39
250	103.35	(106.67)	+3.22
260	104.92	(108.12)	+3.04
270	106.50	(109.56)	+2.88
280	108.08	(111.01)	+2.72
290	109.65	(112.46)	+2.56
300	111.23	(113.91)	+2.41
310	112.81	(115.36)	+2.26
320	114.38	(116.80)	+2.12
330	115.96	(118.25)	+1.98
340	117.54	(119.70)	+1.84
350	119.12	(121.15)	+1.72
360	120.69	(122.60)	+1.58
370	122.27	(124.04)	+1.45
B. Poly(ethylene sebacate), Solid			
120	154.06	157.53	+2.25
130	162.64	167.03	+2.70
140	171.22	176.22	+2.92
150	179.80	185.07	+2.94
160	188.37	193.47	+2.71

Table 5 (continued)

Temperature, K	Experiment	Calculated	Deviation
170	196.95	201.51	+2.31
180	205.53	209.28	+1.82
190	214.11	216.86	+1.28
200	222.69	224.35	+0.75
210	231.27	231.86	+0.25
220	239.85	239.57	−0.12
Poly(ethylene sebacate), Liquid			
360	472.69	(477.97)	+1.12
370	478.25	(483.41)	+1.08
380	483.81	(488.85)	+1.04
390	489.38	494.29	+1.00
400	494.94	499.73	+0.97
410	500.51	505.17	+0.93
C. Poly(butylene adipate), Solid The experimental heat capacity data of solid PBA may contain substantial systematic experimental error and does not meet the ATHAS standard of acceptable data (see Ref. 2)			
80	108.73	98.54	− 9.38
90	118.24	108.84	− 7.95
100	127.74	118.58	− 7.17
110	137.22	127.23	− 7.28
120	146.69	135.69	− 7.50
130	156.16	143.83	− 7.89
140	165.63	151.72	− 8.40
150	175.11	159.33	− 9.01
160	184.59	166.57	− 9.76
170	194.07	173.51	−10.59
180	203.57	180.22	−11.47
190	213.07	186.76	−12.35
Poly(butylene adipate), Liquid			
330	402.60	(397.27)	− 1.33
340	406.13	(401.84)	− 1.06
350	409.66	(406.42)	− 0.79
360	413.19	(410.99)	− 0.53
370	416.72	(415.57)	− 0.28
380	420.25	(420.14)	− 0.03
390	423.78	424.72	+ 0.22
400	427.31	429.30	+ 0.46
410	430.84	433.87	+ 0.70
420	434.37	438.45	+ 0.94
430	437.90	443.02	+ 1.17
440	441.43	447.60	+ 1.40
450	444.96	452.17	+ 1.62

Table 5 (continued)

Temperature, K	Experiment	Calculated	Deviation
D. Poly(ethylene terephthalate), Solid			
80	69.95	80.02	+14.39
90	77.18	87.19	+12.97
100	84.42	94.37	+11.79
110	91.70	100.76	+ 9.88
120	100.10	107.20	+ 7.09
130	105.95	113.62	+ 7.24
140	112.61	120.01	+ 6.57
150	119.38	126.35	+ 5.84
160	126.23	132.60	+ 5.05
170	133.14	138.77	+ 4.23
180	140.09	144.87	+ 3.41
190	147.09	150.90	+ 2.59
200	154.12	156.86	+ 1.78
210	161.17	162.80	+ 1.01
220	168.24	168.73	+ 0.29
230	175.32	174.65	− 0.39
240	182.43	180.58	− 1.01
250	189.54	186.52	− 1.60
260	196.67	192.40	− 2.17
270	203.80	198.20	− 2.75
280	210.94	203.92	− 3.33
290	218.09	209.47	− 3.95
300	225.24	214.91	− 4.59
Poly(ethylene terephthalate), Liquid			
350	335.65	(333.69)	− 0.58
360	338.47	(336.83)	− 0.48
370	341.29	(339.98)	− 0.38
380	344.11	(343.12)	− 0.29
390	346.93	346.27	− 0.19
400	349.75	349.41	− 0.10
410	352.57	352.56	0.00
420	355.39	355.70	+ 0.09
430	358.21	358.85	+ 0.18
440	361.03	361.99	+ 0.27
450	363.85	365.14	+ 0.35
460	366.67	368.28	+ 0.44
470	369.49	371.43	+ 0.53
480	372.31	374.58	+ 0.61
490	375.13	377.72	+ 0.69
500	377.95	380.87	+ 0.77
510	380.77	384.01	+ 0.85
520	383.59	387.16	+ 0.93
530	386.41	390.30	+ 1.01

Table 5 (continued)

Temperature, K	Experiment	Calculated	Deviation
540	389.23	393.45	+ 1.08
550	392.05	(396.59)	+ 1.16
560	394.87	(399.74)	+ 1.23
570	397.69	(402.88)	+ 1.31
580	400.51	(406.03)	+ 1.38
590	403.33	(409.17)	+ 1.45

E1. Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) Random-Copolymer, Solid, 30/70 mole %

230	127.90	128.80	+0.70
240	134.20	134.11	−0.07
250	140.40	139.35	−0.75
260	146.60	144.65	−1.33
270	152.80	149.87	−1.92
280	159.10	155.16	−2.48
290	165.40	162.96	−1.48
300	172.60	166.83	−3.34

Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) Random-Copolymer, Liquid, 30/70 mole %

500	284.60	282.69	−0.67
510	287.00	285.59	−0.49
520	289.50	288.49	−0.35
530	291.90	291.39	−0.18
540	294.40	294.29	−0.04
550	296.80	(297.19)	+0.13
560	299.30	(300.09)	+0.26
570	301.70	(302.98)	+0.43
580	304.20	(305.88)	+0.55
590	306.60	(308.78)	+0.71
600	309.10	(311.68)	+0.84

E2. Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) Random-Copolymer, Solid, 58/42 mole %

230	116.60	118.34	+1.49
240	121.80	123.02	+1.00
250	127.10	127.64	+0.42
260	132.30	132.28	−0.01
270	137.50	136.87	−0.45
280	142.80	141.50	−0.91
290	147.90	147.61	−0.20
300	153.90	151.36	−1.65

Table 5 (continued)

Temperature, K	Experiment	Calculated	Deviation
Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) Random-Copolymer, Liquid, 58/42 mole %			
500	253.58	258.59	+1.97
510	255.97	261.01	+1.97
520	258.36	263.44	+1.97
530	260.75	265.87	+1.96
540	263.14	268.30	+1.96
550	265.53	(270.73)	+1.96
560	267.92	(273.16)	+1.96
570	270.31	(275.58)	+1.95
580	272.70	(278.01)	+1.95
590	275.08	(280.44)	+1.95
600	277.47	(282.87)	+1.95
E3. Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) Random-Copolymer, Solid, 75/25 mole %			
230	111.00	111.99	+0.89
240	115.90	116.28	+0.33
250	120.80	120.53	−0.23
260	125.80	124.77	−0.82
270	130.70	128.98	−1.31
280	135.60	133.20	−1.77
290	140.00	138.29	−1.22
300	145.00	141.97	−2.09
Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl) Random-Copolymer, Liquid, 75/25 mole %			
500	245.41	243.95	−0.59
510	246.50	246.09	−0.16
520	247.58	248.24	+0.26
530	248.67	250.38	+0.69
540	249.76	252.52	+1.11
550	250.84	(254.66)	+1.52
560	251.93	(256.81)	+1.94
570	253.02	(258.95)	+2.34
580	254.10	(261.09)	+2.75
590	255.19	(263.23)	+3.15
600	256.28	(265.38)	+3.55

Table 5 (continued)

Temperature, K	Experiment	Calculated	Deviation
F. Alternating-Copolymer of Vinylene Diphenylsilylene and Vinylene Diphenylgermylene, Solid			
30	70.01	77.53	+10.74
40	95.22	103.69	+8.90
50	120.70	126.59	+4.88
60	143.20	147.42	+2.95
70	162.60	166.15	+2.18
80	179.80	183.55	+2.09
90	195.50	200.38	+2.50
100	210.60	216.40	+2.75
110	225.70	231.90	+2.75
120	240.80	246.80	+2.49
130	256.00	261.60	+2.19
140	271.10	276.30	+1.92
150	286.20	291.30	+1.78
160	301.20	(306.20)	+1.66
170	316.10	(321.50)	+1.71
180	331.30	(337.10)	+1.75
190	346.80	(353.30)	+1.87
200	362.80	(370.10)	+2.01
210	379.40	(387.80)	+2.21
220	396.50	(404.90)	+2.12
230	414.00	(422.10)	+1.96
Alternating-Copolymer of Vinylene Diphenylsilylene and Vinylene Diphenylgermylene, Liquid			
310	671.70	(681.73)	+1.49
320	691.00	(695.13)	+0.60

(COO—+0.75Ph—+0.25Na—) with a standard deviation of the addition scheme for the solid of −0.78±1.04% from 230 to 300 K and for the liquid, 1.50±1.37% from 500 to 600 K.

The last part in Table 5, Part F, contains the comparison of the addition scheme with the heat capacity measurements of alternating copolymers of vinylene diphenylsilylene and vinylene diphenylgermylene [10]. Measurement of the heat capacity of this coplymer was done by adiabatic calorimetry. The listed experimental data in Table 5 were derived by connecting the author's data by spline function fitting. The additivity of this alternating copolymer is PHSiPh—+PhGePh—+2HCCH—. Standard deviations of our addition scheme from the experimental data are 2.2±0.4% for the solid between 60 and 230 K and 1.0±0.4% for the liquid between 310 and 320 K. The deviation is somewhat higher below 50 K, where the reported data were extrapolated using a Tarasov fit with the higher temperature data.

The overall standard deviation of 177 data points (excluding data of solid PBA, the data of solid PET below 120 K and data of the alternating copolymer of PVdPS and PVdPG below 50 K) in Table 5 is 0.60±2.35%, close to experimental precision. Overall, the presented addition scheme seems thus capable to represent and predict heat capacities of many linear macromolecules.

The limits of the empirical addition scheme can be explored using the heat capacity contribution of the solid O— and COO— groups for which a wide variety of measurements have been made (see Table 2). Tables 6 and 7 show that there are, indeed, systematic increases in these goup contributions when calculated from homopolymers with increasing number of CH_2— groups. In the derivation of the

Table 6 Heat Capacity Contributions of the COO— Group in Polyester, C_V, in JK^{-1} mole^{-1}

Temp., K	PGL	PPL	PBL	PVL	PCL	PUDL	PTDL	PPDL
100	20.65	20.99	23.05	22.90	23.47	22.85	23.31	24.36
110	22.01	22.35	24.35	24.21	24.72	24.33	24.68	25.72
120	23.25	23.50	25.54	25.34	25.79	25.50	25.91	26.69
130	24.40	24.56	26.69	26.39	26.80	26.66	27.09	27.52
140	25.47	25.54	27.82	27.39	27.77	27.81	28.41	28.26
150	26.46	26.51	28.97	28.43	28.81	29.03	29.86	29.28
160	27.41	27.78	30.18	29.70	30.26	31.16	32.34	31.70
170	28.32	29.04	31.66	31.04	31.84	33.50	35.09	34.33
180	29.19	30.33	33.18	32.44	33.49	35.99	38.02	37.18
190	30.03	31.63	34.71	33.85	35.16	38.53	41.01	40.10
200	30.84	32.92	36.21	35.24	36.80	41.02	43.95	42.97

Table 7 Heat Capacity Contributions of the O— Group in Linear, Aliphatic Polyoxides, C_V, in JK^{-1} mole^{-1}

Temp., K	POM	POMOE	POE	POMO4M	PO3M	PO4M	PO8M
100	7.23	6.37	7.94	6.49	7.37	9.29	10.97
110	7.48	6.76	8.27	6.98	7.80	9.70	11.00
120	7.77	7.08	8.47	7.54	8.12	10.73	11.28
130	8.12	7.42	8.75	8.14	8.44	11.24	11.41
140	8.51	7.80	8.91	8.88	8.76	11.70	11.92
150	8.96	8.15	9.13	9.34	9.13	12.47	12.45
160	9.45	8.63	9.42	9.91	9.59	13.53	12.43
170	9.98	9.15	9.57	10.69	10.14	—	13.75
180	10.53	9.76	9.80	11.54	10.77	—	14.46
190	11.06	10.45	10.02	—	—	—	15.69
200	11.58	11.51	10.42	—	—	—	17.34

addition scheme this effect was minimized by an appropriate assignment of statistical weights, which also reduces the influence of the experimental error. The two possible major causes of the systematic deviations could be an error in the CH_2— group contribution or a non-additive change in the skeletal vibrations.

The CH_2— heat capacity has experimentally been frequently verified [2]. In addition, the experimental and the calculated heat capacity from the vibrational spectrum agree well in this temperature range [4]. It is thus more likely that a non-additive skeletal vibration is at fault. To prove this hypothesis, one can express the heat capacity contribution of the O— group at constant volume as:

$$C_V(\text{O—})_{\text{Add.Scheme}} = C_V(\text{PO}) - nC_V(\text{CH}_2\text{—}) \tag{6}$$

where $C_V(\text{PO})$ and $C_V(\text{CH}_2\text{—})$ are the heat capacities of the given polyoxide and polyethylene, respectively. Next, each of these heat capacities can be separated into skeletal contributions S and group contribution G. Since it is well established that group vibrations G are additive, one can derive the overall skeletal heat capacity contribution for the polyoxides as follows:

$$S(\text{PO}) = S(\text{O—})_{\text{Add.Scheme}} + nS(\text{CH}_2\text{—}) \tag{7}$$

The skeletal vibrations of CH_2— are well known [4], so that one can write

$$S(\text{O—})_{\text{Add.Scheme}} = C_V(\text{O—})_{\text{Add.Scheme}} - (2\text{C—O} - \text{C—C})_{\text{stretch}} \tag{8}$$

The term in parentheses accounts for the difference in group vibration contributions to the heat capacity and is well known [4]. Fitting now $S(\text{O—})_{\text{Add.Scheme}}$ to a Tarasov function for 2 moles of vibrators yields the result plotted in Fig. 1. The average frequency parameters θ_3 and θ_1 change smoothly, but not linearly, from POM to PE. Using the different average θ-values for the calculation of $S(\text{O—})$, the errors, for example, at 150 K drop to a satisfactory $-2.2 \pm 1.7\%$, from

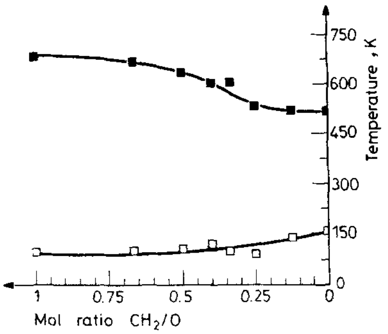


Fig. 1 Change of characteristic temperatures in a Tarasov fit, θ_1 (solid squares) and θ_3 (X) as a function of CH_2—/O—. Heat capacities for the fit were calculated using Eq. 8

$-3.0 \pm 15\%$ for the overall difference of C_p(O—) in Table 7 from column 1 of Table 2 [9.42 JK^{-1} $mole^{-1}$].

As expected, changes of the skeletal vibrations are at the root of the limit of the addition scheme of heat capacities.

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Zusammenfassung — Das früher entwickelte Additionsschema für Wärmekapazitäten wird auf Makromoleküle erweitert, die Nicht-C-Bindungen im Stützgerüst enthalten. Tabellen für 31 Gruppen sind angegeben. Von 713 Meßdaten wurden für Gruppenbeiträge, für die mehr als ein Meßwert zur Verfügung stand, Mittelwerte berechnet, wobei sich eine Abweichung von 0.1 ± 1.5% (interne Konsistenz) ergab. Berechnete Wärmekapazitäten von Homopolymeren und Kopolymeren, für die unabhängige Messungen ausgeführt wurden, weisen einen mittleren Fehler von 0.60% bei einer Standardabweichung von 2.35% auf (177 Meßwerte).

Резюме — Развитая ранее аддитивная схема расчета теплоемкостей применена к макромолекулам, не содержащим углеродных связей в остове молекулы. Приведены таблицы для 31 группы. 713 точечных данных, измеренных более чем один раз и усредненных для групповых вкладов, показали отклонение 0.1 ± 1.58% (внутренняя совместичмость). Теплоемкости для гомополимеров и сополимеров, вычисленные на основе независимых измерений, показали средние ошибки 0,60% и стандартное отклонение ±2,35% (177 точечных данных).