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AN ADDITION SCHEME OF HEAT CAPACITIES OF LINEAR MACROMOLECULES. CARBON BACKBONE POLYMERS

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It is shown that heat capacities of linear macromolecules consisting of all-carbon single-bonded backbones can be calculated from the appropriate contributions of substituted carbon atoms to a precision of about − 0.2 ± 2.5% (155 data points), which is similar to the experimental precision. Heat capacity contributions of 42 groups are given over the full range of measurement and reasonable extrapolation. The quality of the addition scheme is tested on 16 series of measurements on homopolymers, copolymers and blends. The addition scheme works for all these different states of aggregation of the constituent groups. The basis of the addition scheme is discussed.

The possible additivity of heat capacities of different constituents of linear macromolecules has been a topic of long standing interest in our laboratory. A first attempt to establish an addition scheme was published in 1969 [1]. Based on literature data on 30 polymers, it could be shown at that time that from 60 K to the glass transition temperature additivity seemed to exist with an accuracy of ± 5%. In the meantime, our collection of heat capacities of polymers has grown into the ATHAS Data Bank with data on about 100 polymers [2]. During the collection of the data bank it became clear that even polymer melts may show additivity [3]. Of particular interest was that copolymer heat capacities could be generated from the heat capacities of the homopolymer constituents [1]. Heat capacities of multiphase polymers, such as partially crystallized polymers [4] and phase separated block copolymers [5] and blends [6] could also be analyzed by comparison with heat capacities derived from additivity of the components [7]. Even the increase in heat capacity at the glass transition was found to be additive and empirically predictable in terms of the rigid atomic groupings, "beads", in the macromolecule [8].

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Furthermore, the heats and entropies of fusion have many regularities [9] which can be exploited for the prediction of thermodynamic functions. It is our goal to combine all literature data on the heat capacities and related quantities to gain a better understanding of the thermodynamic properties of macromolecules.

In this paper, the additivity of heat capacity of carbon backbone polymers is studied and a set of tables of heat capacity contributions, based largely on the 1980 data bank [2], is presented.

On additivity of heat capacities

In the crystalline and glassy solid states, the heat capacity consists practically fully of vibrational contributions. Additivity of heat capacities must thus mean approximate additivity of vibrational spectra. Each vibration contributes R [8.314 J/(K mol)] to the heat capacity when fully excited. Figure 1 illustrates the change of heat capacity contributions of different vibrations as a function of temperature.

Characterizing a vibration frequency by its θ-temperature [10], a vibration reaches 92% excitation relative to heat capacity at temperature θ K (1 K = $2.08 \cdot 10^{10}$ Hz, 1 K = 0.695 cm^{-1}). Above the θ-temperature there is thus no appreciable change of the heat capacity contribution of a vibration of given frequency, and additivity is trivial. The heat capacity depends in this case only on the number of vibrators (rule of Dulong–Petit).

The largest change in heat capacity contribution is the temperature range about the point of inflection of the Einstein function (see Fig. 1), which occurs at

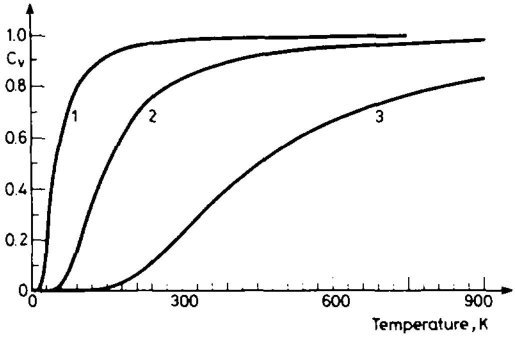

Fig. 1 Heat capacity contributions of vibrations of various θ-temperatures. The curves represent the Einstein function $E(h\nu/kT)$:[10]

$$E(h\nu/kT) = C_v/R = (\theta/T)\exp(\theta/T)/[\exp(\theta/T) - 1]^2$$

[h = Planck's constant; ν = frequency in s^{-1}; k = Boltzmann's constant; T = temperature in K; C_v = heat capacity at constant volume in J/(K mol); R = gas constant; $\theta = h\nu/k$]. Ordinate in multiples of R. Curve 1θ = 150 K; curve 2θ = 450 K; curve 3θ = 1350 K.

$\theta/T = 4.49$. At temperatures below $\theta/T = 6$, the heat capacity contribution is less than 9% of R and becomes quickly negligible. Between θ/T of 1 and 6 additivity can thus exist only if both, frequency *and* number of vibrators do not change for different molecular structures made up of the same base units.

If one now subdivides the vibrations of a linear macromolecule into group and skeletal vibrations [10], one finds that the group vibration of a given atomic base units are, indeed, largely independent of the molecular structure. This is already well known from the constancy of analogous infrared and Raman frequencies in different molecules.

The skeletal vibrations of linear macromolecules must be subdivided into inter- and intramolecular vibrations. Because of the extreme anisotropy of linear macromolecules there is only a limited amount of vibrational coupling between the chains. For selenium, the only well studied polymer with a monatomic repeating unit, the heat capacity is best represented by about 0.66 moles of intermolecular vibrations (Tarasov $\theta_3 = 98$ K) and 2.34 moles in intramolecular vibrations (Tarasov $\theta_1 = 350$ K) [11]. A discussion of the low temperature heat capacities of 35 macromolecules has shown, in addition, that there is not a large variation in the frequency distribution of the intermolecular vibrations. The Tarasov θ_3-temperatures vary, for exemple, between the extremes of 42 K [poly(ethylene terephthalate)] and 158 K (polyethylene) and are, in addition, partially mass dependent. The mass dependence would be corrected for in additivity schemes, and as the temperature approaches θ K, the variation of heat capacity with temperature is lost. The more important intramolecular skeletal vibrations, in turn, can be represented even more accurately by additive contributions. Especially for carbon backbone polymers, the objects of this discussion, all force constants governing the intramolecular skeletal vibrations are the same. Even the geometry is largely similar due to the constant C—C—C-bond angle. This leads to additivity as suggested earlier [10, 11].

Large deviations are expected for macromolecular chains including hetero atoms. For this reason the discussion of their additivity is reserved for a later discussion. As one attempts to go to side-group additivity the results must be considered purely empirical.

In the rubbery and liquid states the heat capacities are still largely governed by vibrational contributions, but an estimation of the additional heat capacity contributions of the longer range motion and the conformational contributions is not known [12]. As long as the change in C_p at the glass transition is, however, empirically additive in terms of "beads" [3], one expects liquid heat capacities to be also largely additive from chain segment contributions, as will be shown below. It is also of interest to note that most of the experimental heat capacities of liquid macromolecules are strictly linear over wide temperature ranges [2], quite in contrast to any attempt to theoretical interpretation of the data.

Crystallinity dependence of heat capacity can, finally, be treated in three temperature ranges. At low temperature (below about 50 K), the amorphous substances are higher in heat capacity. The difference in θ_3-temperatures in a Tarasov-description gives a quantitative measure of this effect (polyethylene 80 K and 158 K, selenium 54 K and 98 K, polypropylene 81 K and 92 K, polyoxytrimethylene 72 K and 102 K for amorphous and crystalline θ_3, respectively). For the few analyzed examples, the crystallinity dependence is largely linear. Too few data are available to include this temperature range in the here presented addition scheme. This is the reason for limiting all data to temperatures higher than or equal to 30 K.

More information is available for the next higher temperature region, to the glass transition. In this temperature region the heat capacity is practically independent of crystallinity [2], i.e. glassy and crystalline solids and all intermediate crystallinities have nearly the same heat capacity. Occasional problems arise from very broad glass transition regions, which may be intrinsic, as in polyethylene [5] and possibly also in other, relatively unsubstituted macromolecules [2]. An effort is made to eliminate these effects for the group contributions in the addition scheme, so that predicted heat capacities may in such cases be somewhat low. The third temperature region, between glass and melting transitions, is again quite linear in crystallinity. The amorphous phase has the higher heat capacity, although the difference in heat capacity between crystal and liquid is decreasing with increasing temperature and is at the melting temperature often close to zero. Complications are caused by a broadening of the glass transition in semicrystalline polymers due to microphase separation and excessive interactions between the phases due to tie molecules. A recently studied example is that of polypropylene [13]. In Tables 1 to 5 an effort was made to eliminate these effects, so that the estimated heat capacities from the addition scheme can be used as a reference against which to judge possible non-additive effects.

Use of the addition scheme

The addition scheme is designed for temperatures above 30 K. Up to the independently determined glass transition the data for all group contributions in the solid state are simply added on a molar composition basis. The same contributions are used for homopolymers, copolymers or blends. In case of multiphase, amorphous materials with multiple glass transitions, solid contributions can be added only below the lowest glass transition. Above the lowest temperature glass transition all group contributions for the liquid or rubbery phase must be added from the tables of liquid heat capacity contributions. In case of multiple glass transitions or additional melting (with independently determined transition temperatures) the newly mobilized fractions of groups are to be excluded from the remaining solid groups and their liquid heat capacity contribution must be added for the total heat capacity. After the final glass or melting transition, all group contributions are to be taken from the tables of liquid heat capacity contributions. Examples are shown in the discussion below.

Other thermodynamic functions can be obtained by numerical integration of the appropriate tables.

$$\Delta H = \int_{T_1}^{T_2} Cp \, \mathrm{d}T \tag{1}$$

$$\Delta S = \int_{T_1}^{T_2} (Cp/T) \, \mathrm{d}T \tag{2}$$

$$(\Delta G = \Delta H - T\Delta S) \tag{3}$$

The reference temperature absolute zero is not accessible through the heat capacity contribution tables and 298.15 K, the usual thermodynamic reference temperature, is often complicated by transitions. It is thus best to choose a reference temperature at which all of the to be compared samples are liquid. In the molten state, macromolecules are most likely close to equilibrium. To integrate functions sensitive to equilibrium (ΔS and ΔG), one must find equilibrium or zero entropy production paths (i.e. paths of constant stability or metastability). Transition enthalpies must be added separately. Transition entropies must be determined at or extrapolated to the corresponding equilibrium conditions.

Tables of group contributions and their justification

The addition scheme is presented in Table 1 to 5. All data for 25 chemical groups are presented where available in two parts, one for the solid and one for the liquid heat capacity contribution. Data based on extrapolations not directly supported by experimental data are placed in parentheses.

By far the most important experimental heat capacity is that of polyethylene, Table 1, columns 1 and 2; CH_2—. The data bank recommended heat capacity was evaluated by comparison of data on over 100 samples of varying crystallinity [2]. The extension of the crystalline data* to 560 K is necessary because of occasional

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* The listed data refer to crystalline polyethylene. Measurements for glassy polyethylene are also available and show somewhat higher heat capacity between 70 and 30 K [7.25, 6.26, 5.14, 3.90 and

Table 1 Heat capacity contributions in J/(K mol)

Temperature, K	CH_2–		$CHCH_3$–		CHC_6H_5–		$CCH_3C_6H_5$–	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
30	1.84	—	5.22	—	15.63	—	(2.77)	—
40	3.19	—	7.01	—	19.94	—	(7.91)	—
50	4.52	—	8.50	—	23.49	—	(14.98)	—
60	5.74	—	9.93	—	26.63	—	23.23	—
70	6.83	—	11.44	—	29.55	—	31.69	—
80	7.79	—	13.11	—	32.38	—	37.43	—
90	8.66	—	14.99	—	35.15	—	43.18	—
100	9.45	—	16.80	—	37.92	—	46.24	—
110	10.20	—	18.49	—	40.68	—	50.93	—
120	10.92		20.11	—	43.46	—	55.24	—
130	11.60	—	21.68	—	46.29	—	59.29	—
140	12.25	—	23.20	—	49.18	—	62.84	—
150	12.87	(24.41)	24.70	(41.24)	52.14	(110.51)	66.51	(55.53)
160	13.45	(24.84)	26.19	(42.32)	55.20	(112.73)	70.32	(60.86)
170	14.00	(25.27)	27.68	(43.40)	58.36	(114.95)	74.23	(66.18)
180	14.53	(25.70)	29.15	(44.48)	61.61	(117.17)	78.23	(71.51)
190	15.05	(26.14)	30.61	(45.56)	64.96	(119.39)	82.31	(76.84)
200	15.57	(26.57)	32.06	(46.65)	68.40	(121.61)	86.44	(82.16)
210	16.10	(27.00)	33.49	(47.73)	71.93	(123.83)	90.61	(87.49)
220	16.66	(27.43)	34.88	(48.81)	75.53	(126.05)	94.80	(92.81)
230	17.25	(27.87)	36.25	(49.89)	78.76	(128.27)	99.01	(98.14)
240	17.88	28.30	37.28	(50.97)	82.28	(130.49)	103.21	(103.46)
250	18.55	28.73	38.28	(52.05)	85.90	(132.71)	107.40	(108.79)
260	19.23	29.16	39.52	(53.13)	89.62	(134.93)	111.62	(114.14)
270	19.91	(29.60)	40.96	(54.21)	93.45	(137.15)	115.87	(119.44)
280	20.58	(30.03)	42.60	(55.29)	97.38	(139.38)	120.15	(127.77)
290	21.21	(30.46)	44.43	(56.37)	101.43	(141.60)	124.49	(130.09)
300	21.81	(30.89)	46.43	(57.45)	105.57	(143.82)	128.89	(135.42)
310	22.38	(31.33)	48.57	(58.53)	109.80	(146.04)	133.33	(140.74)
320	22.95	(31.76)	50.82	(59.61)	114.07	(148.26)	137.79	(146.07)
330	23.56	(32.19)	53.12	(60.69)	118.36	(150.48)	142.23	(151.39)
340	24.30	(32.62)	55.37	(61.77)	122.55	(152.70)	146.54	(156.72)
350	25.25	(33.06)	57.48	(62.85)	126.57	(154.92)	150.66	(162.04)
360	26.51	(33.49)	(59.05)	(63.93)	130.30	(157.14)	154.47	(167.37)
370	28.13	(33.92)	(60.28)	(65.01)	133.71	(159.36)	157.93	(172.69)
380	30.12	(34.35)	(61.19)	(66.09)	—	(161.58)	161.03	(178.02)

2.60 J/(K mol), respectively]. In addition, there is a broad glass transition in polyethylene starting already at 110 K reaching to about 250 K with a T_g (half vitrification) at 237 K. In this broad temperature region of the glass transition the measured heat capacity is intermediate between melt and solid.

Table 1 (cont.)

Temperature, K	CH_2—		$CHCH_3$—		CHC_6H_5—		$CCH_3C_6H_5$—	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
390	(31.78)	34.79	(62.49)	(67.17)	—	163.80	(164.46)	(183.35)
400	(32.91)	35.22	(64.38)	(68.25)	—	166.02	(168.42)	(188.67)
410	(34.06)	35.65	(66.30)	(69.33)	-	168.24	(172.36)	(194.00)
420	(35.26)	36.08	(68.24)	70.41	—	170.46	(176.26)	(199.32)
430	(36.49)	36.52	(70.22)	71.49	—	172.68	(180.12)	(204.65)
440	(37.78)	36.95	(72.20)	72.58	—	174.90	(183.91)	(209.97)
450	(39.12)	37.38	(74.22)	73.66	—	177.12	—	215.30
460	(40.52)	37.81	(76.26)	74.74	—	179.34	—	220.63
470	(42.00)	38.25	(78.32)	75.82	—	181.56	—	225.95
480	(43.56)	38.68	(80.42)	76.90	—	183.79	—	231.28
490	(45.23)	39.11	(82.52)	77.98	—	186.01	—	236.61
500	(47.02)	39.54	(84.65)	79.06	—	188.23	—	(241.94)
510	(48.98)	39.98	(86.77)	80.14	—	190.45	—	(247.26)
520	(51.16)	40.41	(88.86)	81.22	—	192.67	—	(252.59)
530	(53.63)	40.84	(90.88)	82.30	—	194.89	—	(257.92)
540	(56.56)	41.27	(92.71)	83.38	—	197.11	—	(263.25)
550	(60.24)	41.71	(94.12)	84.46	—	199.33	—	(268.57)
560	(65.73)	42.14	—	85.54	—	201.55	—	(273.90)
570	—	42.57	—	86.62	—	203.77	—	(279.23)
580		43.00		87.70	-	205.99	—	(284.56)
590		43.44	—	88.78	—	208.21	—	(289.88)
600		43.87	-	89.96	—	210.43	—	(295.21)

inclusion of CH_2— groups in high temperature polymers. These high temperature data were derived from the calculation of C_v from the vibrational spectrum, using the Nernst–Lindemann equation fitted to experimental compressibility and expansivity data at room temperature for C_v to C_p conversion [14]. The heat capacity of molten polyethylene is based on crystallinity extrapolation in the vicinity of 250 K and on direct experimental data from 330 to 600 K. Data extensions (listed in parentheses) to 150 K, and between 270 and 380 K are linear extrapolations of the recommended data.

Columns 3 and 4 of Table 1 represents the group $CHCH_3$— and is the first obtained by difference. Polyethylene data of columns 1 and 2 are subtracted from heat capacity data on polypropylene. The solid data refer to the crystal. Glassy data are also available from atactic polypropylene and crystallinity extrapolation. They lead to slightly higher heat capacities in the low temperature region of column 3 [from 30 to 250 K: 6.12; 7.97; 9.77; 12.10, 13.66; 15.75; 17.41; 19.06; 20.65;

Table 2 Heat capacity contributions in J/(K mol)

Temperature, K	CHC_2H_5—		CHC_3H_7—		CHC_4H_9—		$CHiC_4H_9$—	$C(CH_3)_2$—	
	1	2	3	4	5	6	7	9	10
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Solid	Liquid
30	8.36	—	—	—	14.58	—	—	6.00	—
40	11.67	—	—	—	20.81	—	—	7.57	—
50	14.74	—	—	—	25.64	—	—	9.17	—
60	17.53	—	—	—	30.97	—	—	11.04	—
70	20.18	—	—	—	35.84	—	—	13.27	—
80	22.90	—	—	—	40.54	—	39.42	15.86	—
90	25.64	—	—	—	45.13	—	43.88	18.68	—
100	28.33	—	—	—	49.63	—	48.07	21.52	—
110	30.96	—	—	—	54.10	—	52.02	24.38	—
120	33.43	—	—	—	58.69	—	55.80	27.23	—
130	35.87	—	—	—	63.08	—	59.46	30.12	—
140	38.23	—	—	—	67.63	—	63.04	32.95	—
150	40.51	(64.97)	—	(75.83)	72.09	(98.76)	66.58	35.72	(48.99)
160	42.77	(66.38)	—	(78.34)	76.24	(102.03)	70.12	38.37	(51.01)
170	45.08	(67.79)	—	(80.85)	81.16	(105.30)	73.66	41.01	(53.02)
180	47.53	(69.20)	—	(83.36)	86.27	(108.56)	77.23	43.54	(55.03)
190	50.09	(70.61)	—	(85.86)	91.40	(111.83)	80.82	(46.17)	(57.05)
200	52.83	(72.02)	72.33	(88.37)	(96.52)	(115.10)	84.44	(47.77)	(59.06)
210	55.78	(73.43)	74.76	(90.88)	(101.64)	(118.37)	88.10	—	(61.07)
220	(58.39)	(74.84)	77.16	(93.39)	(106.72)	(121.64)	91.78	—	(63.09)
230	(61.07)	(76.25)	79.53	(95.89)	—	(124.91)	95.51	—	(65.10)
240	(63.71)	(77.66)	—	98.40	—	128.18	99.26	—	67.12
250	—	(79.07)	—	100.91	—	131.44	103.06	—	69.13
260	—	(80.48)	—	103.42	—	134.71	106.94	—	71.14
270	—	(81.89)	—	(105.92)	—	(137.98)	110.91	—	(73.16)
280	—	(83.31)	—	(108.43)	—	(141.25)	115.00	—	(75.17)
290	—	(84.72)	—	(110.94)	—	(144.52)	119.24	—	(77.18)
300	—	(86.13)	—	(113.45)	—	(147.79)	(123.62)	—	(79.20)
310	—	(87.54)	—	(115.95)	—	(151.05)	—	—	(81.21)
320	—	(88.95)	—	(118.46)	—	(154.32)	—	—	(83.22)
330	—	(90.36)	—	(120.97)	—	(157.59)	—	—	(85.24)
340	—	(91.77)	—	(123.48)	—	(160.86)	—	—	(87.25)
350	—	(93.18)	—	(125.98)	—	(164.13)	—	—	(89.26)
360	—	(94.59)	—	(128.49)	—	(167.40)	—	—	(91.28)
370	—	(96.00)	—	(131.00)	—	(170.67)	—	—	(93.29)
380	—	(97.41)	—	(133.51)	—	(173.93)	—	—	(95.30)
390	—	98.82	—	136.01	—	(177.20)	—	—	(97.32)
400	—	100.23	—	138.52	—	(180.47)	—	—	(99.33)
410	—	101.64	—	141.03	—	(183.74)	—	—	(101.34)
420	—	103.05	—	143.54	—	(187.01)	—	—	(103.36)
430	—	104.46	—	146.04	—	(190.28)	—	—	(105.37)

Table 2 (cont.)

Tem-pera-ture,	CHC_2H_5—		CHC_3H_7—		CHC_4H_9—		$CHiC_4H_9$—	$C(CH_3)_2$—	
	1	2	3	4	5	6	7	9	10
K	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Solid	Liquid
440	—	105.87	—	148.55	—	(193.55)	—	—	(107.39)
450	—	107.28	—	151.06	—	(196.81)	—	—	(109.40)
460	—	108.69	—	153.57	—	(200.08)	—	—	(111.41)
470	—	110.10	—	156.07	—	(203.35)	—	—	(113.43)
480	—	111.52	—	(158.58)	—	(206.62)	—	—	(115.44)
490	—	112.93	—	(161.09)	—	(209.89)	—	—	(117.45)
500	—	114.34	—	(163.60)	—	(213.16)	—	—	(119.47)
510	—	115.75	—	(166.10)	—	(216.42)	—	—	(121.48)
520	—	117.16	—	(168.61)	—	(219.69)	—	—	(123.49)
530	—	118.57	—	(171.12)	—	(222.96)	—	—	(125.51)
540	—	119.98	—	(173.63)	—	(226.23)	—	—	(127.52)
550	—	121.39	—	(176.13)	—	(229.50)	—	—	(129.53)
560	—	122.80	—	(178.64)	—	(232.77)	—	—	(131.55)
570	—	124.21	—	(181.15)	—	(236.04)	—	—	(133.56)
580	—	125.62	—	(183.66)	—	(239.30)	—	—	(135.57)
590	—	127.03	—	(186.16)	—	(242.57)	—	—	(137.59)
600	—	128.44	—	(188.67)	—	(245.84)	—	—	(139.60)

22.19; 23.70; 25.17; 26.61; 28.03; 29.43; 30.82; 32.39; 33.79; 35.82; 37.65; 39.55; 41.52; 43.55 J/(K mol $CHCH_3$)]. The increase closer to 250 K beyond the crystalline data in column 3 are probably due to an incomplete separation of the glass transition effect. The data of column 3 in parentheses from 360 to 560 K are from heat capacities calculated from the vibrational spectrum of crystalline polypropylene [13]. The liquid data below 420 K in column 4 are based on data bank extrapolations [2] using atactic polypropylene and crystallinity extrapolations.

Columns 5 and 6 of Table 1 represent the heat capacity of the polystyrene based CHC_6H_5–group. The solid heat capacity is derived from glassy samples [2]. Data at higher temperature are now available through evaluation of the vibrational frequency spectrum [16]. The liquid data below 390 K are linear extrapolations of the heat capacities above the glass transition temperature [2].

Columns 7 and 8 of Table 1 refer to $CCH_3C_6H_5$–groups calculated by subtracting polyethylene heat capacity from that of poly-α-methylstyrene. The three lowest data points of the solid are based on extrapolated heat capacities of glassy poly-α-methylstyrene using the Tarasov equation [2]. The data from 390 to 440 K are extrapolated, eliminating glass transition effects of poly-α-methyl styrene [2]. The

Table 3 Heat capacity contributions in J/(K mol)

Temperature, K	CF_2—		CHF—	CHCl—		CCl_2—	CFCl—	CHOH—
	1	2	3	5	6	7	9	11
	Solid	Liquid	Solid	Solid	Liquid	Solid	Solid	Solid
30	6.30	—	(3.86)	8.11	—	(5.48)	—	—
40	8.44	—	(5.31)	10.19	—	(9.34)	—	—
50	10.31	—	(7.28)	11.76	—	(12.86)	—	—
60	12.27	—	(8.76)	13.03	—	15.66	—	6.04
70	14.17	—	(10.27)	14.16	—	19.25	—	8.22
80	16.02	—	12.48	15.26	—	22.22	16.44	10.15
90	17.75	—	13.52	16.32	—	24.72	19.02	11.80
100	19.37	—	14.51	17.37	—	26.86	21.44	13.24
110	21.20	—	15.44	18.39	—	28.71	23.43	14.49
120	22.90	—	16.33	19.37	—	30.34	25.34	15.62
130	24.53	—	17.23	20.34	—	31.85	27.16	16.69
140	26.13	—	18.14	21.31	—	33.28	28.87	17.73
150	27.65	(40.18)	19.08	22.28	—	34.66	30.53	18.79
160	29.13	(40.91)	20.06	23.28	—	36.05	32.13	19.89
170	30.62	(41.64)	21.09	24.31	—	37.46	33.64	21.06
180	31.98	(42.38)	22.17	25.35	—	38.91	35.20	22.31
190	33.24	(43.12)	23.15	26.40	—	40.40	36.81	23.64
200	34.47	(43.86)	(23.95)	27.46	—	41.94	38.40	25.07
210	35.67	(44.61)	(24.73)	28.51	—	43.54	39.99	26.59
220	36.82	(45.35)	(25.48)	29.55	—	45.18	41.59	28.19
230	37.94	(46.10)	(26.23)	30.54	—	46.87	43.21	29.91
240	39.03	(46.85)	(26.95)	31.49	—	48.62	44.84	31.72
250	40.10	(47.61)	(27.66)	32.44	—	50.43	46.47	33.66
260	41.13	(48.36)	(28.38)	33.40	—	—	48.14	35.76
270	42.15	(49.12)	(29.13)	34.38	—	—	49.83	38.04
280	43.15	(49.89)	(29.91)	35.37	—	—	51.53	40.54
290	44.13	(50.65)	(30.76)	36.43	—	—	53.26	43.29
300	45.09	(51.42)	(31.67)	37.54	—	—	55.01	46.30
310	46.02	(52.19)	(32.62)	(38.73)	—	—	(56.88)	—
320	46.95	(52.96)	(33.60)	(39.99)	—	—	(58.65)	—
330	47.86	(53.74)	(34.55)	(41.32)	—	—	—	—
340	48.76	(54.52)	(35.39)	(42.66)	—	—	—	—
350	49.63	(55.30)	(36.03)	(43.60)	—	—	—	—
360	50.49	(56.08)	—	—	57.59	—	—	—
370	51.35	(56.87)	—	—	60.64	—	—	—
380	52.17	(57.66)	—	—	63.69	—	—	—
390	52.99	(58.45)	—	—	—	—	—	—
400	53.81	(59.24)	—	—	—	—	—	—
410	54.60	(60.04)	—	—	—	—	—	—
420	55.39	(60.84)	—	—	—	—	—	—
430	56.15	(61.64)	—	—	—	—	—	—

Table 3 (cont.)

Temperature, K	CF_2—		CHF—	CHCl—		CCl_2—	CFCl—	CHOH—
	1	2	3	5	6	7	9	11
	Solid	Liquid	Solid	Solid	Liquid	Solid	Solid	Solid
440	56.91	(62.44)	—	—	—	—	—	—
450	57.65	(63.25)	—	—	—	—	—	—
460	58.39	(64.06)	—	—	—	—	—	—
470	59.10	(64.87)	—	—	—	—	—	—
480	59.82	65.39	—	—	—	—	—	—
490	60.51	65.72	—	—	—	—	—	—
500	61.20	66.05	—	—	—	—	—	—
510	61.88	66.38	—	—	—	—	—	—
520	62.55	66.72	—	—	—	—	—	—
530	63.20	67.05	—	—	—	—	—	—
540	63.86	67.38	—	—	—	—	—	—
550	64.48	67.71	—	—	—	—	—	—
560	65.12	68.04	—	—	—	—	—	—
570	65.75	68.38	—	—	—	—	—	—
580	66.36	68.71	—	—	—	—	—	—
590	66.96	69.04	—	—	—	—	—	—
600	67.58	69.37	—	—	—	—	—	—

liquid column rests only between 450 and 490 K on experiments [2]. The remaining values are linearly extrapolated, the established slope seems excessive.

Table 2 contains heat capacities of a series of groups of importance to branched polyethylenes (for $CHCH_3$ see Table 1). All data are obtained by difference with polyethylene heat capacities, listed in Table 1.

Columns 1 and 2 are drawn from data bank information on poly-1-butene [2]. The solid data are linked to measurements on semicrystalline polymers. In the temperature range 220 to 240 K, low temperature heat capacities were extrapolated. The liquid data were measured from 390 to 600 K, low temperature data were extrapolated.

Columns 3 and 4 are based on less complete data on semicrystalline and amorphous poly-1-pentene [2]. The liquid data are based on measurements from 240 to 470 K and extrapolations up to 600 K. Note that data between 270 and 380 K are placed in parentheses because of extrapolations done in the polyethylene data.

Columns 5 and 6 were calculated from amorphous (glassy and liquid) poly-1-hexene. Direct measurements cover the 30–190 K temperature range (glass) and the 230 to 290 K range (liquid) [2]. Values in parentheses involve extrapolations in the poly-1-hexene or in the polyethylene data.

Table 4 Heat capacity contributions in J/(K mol)

Temperature, K	$CHOCOCH_3$—		$CHCOOCH_3$—		$CHCOOC_2H_5$—		$CHCOOC_4H_9$—		CHCN—
	1	2	3	4	5	6	7	8	9
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
30	—	—	(9.86)	—	—	—	—	—	(3.10)
40	—	—	(16.16)	—	—		—	—	(6.36)
50	—	—	22.05	—	—	—	—	—	(9.25)
60	—		27.35	—	—	—	—	—	12.35
70	—	—	32.07	—	—	—	—	—	14.86
80	20.02	—	36.29	—	—	—	63.96	—	17.08
90	22.51	—	40.09	—	49.33	—	69.54	—	19.03
100	25.09	—	43.53	—	53.05	—	75.02	—	20.77
110	27.71	—	46.68	—	56.63	—	80.90	—	22.34
120	30.35	—	49.58	—	60.14	—	86.63	—	23.75
130	33.04		52.31	—	63.60	—	92.41	—	25.08
140	35.75	—	54.89	—	67.03	—	98.21	—	26.34
150	38.50	(117.43)	57.36	(103.21)	70.44	(122.01)	104.04	(159.40)	27.57
160	41.29	(117.98)	59.76	(104.40)	73.87	(123.75)	109.91	(162.27)	28.78
170	44.10	(118.52)	62.12	(105.59)	77.30	(125.48)	115.81	(165.13)	30.00
180	46.94	(119.07)	64.42	(106.79)	80.73	(127.21)	121.74	(168.00)	31.22
190	49.78	(119.62)	66.70	(107.98)	84.15	(128.94)	127.67	(170.87)	32.46
200	52.63	(120.16)	68.94	(109.17)	87.56	(130.67)	133.60	(173.73)	33.70
210	55.47	(120.71)	71.15	(110.36)	90.95	(132.40)	139.52	(176.60)	34.94
220	58.27	(121.26)	73.33	(111.56)	94.30	(134.13)	—	(179.46)	36.19
230	61.05	(121.80)	75.47	(112.75)	97.62	(135.87)	—	(182.33)	37.43
240	63.78	(122.35)	77.58	(113.94)	100.88	(137.60)	—	185.19	38.68
250	66.48	(122.89)	79.66	(115.13)	—	139.33		188.06	39.92
260	69.17	(123.44)	81.75	(116.33)	—	141.06	—	190.92	41.20
270	71.85	(123.99)	83.86	(117.52)	—	(142.79)	—	(193.79)	42.54
280	74.55	(124.53)	—	(118.71)	—	(144.52)	—	(196.66)	43.93
290	77.28	(125.08)	—	(119.90)	—	(146.25)	—	(199.52)	45.43
300	80.05	(125.62)	—	(121.10)	—	(147.99)	—	(202.39)	47.02
310	—	(126.17)	—	(122.29)	—	(149.72)	—	(205.25)	48.70
320	—	(126.72)	—	(123.48)		(151.45)	—	(208.12)	50.46
330	—	(127.26)	—	(124.67)	—	(153.18)	—	(210.98)	52.24
340	—	(127.81)	—	(125.87)		(154.91)	—	(213.85)	53.97
350	—	(128.35)	—	(127.06)	—	(156.64)	—	(216.71)	55.57
360	—	(128.90)	—	(128.25)	—	(158.38)	—	(219.58)	56.94
370	—	(129.45)	—	(129.44)	—	(160.11)		(222.44)	58.03
380	—	(129.99)	—	(130.64)	—	(161.84)	—	(225.31)	—
390	—	(130.54)	—	131.83	—	163.57	—	228.18	—
400	—	(131.09)	—	133.02	—	165.30	—	231.04	
410	—	(131.63)	—	134.21	—	167.03	—	233.91	—
420	—	(132.18)	—	135.41	—	168.76	—	236.77	—
430	—	(132.72)	—	136.60	—	170.50	—	239.64	—

Table 4 (cont.)

Temperature, K	$CHOCOCH_3$—		$CHCOOCH_3$—		$CHCOOC_2H_5$—		$CHCOOC_4H_9$—		CHCN—
	1	2	3	4	5	6	7	8	9
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
440		(133.27)	—	137.79	—	172.23	—	242.50	—
450	—	(133.82)	—	138.98	—	173.96	—	(245.37)	—
460		(134.36)	—	140.18		175.69	—	(248.23)	—
470	—	(134.91)	—	141.37	—	177.42		(251.10)	—
480	—	(135.45)	—	142.56	—	179.15	—	(253.97)	—
490	—	(136.00)	—	143.75	—	180.88	—	(256.83)	
500	—	(136.55)	—	144.95	—	182.62	—	(259.70)	—
510	—	(137.09)	—	(146.14)	—	(184.35)	—	(262.56)	
520	—	(137.64)	—	(147.33)	—	(186.08)	—	(265.43)	—
530	—	(138.18)	—	(148,52)	—	(187.81)		(268.29)	—
540		(138.73)	—	(149.72)	—	(189.54)	—	(271.16)	—
550	—	(139.28)	—	(150.91)		(191.27)	—	(274.02)	—
560	—	(139.82)	—	(152.10)		(193.01)	—	(276.89)	
570	-	(140.37)	—	(153.29)	—	(194.74)	—	(279.75)	—
580	—	(140.91)	—	(154.49)	—	(196.47)		(282.62)	—
590	—	(141.46)	—	(155.68)	—	(198.20)	—	(285.49)	
600	—	(142.01)		(156.87)		(199.93)	—	(288.35)	—

Poly-4-methyl-1-pentene was measured only in the solid state [2]. The data are listed in column 7.Column 8 is omitted for lack of data.

The last set of data result from glassy and liquid polyisobutylene [2]. Direct measurements cover the range 30 to 180 K for the glass and 210 to 380 K for the liquid. Other values are extrapolated before substracting polyethylene heat capacities.

In Table 3 the heat capacity contributions of a number of carbon backbone atoms substituted with heavy atoms are collected (compare also to $CHCH_3$— in Table 1, $C(CH_3)_2$— in Table 2, and CHCN— in Table 4).

Columns 1 and 2 of Table 3 show data for polytetrafluoroethylene CF_2—. They are based on the recommended data of 1984 [15] since not enough information was available at the time the original data bank was assembled. All solid heat capacity data refer to crystalline samples (column 1) and are backed by direct experimental data to 480 K and a full frequency spectrum calculation as in polyethylene. The melt data down to 480 K were newly measured and compared to all prior published values [15]. The low temperature data are from crystallinity extrapolations. The data in parentheses are linear extrapolations below the upper end of the glass

Table 5 Heat capacity contributions in J/(K mol)

Temperature, K	CCH_3COOCH_3—		$CCH_3COOC_2H_5$—		$CCH_3COOC_4H_9$—		$CHOCOC_6H_5$—	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
30	12.83	—	—	—	—	—	—	—
40	18.19		—	—	—	—	—	—
50	23.15	—	—	—	—	—	—	—
60	28.79	-	—	—	—	—	—	—
70	34.47	—	—	—	—	—	—	—
80	39.50	—	51.05	—	70.02	—	—	—
90	43.98	—	54.94	—	76.19	—	—	—
100	48.04	—	58.97	—	82.51	—	—	—
110	51.77	—	63.08	—	88.93	—	—	—
120	55.26	—	67.25	—	95.40	—	—	—
130	58.60	—	71.48	—	101.94	—	—	—
140	61.85	—	75.76	—	108.52	—	—	—
150	65.07	(124.15)	80.07	(124.06)	115.14	(165.79)	—	(176.11)
160	68.29	(126.10)	84.43	(127.33)	121.82	(170.24)	—	(178.56)
170	71.55	(128.04)	88.83	(130.60)	128.53	(174.69)	—	(181.00)
180	74.87	(129.98)	93.26	(133.87)	135.27	(179.13)	—	(183.45)
190	78.47	(131.92)	97.70	(137.13)	142.02	(183.58)	91.34	(185.90)
200	81.95	(133.86)	102.14	(140.40)	148.77	(188.03)	96.00	(188.34)
210	85.42	(135.80)	106.57	(143.67)	155.52	(192.48)	100.65	(190.79)
220	88.87	(137.74)	110.98	(146.94)	162.24	(196.93)	105.27	(193.23)
230	92.29	(139.69)	115.36	(150.20)	168.93	(201.38)	109.85	(195.68)
240	95.68	(141.63)	119.70	(153.47)	175.59	(205.83)	114.40	(198.12)
250	99.03	(143.57)	124.00	(156.74)	182.20	(210.27)	118.91	(200.57)
260	102.37	(145.51)	128.29	(160.01)	188.81	(214.72)	123.41	(203.01)
270	105.72	(147.45)	132.58	(163.27)	195.42	(219.17)	127.91	(205.46)
280	109.08	(149.39)	136.89	(166.54)	202.04	(233.62)	132.41	(207.91)
290	112.48	(151.33)	141.23	(169.81)	208.70	(228.07)	136.96	(210.35)
300	115.91	(153.28)	145.61	(173.08)	—	(232.52)	141.54	(212.80)
310	119.37	(155.22)	150.01	(176.34)	—	(236.96)	(146.15)	(215.24)
320	122.83	(157.16)	154.42	(179.61)	—	(241.41)	(150.76)	(217.69)
330	126.26	(159.10)	158.78	(182.88)	—	(245.86)	(155.32)	(220.13)
340	129.55	(161.04)	—	(186.15)	—	(250.31)	(159.76)	(222.58)
350	132.64	(162.98)	—	(189.41)	—	(254.76)	—	(225.02)
360	135.42	(164.93)	—	(192.68)	—	(259.21)	—	(227.47)
370	137.84	(166.87)	—	(195.95)	—	(263.66)	—	(229.91)
380	—	(168.81)	—	(199.22)	—	(268.10)	—	(232.36)
390	—	170.75	—	(202.48)	—	272.55	—	234.81
400	—	172.69	—	(205.75)	—	277.00	—	237.25
410	—	174.63	—	(209.02)	—	281.45	—	239.70
420	—	176.57	—	(212.29)	—	285.90	—	242.14
430	—	178.52	—	(215.55)	—	290.35	—	244.59

Table 5 (cont.)

Temperature, K	CCH_3COOCH_3—		$CCH_3COOC_2H_5$—		$CCH_3COOC_4H_9$		$CHOCOC_6H_5$—	
	1	2	3	4	5	6	7	8
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
440	—	180.46	—	(218.82)	—	294.80	—	247.03
450	—	182.40	—	(222.09)	—	(299.24)	—	249.48
460	—	184.34	—	(225.36)	—	(303.69)	—	251.92
470	—	186.28	—	(228.62)	—	(308.14)	—	254.37
480	—	188.22	—	(231.89)	—	(312.59)	—	256.82
490	—	190.16	—	(235.16)	—	(317.04)	—	259.26
500	—	192.11	—	(238.43)	—	(321.49)	—	261.71
510	—	194.05	—	(241.69)	—	(325.93)	—	(264.15)
520	—	195.99	—	(244.96)	—	(330.38)	—	(266.60)
530	—	197.93	—	(248.23)	—	(334.83)	—	(269.04)
540	—	199.87	—	(251.50)	—	(339.28)	—	(271.49)
550	—	201.81	—	(254.76)	—	(343.73)	—	(273.93)
560	—	(203.76)	—	(258.03)	—	(348.18)	—	(276.38)
570	—	(205.70)	—	(261.30)	—	(352.63)	—	(278.82)
580	—	(207.64)	—	(264.57)	—	(357.07)	—	(281.27)
590	—	(209.58)	—	(267.83)	—	(361.52)	—	(283.72)
600	—	(211.52)	—	(271.10)	—	(365.97)	—	(286.16)

transition of polytetrafluoroethylene. These values may be needed for the estimation of heat capacities of low glass transition copolymers.

Column 3 was calculated from measurements on solid poly(vinyl fluoride) from 80 to 190 K [2]. The additional values in parentheses result from calculations made using vibrational frequency information [17]. No data on the liquid state are available, so column 4 is left out in Table 3. The analogous chlorinated carbon atom data are listed in columns 5 and 6, data being derived from poly(vinyl chloride) and polyethylene. The data on the solid CHCl— are based on experimental heat capacities of glassy poly(vinyl chloride) from 30 to 300 K. Liquid data were measured only from 360–380 K, too short a range for meaningful extrapolation.

Column 7 refers to heat capacities of CCl_2— and should be compared to the CF_2—and CH_2—data of Columns 1 and 2 and Table 1, respectively. Again, only data on solid poly(vinylidene chloride) measured from 60 to 250 K are available in the data bank. The three low temperature heat capacities were extrapolated using the Tarasov equation [2]. Column 8 had to be omitted because of lacking data on liquid poly(vinylidene chloride).

Column 9 shows data on CFCl-derived from polychlorotrifluoroethylene. For this chemical group heat capacities of semicrystalline polychlorotrifluoroethylene

Table 6 Comparison of calculated heat capacities of Tables 1–5 with experimental data [Heat capacities in J/(K mol), deviations in %]

Temperature, K	Experiment	Calculated	Deviation
A. Poly(vinylidene fluoride), solid			
30	9.10	8.14	−10.55
40	12.20	11.63	−4.67
50	15.00	14.83	−1.13
60	17.90	18.01	+0.61
70	20.90	21.00	+0.48
80	23.80	23.81	+0.04
90	26.10	26.41	+1.19
100	28.47	28.82	+1.23
B. Polytrifluoroethylene, solid			
80	26.43	28.50	+7.83
90	29.99	31.27	+4.27
100	33.21	33.88	+2.02
110	36.15	36.64	+1.36
120	38.89	39.23	+0.87
130	41.48	41.76	+0.68
140	43.97	44.27	+0.68
150	46.39	46.73	+0.73
160	48.78	49.19	+0.84
170	51.16	51.71	+1.08
180	53.36	54.15	+1.48
190	55.99	56.39	+0.71
C1. Ethylene/Propylene random copolymer, solid, 0.075 $CHCH_3$—			
80	8.67	8.39	−3.29
90	9.51	9.32	−2.02
100	10.30	10.17	−1.26
110	11.06	10.98	−0.73
120	11.81	11.77	−0.41
130	12.56	12.51	−0.40
140	13.30	13.22	−0.62
150	14.05	13.90	−1.09
160	14.82	14.54	−1.85
170	15.60	15.16	−2.82
180	16.39	15.75	−3.92
C2. Ethylene/Propylene random copolymer, solid, 0.155 $CHCH_3$—			
80	9.06	9.02	−0.39
90	10.06	10.02	−0.39
100	11.04	10.94	−0.90
110	12.01	11.82	−1.59
120	12.97	12.67	−2.34

Table 6 (cont.)

Temperature, K	Experiment	Calculated	Deviation
130	13.92	13.48	−3.20
140	14.86	14.25	−4.10
150	15.79	15.00	−5.03
160	16.72	15.71	−6.04
170	17.64	16.39	−7.05
180	18.54	17.05	−8.03
C3. Ethylene/Propylene random copolymer, liquid, 0.205 $CHCH_3$—			
240	33.07	(32.95)	−0.38
250	33.61	(33.51)	−0.30
260	34.16	(34.08)	−0.24
270	34.70	(34.64)	−0.17
280	35.24	(35.21)	−0.10
290	35.79	(35.77)	+0.04
300	36.33	(36.34)	+0.02
310	36.87	(36.90)	+0.08
320	37.42	(37.47)	+0.14
330	37.96	(38.03)	+0.19
340	38.50	(38.60)	+0.25
350	39.05	(39.16)	+0.30
360	39.59	(39.73)	+0.35
370	40.13	(40.30)	+0.40
380	40.68	(40.86)	+0.45
390	41.22	(41.43)	+0.50
400	41.76	(41.99)	+0.54
410	42.31	(42.56)	+0.59
420	42.85	43.12	+0.63
430	43.40	43.69	+0.67
440	43.94	44.25	+0.71
450	44.48	44.82	+0.75
C4. Ethylene/Propylene random copolymer, liquid, 0.350 $CHCH_3$—			
240	35.68	(36.23)	+1.55
250	36.43	(36.89)	+1.27
260	37.18	(37.55)	+1.01
270	37.92	(38.21)	+0.75
280	38.67	(38.87)	+0.51
290	39.42	(39.53)	+0.28
300	40.17	(40.19)	+0.05
310	40.92	(40.85)	−0.17
320	41.66	(41.51)	−0.37
330	42.41	(42.17)	−0.58
340	43.16	(42.83)	−0.77
350	43.91	(43.48)	−0.96
360	44.65	(44.14)	−1.14

Table 6 (cont.)

Temperature, K	Experiment	Calculated	Deviation
370	45.40	(44.80)	−1.32
380	46.15	(45.46)	−1.49
390	46.90	(46.12)	−1.65
400	47.64	(46.78)	−1.81
410	48.39	(47.44)	−1.97
420	49.14	48.10	−2.12
430	49.89	48.76	−2.26
440	50.64	49.42	−2.40
450	51.38	50.08	−2.54
D1. Ethylene/Propylene Block-copolymer, solid, 0.06 $CHCH_3$—			
80	8.05	8.11	+0.72
90	8.85	9.04	+2.19
100	9.61	9.89	+2.93
110	10.35	10.70	+3.40
120	11.06	11.47	+3.73
130	11.75	12.20	+3.83
140	12.44	12.91	+3.79
150	13.11	13.58	+3.59
160	13.78	14.21	+3.17
170	14.45	14.82	+2.58
180	15.12	15.41	+1.88
190	15.81	15.98	+1.11
200	16.51	16.56	+0.32
D2. Ethylene/Propylene block-copolymer, liquid, 0.06 $CHCH_3$—			
450	39.22	39.56	+0.85
460	39.97	40.03	+0.16
470	40.71	40.50	−0.51
480	41.45	40.97	−1.16
490	42.20	41.44	−1.79
500	42.94	41.91	−2.39
E1. Ethylene/1-Butene block-copolymer, solid, 0.075 CHC_2H_5—			
80	9.03	8.92	−1.22
90	10.06	9.93	−1.22
100	10.98	10.87	−1.07
110	11.82	11.76	−0.57
120	12.64	12.61	−0.25
130	13.29	13.42	+1.01
140	14.21	14.20	−0.05
150	14.95	14.94	−0.07
160	15.68	15.65	−0.17
170	16.39	16.33	−0.36
180	17.10	17.01	−0.55

Table 6 (cont.)

Temperature, K	Experiment	Calculated	Deviation
E2. Ethylene/1-Butene block-copolymer, liquid, 0.075 CHC_2H_5—			
400	38.25	40.09	+4.83
410	38.73	40.60	+4.83
420	39.20	41.11	+4.87
430	39.68	41.61	+4.86
440	40.17	42.12	+4.86
450	40.63	42.62	+4.90
F1. Styrene/α-Methylstyrene block-copolymer, solid, 0.42 CHC_6H_5—			
310	142.20	142.06	−0.10
320	147.20	146.99	−0.15
330	152.40	151.94	−0.30
340	157.00	156.93	−0.05
350	161.50	161.93	+0.27
360	166.30	166.96	+0.40
370	171.60	172.01	+0.24
F2. Styrene/α-Methylstyrene block-copolymer, liquid, 0.42 CHC_6H_5—			
450	237.60	230.54	−2.97
460	240.30	234.50	−2.42
470	243.20	238.45	−1.95
480	246.00	242.41	−1.46
490	248.40	246.37	−0.82
G1. Polystyrene/Poly-α-methylstyrene, blend, solid, compatible, 0.53 CHC_6H_5—			
310	143.40	143.24	−0.11
320	147.70	148.17	+0.32
330	152.60	153.14	+0.35
340	157.40	158.13	+0.46
350	162.40	163.14	+0.45
360	167.20	168.17	+0.58
370	172.60	173.22	+0.36
G2. Polystyrene/Poly-α-methylstyrene, blend, liquid, compatible, 0.53 CHC_6H_5—			
450	237.90	232.45	−2.29
460	240.90	236.56	−1.80
470	245.10	240.67	−1.81
480	248.80	244.79	−1.61
490	251.40	248.90	−0.99
G3. Polystyrene/Poly-α-methylstyrene, blend, solid, incompatible, 0.53 CHC_6H_5-			
310	143.60	143.24	−0.25
320	148.50	148.17	−0.22
330	153.50	153.14	−0.24
340	158.50	158.13	−0.24
350	163.60	163.14	−0.28

Table 6 (cont.)

Temperature, K	Experiment	Calculated	Deviation
360	169.20	168.17	−0.61
370	175.30	173.22	−1.18
G4. Polystyrene/Poly-α-methylstyrene, blend, liquid, incompatible, 0.53 CHC_6H_5			
470	244.80	240.67	−1.69
480	247.90	244.79	1.26
490	251.10	248.90	−0.88

measured from 80 to 300 K was modified by subtraction of heat capacities of the CF_2— group listed in columns 1 and 2. For 310 and 320 K these data are extrapolated. Again no heat capacities have been measured for the liquid so that column 10 had to be omitted.

Similarly poly(vinyl alcohol) experimental heat capacity data from 60 to 300 K were used to establish the data for solid CHOH— in column 11. Column 12 is omitted because of lack of data.

In Table 4 data from a series of atactic acrylic and related polymers are collected starting in columns 1 to 4 with the two geometrical isomeric groups from poly(vinyl acetate) $CHOCOCH_3$— and from poly(methyl acrylate) $CHCOOCH_3$—. The 80 to 300 K heat capacities in column 1 are from measurements on glassy poly(vinyl acetate) [2]. The liquid column is all in parentheses. It rests in the temperature region from 310 to 370 K on measurement [2] and linear extrapolation outside of these temperatures, but in this region the polyethylene data are extrapolated; still, the data are considered quite acceptable. Quite similar is the status of the poly(methyl acrylate) heat capacity needed for columns 3 and 4 together with polyethylene. Measurements on glassy samples range from 50 to 270 K and liquids, from 280 to 500 K [2]. Additionally two polyacrylates (isobutyl and octadecyl) and polyacrylic acid have previously been analyzed with respect to their heat capacity additivity [18]. These data are not repeated here.

Columns 5 to 8 result, analogously, from a subtraction from polyethylene heat capacities from glassy (90–240 K and 80–210 K) and liquid (250–500 K and 220 to 440 K) heat capacities of poly(ethyl acrylate) ($CHCOOC_2H_5$—) and poly(*n*-butyl acrylate), ($CHCOOC_4H_9$—), respectively [2]. The additional data on the liquid samples are linear extrapolations beyond the measured regions, which itself show strictly linear changes of heat capacity with temperature.

Column 9, finally the CHCN— heat capacity contribution is calculated from measurements on glassy polyacrylonitrile with the three low temperature entries resulting from a Tarasov-type extrapolation [2].

Table 5 shows analogous to Table 4 the methacrylate related data and, in addition, the poly(vinyl benzoate) derived group. Additionally, three polymethacrylates (isobutyl, dodecyl, and octadecyl) have been analyzed with respect to their heat capacity additivity [18]. These data are not repeated here [18]. Columns 1 and 2 are the data for CCH_3COOCH_3—. All data, except those for the liquid from 150 to 370 K and 560 to 600 K, are derived from measurement evaluated in the data bank [2]. The $CCH_3OOC_2H_5$— and $CCH_3OOC_4H_9$— heat capacities of columns 3 to 6 are derived similarly. The liquid ranges of measurement of the corresponding polymethacrylates were 340 to 380 K and 300 to 440 K, respectively.

The last group, $CHOCOC_6H_5$—, is based on data bank [2] results on glassy poly(vinyl benzoate) from 190 to 300 K, extrapolated to 340 K to eliminate glass transition effects, and on liquid poly(vinyl benzoate) from 370 to 500 K, linearly extrapolated as indicated in Column 8.

Comparison of the addition scheme with measurements

The best way to assess the quality of the addition scheme is to compare its prediction with actual measurements. Table 6 contains seven examples.

The first example compares measured data on poly(vinylidene fluoride) [2] CH_2—CF_2— with those of the addition scheme. Note that the CF_2— group of the addition scheme was derived from independent measurements on polytetrafluoroethylene. Excepting the 30 K value which is still too much influenced by the heat capacity contributions of the intermolecular vibrations the standard deviation is $-0.3\pm2.1\%$. Heat capacities of solid poly(vinylidene fluoride) above 100 K have been calculated using a full analysis of the vibrational frequency spectrum [17]. These agree with the here presented empirical addition scheme up to 500 K to $2.3\pm2.2\%$. The second example represents a similar internal check, using the measured heat capacity of polytrifluoroethylene [2] and the addition scheme values which were derived from poly(vinyl fluoride), polyethylene, and polytetrafluoroethylene. The data from 80 to 190 K show a standard deviation of $1.8\pm2.1\%$. Again further comparison of data gained from a frequency spectrum analysis agree with the addition scheme from 200 to 400 K to $-3.1\pm2.3\%$. These examples show that the group contributions, when combined to give different homopolymers yield, within experimental error, proper values of the heat capacities.

Next, heat capacity measurements on one random and three block-copolymers are compared to the predictions of the addition scheme. Clegg et al. [19] measured heat capacities of eight poly(ethylene-*co*-propylenes). Of these, two were analyzed by adiabatic calorimetry in the solid region from 80 to 180 K. Above 180 K the influence of the glass transition is noticeable. Table 6 shows the comparison with the addition scheme (C1 and C2, standard deviations $-1.7 \pm 1.2\%$, and $-3.6 \pm 2.7\%$, respectively). Note that the addition is in terms of one carbon backbone atom, i.e. the addition for sample C2 is: $0.845{*}Cp(\mathrm{CH_2}—)+0.155{*}Cp(\mathrm{CHCH_3}—)$. Liquid data were reported as differential scanning calorimetry. Table 6 displays the results of two copolymers, one of 41 mol-% and one of 70 mol-% propylene (0.205 and 0.350 $\mathrm{CHCH_3}$—) from 240 to 450 K (C3 and C4, respectively, standard deviations $0.25 \pm 0.34\%$ and $-0.73 \pm 1.26\%$, respectively). Note that in much of this temperature range the liquid $\mathrm{CH_2}$— contribution is extrapolated. Still, the agreement is excellent. As was noticed already by Clegg et al. [19] the tacticity and positioning of the $\mathrm{CHCH_3}$— seems to play little role. The heat capacities are well reproduced by the addition scheme.

Two semicrystalline block copolymers of ethylene and propylene showing both polyethylene and polypropylene crystallinity were also analyzed by Clegg et al [20]. The adiabatic calorimetry data on the solid 12 mole-% propylene sample are shown in Table 6 (D1, 0.06 $\mathrm{CHCH_3}$—, 80–200 K, standard deviation from addition scheme $2.76 \pm 1.18\%$). The liquid range of the block copolymers was analyzed by differential scanning calorimetry and led to the results displayed in part D2 of Table 6 (the data are chosen from 420 to 500 K, the region above melting, standard deviation from addition scheme $-0.81 \pm 1.21\%$).

Another block copolymer thus analysed by Clegg et al. is that of ethylene and 1-butene [21]. Table 6 contains in Parts E1 and E2 the adiabatic calorimetry results between 80 and 180 K and the differential scanning calorimetry results beyond melting from 400 to 450 K (0.075 mol-% $\mathrm{CHC_2H_5}$—, both polyethylene and poly-1-butene crystallinity, solid and liquid samples showed standard deviations from the addition scheme of $-0.22 \pm 0.74\%$ and $4.86 \pm 0.03\%$, respectively). With these eight examples of short-chain branched polymers fitting the addition scheme it is reasonable to assume that all combinations of such branches can be used to predict, for example, the heat capacities of all linear low density polyethylenes.

A block-copolymer system with larger side-chains was analyzed in our ATHAS laboratory [22] by differential scanning calorimetry. Full additivity of the three analyzed di- and tri-block copolymers was recognized at that time [22], as shown in Fig. 2 (error $\pm 1.7\%$). One example of a triblock-copolymer is shown in Table 6 (Part F1, solid, $1.0{*}\mathrm{CH_2}—+0.58{*}\mathrm{CHC_6H_5}+0.42{*}\mathrm{CCH_3C_6H_5}$, standard deviation from the addition scheme from 310 to 370 K $0.04 \pm 0.26\%$, Part F2, liquid, same block copolymer standard deviation from the addition scheme from 450 to 490 K $-1.9 \pm 0.83\%$). The temperature was chosen to be outside the rather broad glass transition range.

A final application covers a blend of two homopolymers, polystyrene and poly-α-methyl styrene. The heat capacity measurements [6] showed in this case that for six 50/50 weight blends of varying molecular weights, covering the range of full

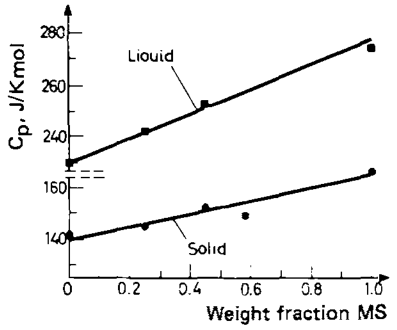

Fig. 2 Additivity of the heat capacity of α-methyl styrene and styrene blocks in the solid phase (at 330 K below the glass transition of both blocks) and in the liquid phase (melt, 470 K, above the glass transition of both blocks). *MS* = methyl styrene

miscibility to complete immiscibility, the solid data (310–365 K) agreed to within ±0.3% with data bank data on the homopolymers appropriately added. In the liquid range analyzed (455–490 K) the agreement was within ±1.9%. Table 6 contains a compatible (G1, solid; G2, liquid; polystyrene 37,000 MW, poly-α-methylstyrene of 90,000 MW) and an incompatible 50:50 blend (G3, solid; G4, liquid; polystyrene of $1.0 \cdot 10^6$ MW and poly-α-methylstyrene of $5.1 \cdot 10^5$ MW). The combined standard deviation of all data points of part G of Table 6 from the addition scheme is $-0.47 \pm 0.95\%$. Note that the computation is done using $1.0{*}CH_2 + 0.53{*}CHC_6H_5 + 0.47{*}CCH_3C_6H_5$.

Conclusion

As expected from a quantitative analysis of a large number of heat capacities of crystalline, glassy, and semicrystalline macromolecules, there exists additivity almost within experimental precision as long as the backbone atoms are all single-bonded carbon atoms. The additivity is documented from about 30 K to the glass or melting transition which limit the existence range of the solid states under consideration.

Additivity of similar precision exists in the liquid state, although the additivity in this temperature range is purely empirical.

Finally, it is documented that the additivity from group contributions applies not only to homopolymers, but also to random and block copolymers as well as blends. Also, conformational, and even sometimes geometrical isomerism seem of little influence on heat capacity in the solid and liquid states.

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Zusammenfassung — Es wird gezeigt, daß Wärmekapazitäten von aus Hauptketten mit ausschließlich C—C-Einfachbindungen bestehenden Makromolekülen aus geeigneten Beiträgen der substituierten Kohlenstoffatome mit einer Genauigkeit bis etwa $-0.2\pm2.5\%$ (155 Datenpunkte) berechnet werden können, was der experimentellen Genauigkeit nahe kommt. Wärmekapazitätsbeiträge von 42 Gruppen wurden über den vollen Meßbereich hinweg und durch sinnvolle Extrapolation bestimmt und angegeben. Die Zuverlässigkeit des Additionsschemas wurde in 16 Meßreihen an Homopolymeren, Kopolymeren und Mischungen getestet. Das Additionsschema ist für alle diese verschiedenen Anordnungen der konstitutionellen Gruppen zutreffend. Die Grundlagen des Additionsschemas werden diskutiert.

Резюме — Показано, что теплоемкосщи линейных макромолекул, состоящих только из углерод-углерод одинарных связей, могут быть вычислены, исходя из отдельных вкладов замещенных атомов углерода, с точностью около $-0{,}2 \pm 2{,}5\%$ (155 точечных данных), что соответствует экспериментальной точногти. Теплоемкости 42 групп-вкладов приведены в широкой области измерений и дана их приемлемая экстраполяция. Качество этой аддитивной схемы проверено на 16 серии измерений гомополимеров, сополимеров и смесей. Аддитивная схема справедлива для всех различных типов сочетания этих составных групп. Обсуждены основы предложенной аддитивной схемы.