Heat capacities of high melting polymers containing phenylene groups

Stephen Z. D. Cheng, Stephanie Lim, Lawrence H. Judovits and Bernhard Wunderlich
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12181, USA
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Heat capacities of solid polyparaphenylene, two variously substituted poly(oxy-1,4-phenylene)s, poly(thio-1,4-phenylene), polyparaxylylene, poly(4,4′-isopropylidenediphenylene carbonate), poly(ethylene terephthalate) and poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) were analysed using an approximate group vibration spectrum and fitting of the skeletal heat capacity to a corrected Tarasov function. The prior developed calculation scheme needed adjustment by two vibrational modes when introducing the phenylene groups. The characteristic parameter θ_1 of these polymers has been found to follow a linear relationship with the square root of the weight fraction of phenylene groups in the repeating units, and θ_3 varies little from polymer to polymer in this group ($\theta_3 = 40\,K$). An addition scheme based on approximate frequency spectra for heat capacities of polymers containing phenylene groups is proposed. Its precision is close to experimental accuracy.

(Keywords: glass; heat capacity; poly(ethylene terephthalate); poly(4,4′-isopropylidenediphenylene carbonate); poly(oxy-2,6-dimethyl-1,4-phenylene); poly(oxy-1,4-phenylene); poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4 phenylene); polyparaphenylene; polyparaxylylene; poly(thio-1,4-phenylene); semicrystalline; vibrational spectra)

INTRODUCTION

In several prior papers we established in the framework of ATHAS, our Advanced THermal Analysis System, the connection between measured and calculated heat capacities of a series of solid, linear macromolecules. The prior analysed polymers were polyethylene and linear aliphatic polyoxides[1], polypropylene[2], fluorinated and chlorinated polyethylenes[3–5], polystyrene and poly-*p*-xylylene[6], polybutadienes[7], and polyesters[8]. The calculations are based on an approximate vibrational frequency spectrum synthesized from group and skeletal vibrations. Inversion of the vibrational spectrum to heat capacity is done with the Einstein function using appropriate computer programs[9]. Agreements between calculations and experiments are usually better than ±5%, close to the overall experimental precision. For chemically similar molecules it has been possible to derive predictions of heat capacities based on the frequency spectrum[1,5].

High temperature polymers containing phenylene groups are widely used for engineering purposes. Their thermal properties are interesting not only for fundamental research, but also for applications. In this paper, eight linear macromolecules containing phenylene groups are studied. Polyparaphenylene (PPP), two variously substituted poly(oxy-1,4-phenylene)s [poly(oxy-1,4-phenylene) PO, poly(oxy-2,6-dimethyl-1,4-phenylene) PPO], poly(thio-1,4-phenylene) (PPS), polyparaxylylene (PPX), poly(4,4′-isopropylidene-diphenylene carbonate) (polycarbonate, PC), poly(ethylene terephthalate) (PET), and poly(oxy-1,4-phenylene-oxy-1,4-phenylene=carbonyl-1,4-phenylene) [poly(aryl-ether-ether-ketone), PEEK]; all of which are semicrystalline. Even PC, has been reported to be able to reach high crystallinity when properly crystallized[10]. Commonly reported glass transition and melting transition temperatures, as well as some other thermal properties needed for later discussion are listed in *Table 1*[6,11–18]. Focussing on the prediction of heat capacities of solid, high temperature polymers containing phenylene groups based on approximations of the normal modes of vibration, the Tarasov function for the skeletal vibrations of linear macromolecules has been amended to account for the special nature of the phenylene group. The side group vibrations are treated solely as group vibrations, as before.

First, the calculation of heat capacity of polyparaphenylene as the basic phenylene containing polymer is discussed, and calculations based on a vibrational dispersion curve and on isolated vibrational frequencies are compared. This contribution of the phenylene group to heat capacity is the key to the heat capacities of the other polymers.

COMPUTATIONS

The computations follow largely the procedure established in the previous works[1–9,19,20]. The experimental heat capacities are taken from the prior established data bank[11–13], and some updates[21]. First, the contribution of the group vibrations to heat capacity are calculated and subtracted from the experimental, constant pressure heat capacity, C_p, after conversion to the constant volume heat capacity, C_v. The remaining skeletal heat capacity is fitted to the Tarasov equation $T(\theta_1/T,\ \theta_3/T)$ to obtain the limiting one- and three-dimensional vibration frequencies θ_1 and θ_3.

All frequencies in this discussion are, for convenience,

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expressed in kelvin ($1\,\mathrm{cm}^{-1}=1.4388\,\mathrm{K}$). The detailed computer programs were given in a previous publication[19]. The C_p-to-C_v conversion is done using the Nernst–Lindemann equation since experimental data for the conversion are never available over the full temperature range:

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

where A_0, when expressed per mole of heavy atoms (C, O and S, in our case) is often a universal constant[22] $5.11\times10^{-3}\,\mathrm{K\,mol\,J^{-1}}$, and T_m° is the equilibrium melting temperature. The difference between C_p and C_v becomes only above about 200 K larger than the experimental uncertainty in heat capacity. Typical variations in A_0 from the universal value are between a factor of 1/2 and 2.[22] If the constancy of θ_1 at higher temperature can be improved by changing A_0 within this range and no experimental information on A_0 is available, then A_0 is made a third adjustable parameter (in addition to θ_1 and θ_3).

With the approximate vibrational group frequencies and θ-temperatures, heat capacities are calculated[9] and compared to the experiment. Note that only two fitting parameters (θ_1 and θ_3) are extracted from the experimental data, all other information is independent of heat capacity measurement.

The eight high temperature polymers have a common feature: they contain phenylene groups. From *Table 1*, one can see that the weight fraction of phenylene groups per repeating unit, f_ϕ changes from 0.40 for PET to 1.00 for PPP. The vibrational modes of the phenylene group become, obviously, the main problem in the present calculation and discussion of heat capacities. The solution to the phenylene group vibration modes is already contained in the description of the normal modes of benzene, or more precisely, *p*-xylene, suggested by Pitzer and Scott some time ago[23]. *Table 2* contains the 30 normal modes expressed in units of K not only for benzene, but also for toluene, *p*-xylene and mesitylene. The motional description of the assignment is shown in *Figure 1*. More recently, Zannoni and Zerbi[24] derived the full vibrational dispersion curve for PPP using lattice dynamics calculations. The detailed assignments and frequencies are listed in *Table 3*. Comparing *Table 3* with the *p*-xylene column of *Table 2*, the degree of correspondence between the small molecule and the polymer repeating unit can be found (also listed in *Table 3*).

We failed, however, for all polymers of interest in this paper, to invert the skeletal heat capacity with the Tarasov function to find θ_1 (from higher temperature experimental heat capacity), or θ_1 and θ_3 (for both low and high temperaure experimental heat capacity). A similar observation was already made earlier in an attempt to describe the heat capacity of polystyrene[6], and similar difficulties arose in the description of heat capacities with alternating heavy and light backbone groups as in poly(vinylidene fluoride) and poly(vinylidene chloride)[4,5]. Clearly in these cases the limit of usefulness of the Tarasov equation has been reached. Assuming, in accord with *Figure 1*, that a phenylene group should contribute five skeletal vibrational and 25 group vibrational modes[6], we find for all phenylene containing polymers that θ_1 increases and θ_3 decreases continuously and sharply with temperature within the experimental temperature range. The difference between maximum and minimum θ_1 is above 300 K, and in some cases cannot even be determined because of a too high skeletal heat capacity. The solution to the problem is suggested by the integral frequency spectrum derived from *Table 3* and plotted in *Figure 2*. The low frequency portion must be replaced by a three-dimensional Debye function to account for the intermolecular forces, omitted in the isolated chain calculation. The Tarasov function accomplished this by changing the low frequency portion without altering the total number of vibrations up to θ_3, i.e. the integral vibrational spectrum at high frequency extrapolates linearly to zero at zero frequency. Extrapolating the PPP high frequency spectrum (which is still close to linear, as generally found for linear macromolecules) to zero frequency shows, however, a discrepancy of about two vibrational modes. To stay within the framework of our calculation program, we added these two vibrational modes as a box distribution ($N=2$) between 60 and 90 K. This was found to fit the heat capacities best, and agrees also with absorption lines found in the far-infra-red spectrum of similar polymers[24b]. The frequency assignment of the group vibrations can then be deduced from *Figure 1* and *Tables 2* and *3*. To keep the number of vibrators constant, the number of skeletal vibrations per phenylene groups was then reduced from 5 to 3. The same treatment was satisfactory for all phenylene containing polymers.

Polyparaphenylene (PPP)

Experimental heat capacity data, C_p, of PPP are available only in the temperature range 80–300 K.[18] Following the above outlined treatment, the number of skeletal vibrational modes is 3, and of group vibrational modes is 27. The universal A_0 ($0.00511\,\mathrm{K\,mol\,J^{-1}}$) was used to convert the experimental C_p to C_v.[22] Only θ_1 can

Table 1 Some physical properties of high melting polymers

Polymer	$(\mathrm{M.wt.})_{\mathrm{rept.}}$	T_g (K)	T_m° (K)	No. of skeletal vib.	No. of group vib.	$\theta_1{}^a$ (K)	$\theta_3{}^a$ (K)	$f_\phi^{3\,b}$
PPP	76.10	>1000	>1000	3	27	543.7	(40)	1.0
PO	92.10	358	535	5	28	555.0	(40)	0.83
PPS	108.16	358	560	5	28	566.3	(40)	0.70
PPX	104.15	286	679	7	41	562.3	(40)	0.73
PPO	120.15	484	545	5	46	564.1	(40)	0.62
PET	192.16	342	553	15	51	586.4	37.0	0.40
PC	254.27	418	575	14	85	568.8	39.9	0.60
PEEK	288.30	418	668	15	87	559.6	(40)	0.79

[a] Values in parentheses are estimated as described in the text

[b] f_ϕ is weight fraction of phenylene groups in the repeating unit

Table 2 Normal vibrational modes of benzene, toluene, *p*-xylene, mesitylene and 1,2,4,6-tetramethylbenzene converted to θ-temperatures[a] in K

Type (from *Figure 1*)	Benzene	Toluene	*p*-Xylene	Mesitylene	1,2,4,6-Methylbenzene[b]
1	1430	1440	1190	1430	1190
2	4400	4400	4400	4400	4400
3	1870	1840	1730	1750	1730
4	990	1000	980	990	980
5	1460	1360	1380	1210	1210
6A	870	750	600	740	600
6B	870	890	930	740	740
7B	4380	4380	4380	4380	4380
8A	2290	2310	2320	2310	2310
8B	2290	2280	2270	2310	2270
9A	1700	1700	1700	1690	1670
10A	1220	1220	1220	400	400
12	1450	1130	1040	830	830
13	4400	4400	4400	1870	1870
14	2430	2340	2360	2370	2340
15	1680	1540	1580	560	560
16A	580	580	580	630	580
16B	580	670	560	630	560
17A	1420	1420	1400	1220	1220
17B	1420	1280	1150	1220	1150
18A	1490	1480	1480	330	330
19A	2140	2130	2190	1990	1990
19B	2140	2100	2090	1990	1990
20B	4430	4430	4430	1340	1340
9B	1690	1660	450	1670	450
7A	4380	1740	1730	4380	1730
11	965	310	245	260	245
18B	1490	490	490	330	330
20A	4430	4430	1730	1340	1340
10B	1220	1050	450	1670	450

[a] θ-Temperature of benzene, toluene, *p*-xylene and mesitylene normal modes are from ref. 23

[b] θ-Temperature of 1,2,4,6-tetramethylbenzene are derived from the calculated data for toluene, *p*-xylene and mesitylene (see text)

be determined, and is 543.7±2.5 K when subtracting group vibrations calculated from Zannoni and Zerbi's dispersion curve[24], and 586.1±44 K when using the isolated frequencies suggested by Pitzer and Scott[23] over this temperature range. θ_3 is set to be 40 K as a likely θ_3. The reason for this choice will be discussed below. It will not influence the calculated heat capacities above 80 K. For both calculated cases the average standard percentage deviation of C_p from the experimental data are ±0.12% and ±1.3%, respectively. *Figure 3* shows the deviations at different temperatures. The calculated skeletal and group vibration C_v's for the better fit are shown in *Figure 4* together with the experimental values for C_p.

Poly(oxy-1,4-phenylene) (PO)

Below the glass transition temperature (358.0 K), experimental heat capacity data of PO have been reported in a narrow temperature range (300–350 K)[12]. From these data, the θ_1 temperature may still be estimated. For PO, the number of skeletal vibrational modes is 5 due to the introduction of the oxygen atom, and the number of group vibrational modes is 28. The additional group vibrations are ϕ–0 stretching vibrations well-established at 1800 K[25]. Again, the universal A_0 is used to convert C_p to C_v. θ_1 of PO in the temperature range 300–350 K is 555.0±5 K when Zannoni and Zerbi's dispersion curve for the phenylene group is used[24]. If θ_3 is assumed to be 40 K (see below) the average standard deviation between experimental and calculation data is ±0.16% in the 300–350 K range. *Figure 5* shows the calculated skeletal and group vibrational contributions to the heat capaicity with the narrow experimental C_p data.

Poly(oxy-2,6-dimenthyl-1,4-phenylene) (PPO)

In the ATHAS data bank the heat capacity of PPO, a widely used polymer, has been reported from 80 K to 570 K[12] based on one investigation by Karasz *et al.*[26] Bopp *et al.* reported PPO data from 310 to 600 K in 1982[27]. More recently, new experimental data were reported by Jauhiainen[28] in the temperature range 160 K to 280 K. Jauianen's data are different from the former report. Their heat capacity is lower at lower temperature and shows a quicker increase of C_p with temperature. At 160 K, the deviation between two author's data is −2.1%. One can extrapolate from these data that at lower temperatures even larger deviations will occur. At, for example, 80 K, the difference may be −9%. From data of our laboratory on PPO in the temperature range of 325 K to 420 K, a positive deviation compared with the earlier measurements was found and it increases with temperature[21]. Our data matches well those of Jauhiainen's[28] and both were therefore accepted to provide an improved set of recommended heat capacities (1985) of PPO. The new recommended data are listed in *Table 4*. The deviation from the recommended data (1980) are listed for comparison as well as θ_1 for both data sets in the temperature range 80–410 K.

From the recommended data (1985) the θ_1 temperature was determined, but the vibrational spectrum of PPO was more difficult to derive due to the complication of the introduction of the 2,6-methyl groups into the phenylene groups. From the vibrational spectra of small model

Table 3 Vibrational frequencies of polyparaphenylene[a] and phenylene group of PPO[b]

Assignment	N	PPP frequencies	Δ[c]	Phenylene group of PPO
1	0.33	1162–1217	0	1162–1217
	0.56	932–1162	0	932–1162
	0.11	926–932	0	926–932
2	1	4400	0	4400
3	0.29	1910	0	1910
	0.50	1910–1966	0	1910–1966
	0.21	1966	0	1966
4	1	1016–1093	0	1016–1093
5	1	1359	170	1189
6A	1	866–892	0	866–892
6B	0.30	636–662	190	466–472
	0.59	439–636	190	249–446
	0.11	433–439	190	243–249
7B	1	4400	0	4400
8A	1	2352–2389	10	2342–2379
8B	0.3	2369–2379	0	2369–2379
	0.7	2284–2369	0	2284–2369
9A	1	1621	30	1591
10A	1	1200	820	380
12	0.22	1392	210	1182
	0.55	1392–1464	210	1182–1254
	0.23	1464	210	1254
13	1	4400	2530	1870
14	0.44	2071	20	2051
	0.56	2071–2136	20	2051–2116
15	1	1546	1020	526
16A	0.56	659–770	0	659–770
	0.44	770–806	0	770–806
16B	1	577	0	577
17A	1	1382	180	1202
17B	1	1136–1207	0	1136–1207
18A	1	1480–1512	1150	330–362
19A	0.26	2172	200	1972
	0.55	2172–2251	200	1972–2051
	0.19	2251	200	2051
19B	1	1824–1858	100	1724–1758
20B	1	4400	3060	1340
7A	1	1838–1854	(0)	1838–1854
9B	1	210–578	(0) S[d]	210–578
11	0.19	0	(0) S	0
	0.37	0–52	(0) S	0–52
	0.44	52–175	(0) S	52–172
18B	0.32	0–40	(?) S	0–40
	0.57	40–230	(?) S	40–230
	0.11	230	(?) S	230
20A	0.62	0–453	(?) S	0–453
	0.27	453–596	(?) S	453–596
	0.11	596–616	(?) S	596–616
10B	1	0–17	(0) S	0–17

[a] Dispersion curve calculated for the isolated macromolecule, given in ref. 24, approximated by constant (Einstein) frequencies and ranges of linear distributions (Box-distribution)

[b] For PPO, CH_3 systemmetric and asymmetric stretching are 4147, 4259 and 4262 K, respectively; symmetric and asymetric bending vibrations are about 1980 K, 2101 K and 2107 K; rocking and wagging vibrations are box-distributions in-between about 1600–1800 K, and finally, the torsion vibration is at 296.2 K. Total number of group vibrational modes of PPO is 46

[c] Δ is defined as the vibrational frequencies difference between p-xylene and 1,2,4,6-tetramethyl benzene listed in *Table 2*

[d] S means skeletal vibrational modes

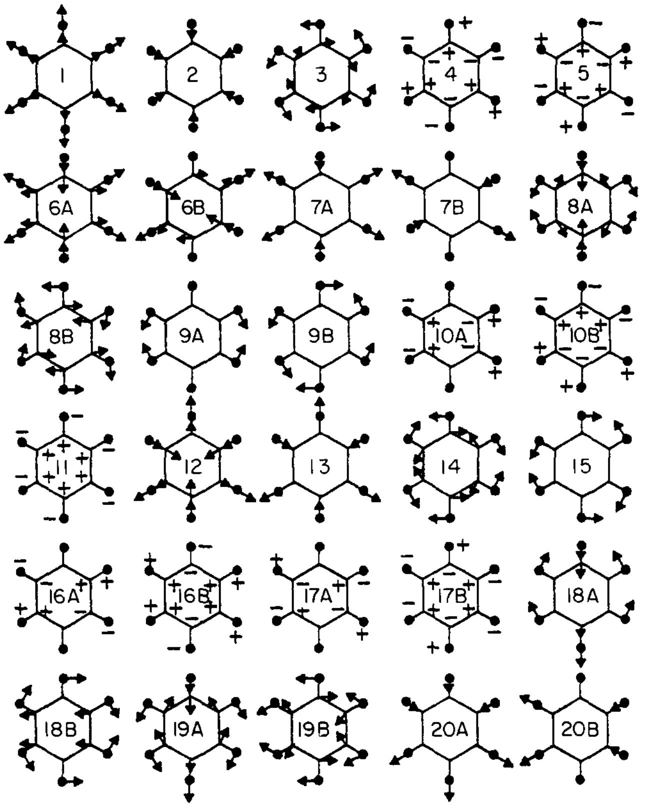


Figure 1 Normal vibration modes of benzene assigned by Pitzer and Scott[23]. For frequencies see *Table 2*, for assignment as skeletal and group vibration see *Table 3*

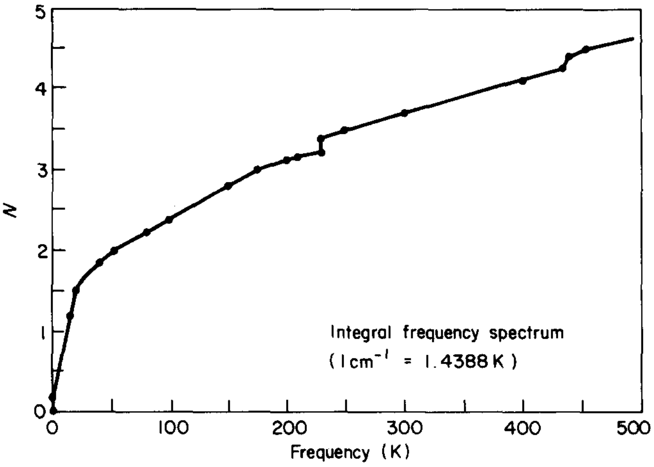


Figure 2 Integral frequency spectrum of PPP in the frequency range 0–500 K

molecules, that of 1,2,4,6-tetramethyl benzene was derived by comparison of toluene, p-xylene and mesitylene (see *Table 2*). We assumed that the difference in vibrational spectrum between p-xylene and 1,2,4,6-tetramethyl benzene is equal to that between the phenylene group in PPP (or better PO) and 2,6-dimethyl-1,4-phenylene in PPO. This difference is listed in *Table 3*, for comparison (Δ). Adding then the 18 well-known group vibrations for the two CH_3 groups[2,29] (see *Table 3*), the O–C stretching vibrations as in PO, and the two phenylene correction frequencies as discussed in the PPP section, allows the calculation of the group vibrational contribution to the heat capacity. The remaining five skeletal vibrations (three for the phenylene ring and two for the oxygen atom) were then fitted to a Tarasov-function with a θ_1 of 564.1 K and an assumed value of θ_3 of 40 K (see below). For A_0 of PPO we used 0.0032 K mol J^{-1}, close to the reported A_0 in ref. 22. The average standard deviation from the recommended data (1985) is $\pm 0.5\%$, that from the recommended data (1980) is $\pm 2.0\%$, supporting the new

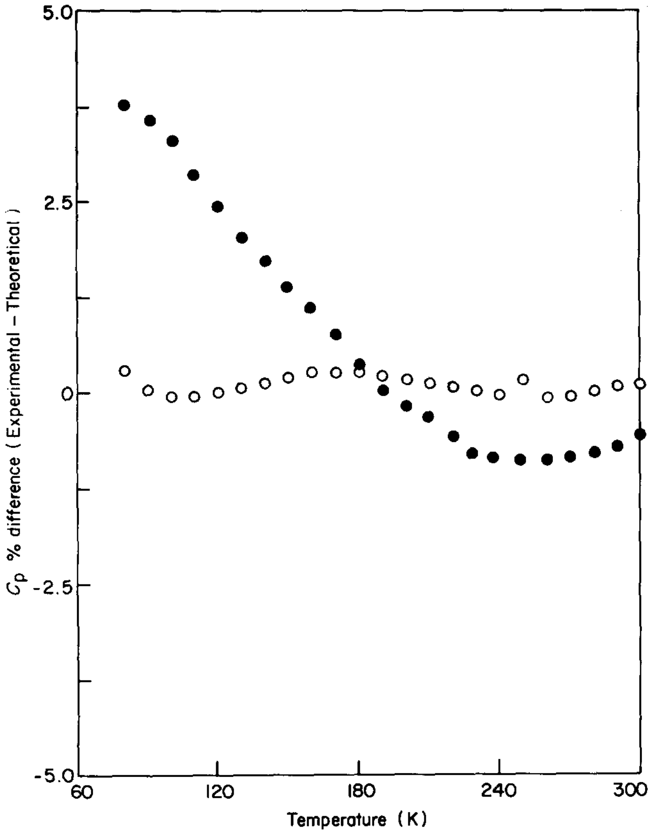


Figure 3 Deviation percentage between calculated and experimental data of PPP in the temperature range 80–300 K. Asterisks: deviation percentage of calculation based on the Zannoni and Zerbi dispersion curve; (●) calculation based on the isolated vibrational frequencies suggested by Pitzer and Scott

set of measurements (temperature range 160 to 420 K). *Figures 6* and *7* show the results.

Poly(thio-1,4-phenylene) (PPS)

The first report of the experimental C_p data of PPS will be published elsewhere[21]. The temperature range of the C_p data for the solid state is between 220 K and the glass transition temperature (358.0 K). The number of skeletal vibrational modes of PPS is the same as in the PO case, namely 5, in which three are contributed by the phenylene group and two by the sulphide atom. Again, 28 group vibrational modes have been determined to be similar to PO. Different vibrational frequencies of PPS compared to PO are only the ϕ–S stretching vibrations. The Raman-active ϕ–S stretching vibrational frequencies have been reported for diphenyl sulphide[30] to be 1558 K and 1575 K because of the nonequivalence of the rings in the crystal. A box distribution is suggested here for the purpose of calculation of heat capacity. To convert C_p to C_v an A_0 of 0.0105 K mol J^{-1} was chosen which is different from the values used before, but fits the data best. A detailed reason for this change is not known. θ_1 has been found now to be 566.3 K $\pm$ 2.2 K in the temperature range 230–320 K. After using $\theta_3 = 40$ K, as before, the standard deviation between the calculation and experimental data is only $\pm 0.17\%$ as shown in *Figure 8*. The contribution to the heat capacity from skeletal and group vibrations, C_v's, as well as experimental values for C_p are shown in *Figure 9*.

Polyparaxylene (PPX)

Experimental heat capacity C_p data as well as the calculation method have been reported for PPX and θ_1

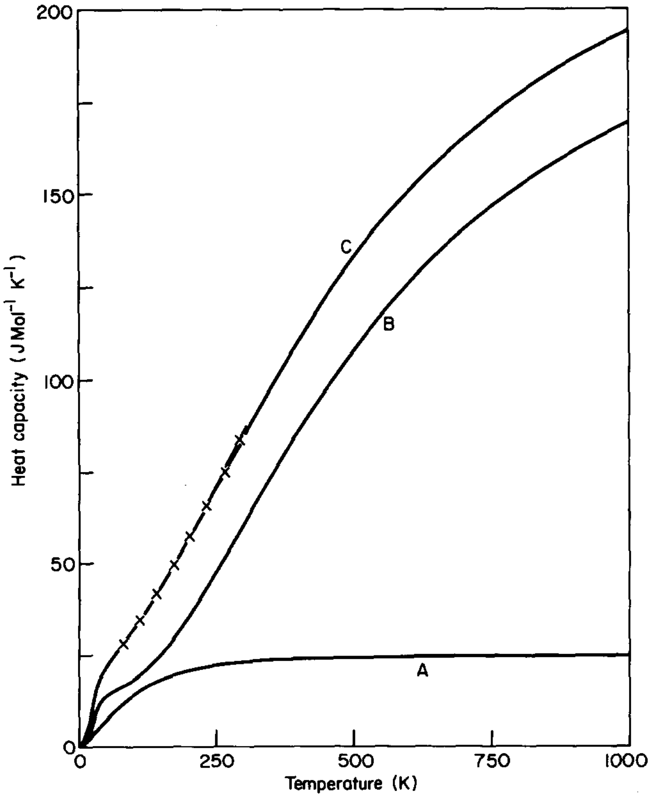


Figure 4 Heat capacity of PPP based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 543.7$ K, $\theta_3 = 40$ K; group vibrations contribution to C_v (B); total C_v (C); experimental C_p(×)

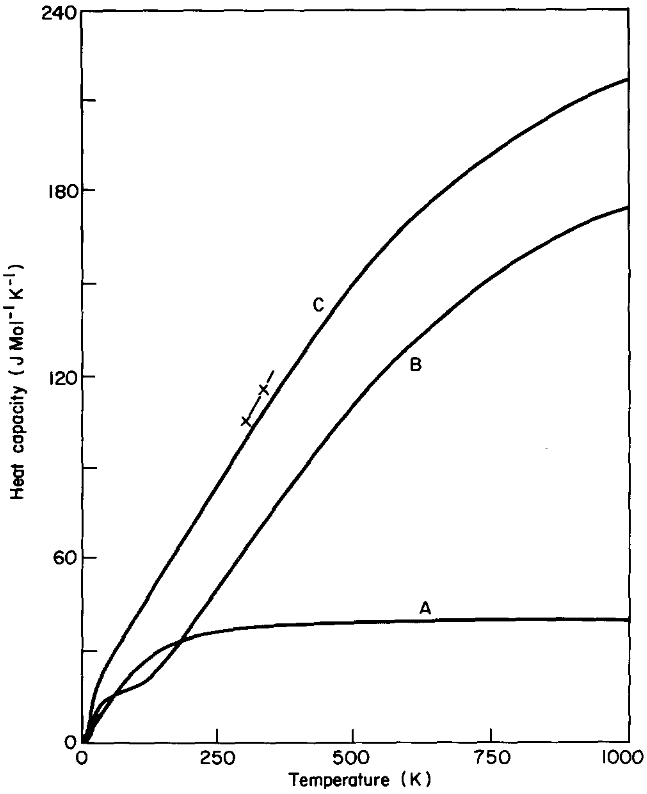


Figure 5 Heat capacity of PO based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 555.0$ K, $\theta_3 = 40$ K; group vibrations contribute to C_v (B); total C_v (C); experimental C_p (×)

Table 4 Recommended heat capacity of PPO (1985) in J K^{-1} mol^{-1}

T (K)	$C_p{}^a$ (1980)	$\theta_1{}^a$ (K)	$C_p{}^b$ (1985)	$\theta_1{}^b$ (K)	Deviation[c] (%)
80.0	53.08	410.3	(48.30)[d]	(532.4)	(−9.0)[d]
90.0	58.27	435.5	(54.04)	(548.0)	(−7.3)
100.0	63.46	451.2	(59.51)	(559.7)	(−6.2)
110.0	68.54	464.3	(64.76)	(572.3)	(−5.5)
120.0	73.33	477.6	(69.82)	(582.6)	(−4.8)
130.0	77.66	493.9	(74.73)	(586.0)	(−3.8)
140.0	82.22	500.0	(79.50)	(589.8)	(−3.3)
150.0	86.49	509.9	(84.17)	(591.1)	(−2.7)
160.0	90.64	516.1	88.74	586.2	−2.1
170.0	94.88	518.6	93.24	583.0	−1.7
180.0	98.87	528.0	97.67	575.1	−1.2
190.0	103.3	514.0	102.1	567.5	−1.2
200.0	107.6	506.6	106.4	559.7	−1.1
210.0	111.7	503.4	110.7	553.9	−0.9
220.0	116.0	493.9	115.0	548.0	−0.9
230.0	119.0	505.8	119.3	537.4	−0.5
240.0	124.1	499.3	123.5	537.2	−0.5
250.0	128.3	498.6	127.8	528.4	−0.4
260.0	132.6	493.9	132.0	531.4	−0.5
270.0	136.5	517.7	136.3	530.7	−0.1
280.0	140.7	520.5	140.6	532.3	−0.1
290.0	145.7	466.5	144.8	538.2	−0.6
300.0	148.3	493.9	149.1	544.8	0.5
310.0	153.6	538.3	153.4	553.9	−0.1
320.0	157.9	549.4	157.8	557.4	−0.1
330.0	162.1	570.9	162.1	570.9	0
340.0	166.2	603.2	166.5	577.9	0.2
350.0	170.2	646.4	170.9	585.9	0.4
360.0	174.5	665.6	175.3	588.1	0.5
370.0	178.6	709.6	179.7	596.9	0.6
380.0	182.7	747.9	184.2	595.7	0.8
390.0	186.8	786.7	188.7	593.5	1.0
400.0	190.5	868.5	193.3	571.8	1.5
410.0	194.5	916.4	197.9	553.6	1.7
420.0	198.2		202.0		1.9

[a] Recommended data of PPO heat capacity using Karasz *et al.*[26] θ_1 were calculated according to those data

[b] New recommended data of PPO heat capacity. Jauhiainen's data[27] were used in the temperature range 160 K and 280 K. Our measurements were carried out in the temperature range 325 K and 420 K for the solid state PPO heat capacity data, which can be described as:

$$C_p = \exp\{0.0759\,(\ln T)^3 - 1.1905\,(\ln T)^2 + 7.0355\,(\ln T) - 10.4728\} \quad (2)$$
$$(\mathrm{J\,K^{-1}\,mol^{-1}})$$

The data are shown in C_p (1985) column. θ_1 values were also calculated based on the data of equation (2)

[c] Deviation between new and old recommended data

[d] Values in the parentheses are the extrapolated data using equation (2). The corresponding θ_1 and deviation were also calculated

was found to be 515.1 K for nine skeletal vibrational modes and 39 group vibrational modes[6]. Following our new treatment, using two fixed phenylene skeletal modes in the 60 to 90 K range which reduces the skeletal vibrational modes fitted to the experimental data to seven, changes θ_1 to 562.3 K. The vibrational spectrum of PPX consists of the 30 vibrational modes of the phenylene group, listed in *Table 3* (27 group and three skeletal vibrational modes), and leaves 14 group and four skeletal vibrational modes contributed by the two CH_2 groups. The group vibrations were taken to be identical to polyethylene[1]: stretching (2 asym. 4148.1 K, and 2 sym. 4097.2 K); 2 CH_2 bending (2074.7 K); 2 CH_2 wagging (1698.3 K–1976.6 K); 2 CH_2 twisting (1689.6–1874.3 K); 2 CH_2 rocking (1038.0–1494.1 K); 1 C–C stretching (1377.6–1637.5 K), and 1 C–ϕ stretching (1830 K). If θ_3 is 40 K, and universal A_0 is used, the calculated data fit the

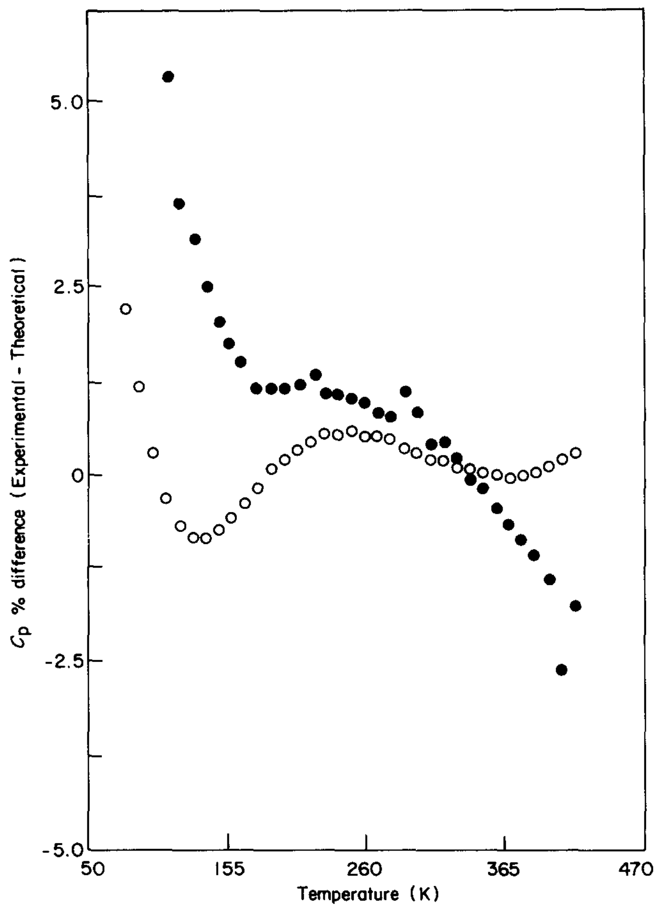


Figure 6 Deviation between calculated and experimental data of PPO in the temperature range 80–420 using recommended data (1985) (○); (●) old recommended data (1980)

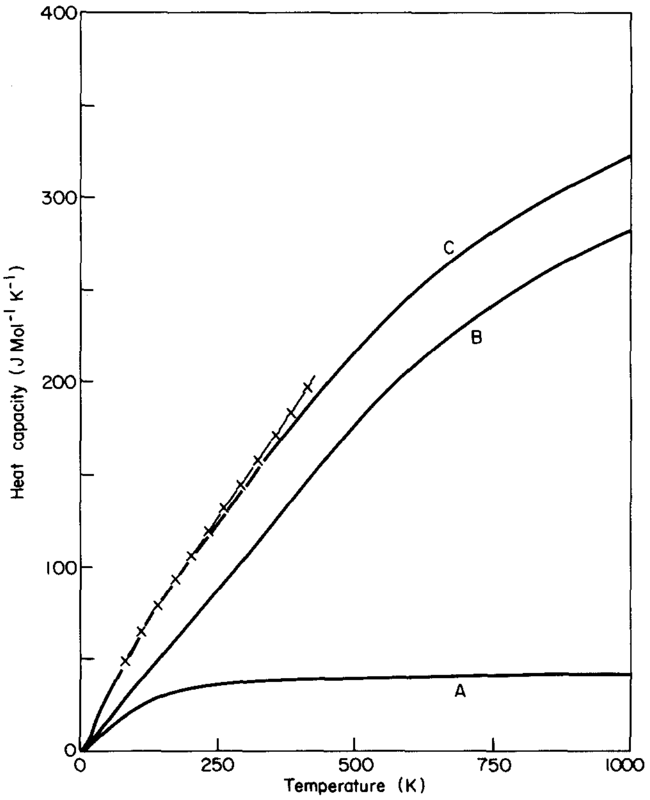


Figure 7 Heat capacity of PPO based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 564.1$ K, $\theta_3 = 40$ K; group vibrations contributions to C_v (B); total C_v (C); experimental C_p (×)

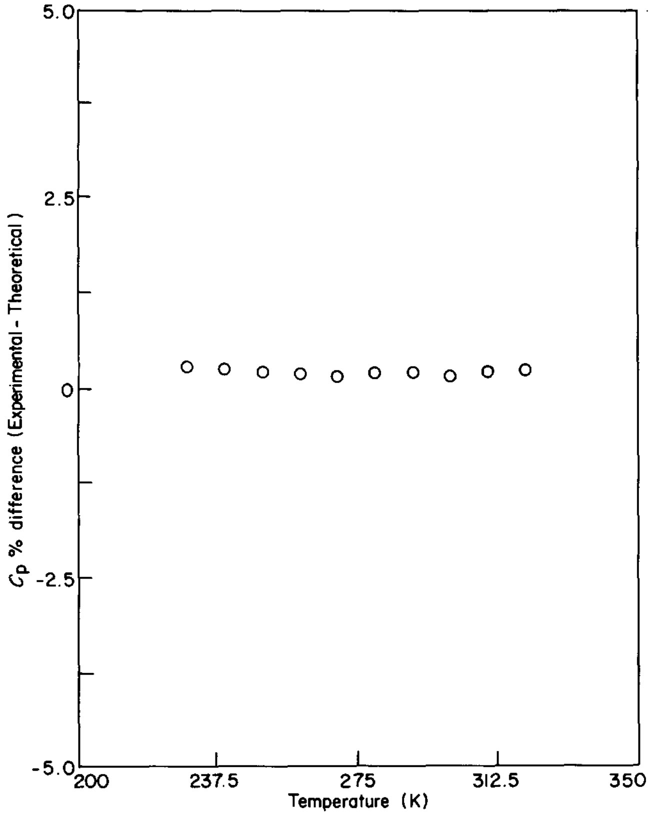


Figure 8 Deviation between calculation and experimental data of PPS in the temperature range 230–320 K

experimental data very well, ($\pm 1\%$ even though solid state heat capacity data have been reported only over a narrow temperature range 220 K–250 K). CH_2 vibrational modes can also be obtained from those for PET for which isolated chain vibrational frequencies have been calculated (see PET). The small changes do not affect the calculations significantly. The calculated data from skeletal and group vibration and total C_v data are shown in *Figure 10*, together with narrow temperature range experimental values of C_p.

Polycarbonate (PC)

Experimental heat capacity C_p data of PC are reported in the ATHAS data bank over the wide temperature range from 0 K to 560 K[13]. To represent the skeletal vibration, both θ_1 and θ_3 can thus be determined. The total number of vibrational modes of PC is 99, and in the present calculation scheme the number of skeletal vibrational modes is 14, the group vibrational modes are, therefore, 85. Of these 54 are contributed by two phenylene groups (see *Table 3*). Of the remaining 31, six are CH_3 stretching (4 asymmetric and 2 symmetric): 4258 K, 4245 K and 4127 K[2]; six are CH_3 bending (4 asymmetric, 2 symmetric): 2101 K, 2092 K and 1983 K[2]: six are C–C stretching and rocking: 1164–1680 K[2]; two are CH_3 torsion, 296.2 K[2]; two are C–O stretching: 1610–1830 K; 1 is C=O stretching: 2498 K; 1 is C=O out-of-plane and 1 is C=O in-plane bending: 1040 K and 693 K; 1 is C–ϕ stretching: 1830 K; 1 is C–ϕ stretching: 1800 K; and finally, 4 are C–C–C bending in the low frequency range (400–700 K)[2]. In order to convert experimental C_p data to C_v, the universal A_0 is used. θ_D has been chosen within temperature range 1–10 K. It is 96.6 K. θ_1 is 568.8 ± 21 K, and θ_3 is 39.9 ± 0.7 K when averaged from 10 to 350 K

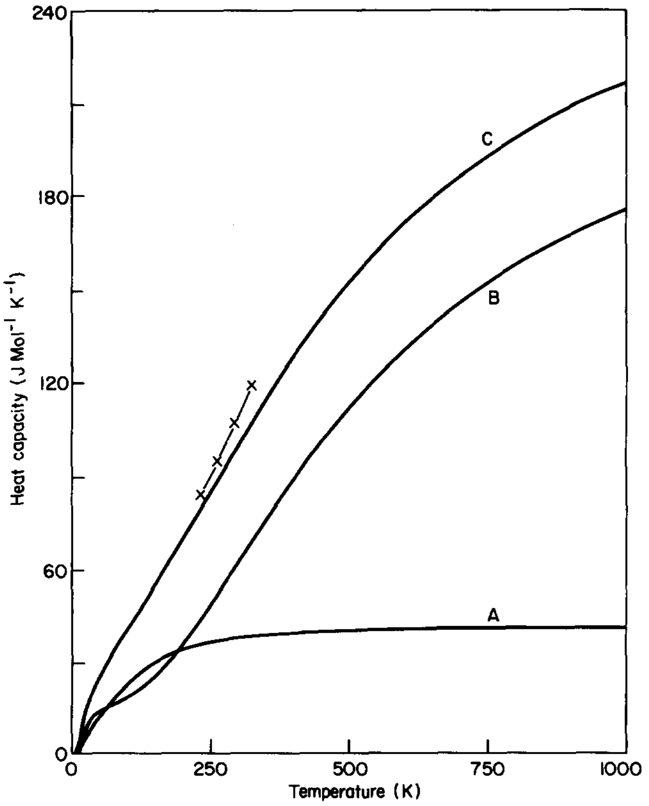


Figure 9 Heat capacity of PPS based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 566.3$ K, $\theta_3 = 40$ K; vibration contribution to C_v (B); total C_v (C); experimental C_p (×)

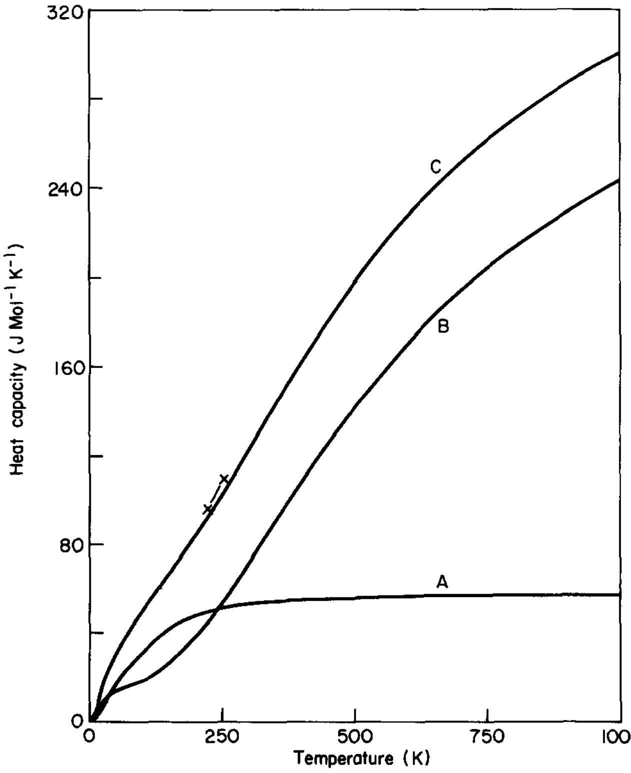


Figure 10 Heat capacity of PPX based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 562.3$ K, $\theta_3 = 40$ K; group vibration contribution to C_v (B), total C_v (C), experimental C_p (×)

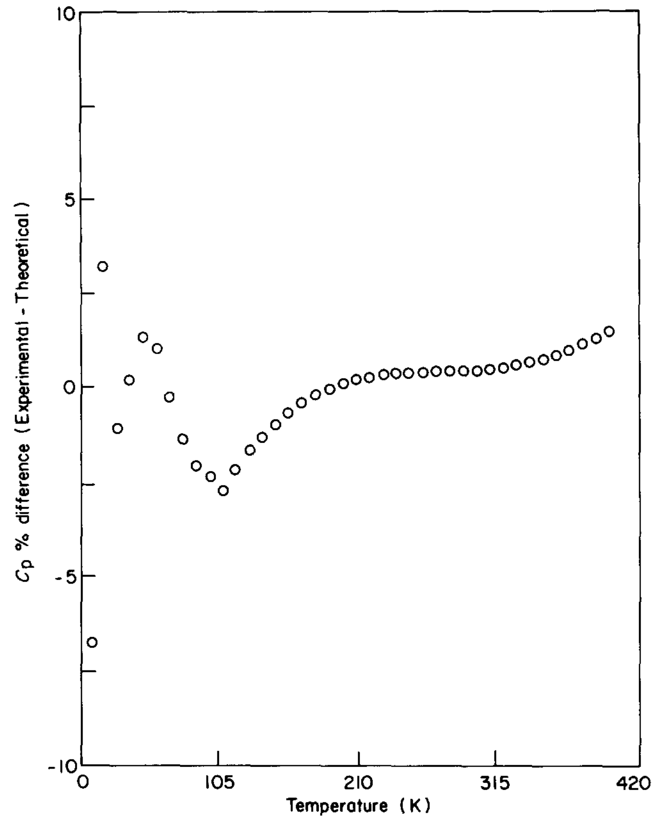


Figure 11 Deviation between calculation and experimental data of PC in the temperature range 10–400 K. Calculation based on the Zannoni and Zerbi dispersion curve

and the Zannoni and Zerbi dispersion curve of the phenylene group[24] is used. θ_1 changes to 582.1 ± 14 K and θ_3 to 39.4 ± 0.5 K when the isolated vibrational frequencies suggested by Pitzer and Scott[23] for the low molecular weight model are used in the same temperature range. For the two cases, the average standard error percentages are $\pm 0.9\%$ and $\pm 0.8\%$, respectively. *Figure 11* shows the error at different temperatures, and the calculated C_v, compared with experimental C_p data, as well as contribution of skeletal and group vibration to C_v are shown in *Figure 12* for the use of Zannoni and Zerbi's phenylene group dispersion curve.

Poly(ethylene terephthalate) (PET)

Experimental heat capacity C_p data are complete for PET in the temperature range 0–590 K, so that both θ_1 and θ_3 of the Tarasov approximation can be obtained. The phenylene group contained in the PET chain contributes 27 group vibrational modes and three skeletal vibrational modes. The total number of skeletal vibrational modes of PET is 15, and the group vibrational modes of PET are 51 (total modes, 66). The 24 additional group vibrations added to the phenylene groups are[31]: four CH_2 stretching modes (2 asym. and 2 sym.), 4270 K and 4160 K; two CH_2 bending modes, 2090 K; two CH_2 wagging modes, 2010 K; two CH_2 twisting modes, 1850 K, two CH_2 rocking modes, 1690 K; two C=O stretching modes, 2498 K; two C=O out-of-plane and two C=O in-plane bending modes, 1040 K and 693 K; 1 C–C stretching mode, 1220–1610 K; 1 C–ϕ stretching mode, 1830 K; two C–O stretching modes, 1610–1830 K; and, finally two $\overset{\overset{O}{\|}}{C}$–O stretching modes, 1440 K. For PET, A_0 is taken as 0.0075 K mol J^{-1}, slightly different from the universal A_0, but still within reasonable range. θ_D is found from the experimental data in the temperature range 1–10 K, as 92.9 K. The Tarasov approximation parameters, θ_1 and θ_3, are then 586.4 ± 22 K and 37.0 ± 0.8 K in temperature range 30–300 K, respectively, if the Zannoni and Zerbi dispersion curve[24] of the phenylene group is used for the phenylene group of PET (*Table 3*). When the approximate vibrational frequencies of *Table 2* are applied, θ_1 and θ_3 change very little, and are 587.9 ± 29 K and 37.0 ± 0.9 K in the same temperature range. The average standard percentage errors for the two cases are $\pm 1.4\%$ and $\pm 1.7\%$, respectively, and are shown in *Figure 13*. Both experimental C_p and calculation data C_v together with skeletal and group vibrational contributions to C_v are shown in *Figure 14*.

Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) [poly(aryl-ether-ether-ketone) (PEEK)]

The heat capacity of PEEK has been measured recently in the temperature range 130–670 K.[21] Again, the low temperature amorphous data are sufficient to determine θ_1 only for the Tarasov approximation. Following the same treatment as before, 87 group vibrational and 15 skeletal vibrational modes are to be considered to which each phenylene group contributes three skeletal and 27 group vibrational modes. Besides the 81 group vibrational modes contributed by the phenylene groups, there are two O–ϕ stretching modes (1800 K); 1 C–ϕ stretching mode (1830 K); 1 C=O stretching mode (2498 K); and finally, one out-of-plane and one in-plane bending mode of C=O (1040 K and 693 K). For PEEK, again, the universal A_0 (0.00511 K mol J^{-1}) was taken. The tarasov approximation parameter θ_1 is found to be

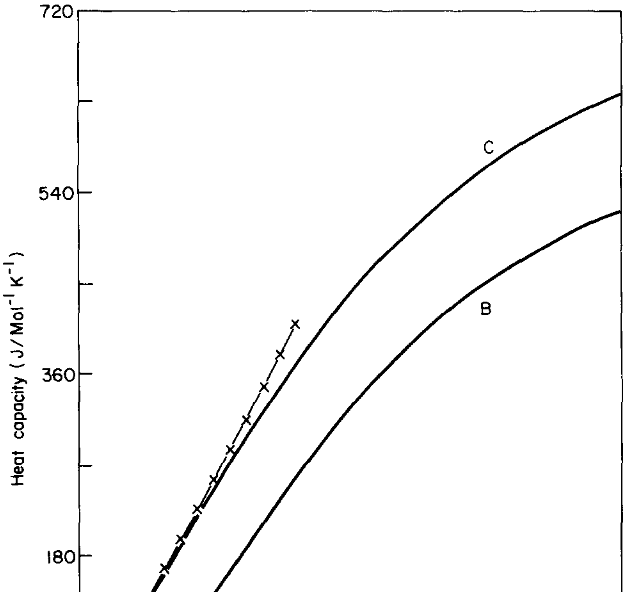


Figure 12 Heat capacity of PC based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 568.8$ K, $\theta_3 = 39.9$ K; group vibrations contribution to C_v (B); total C_v (C); experimental C_p (×)

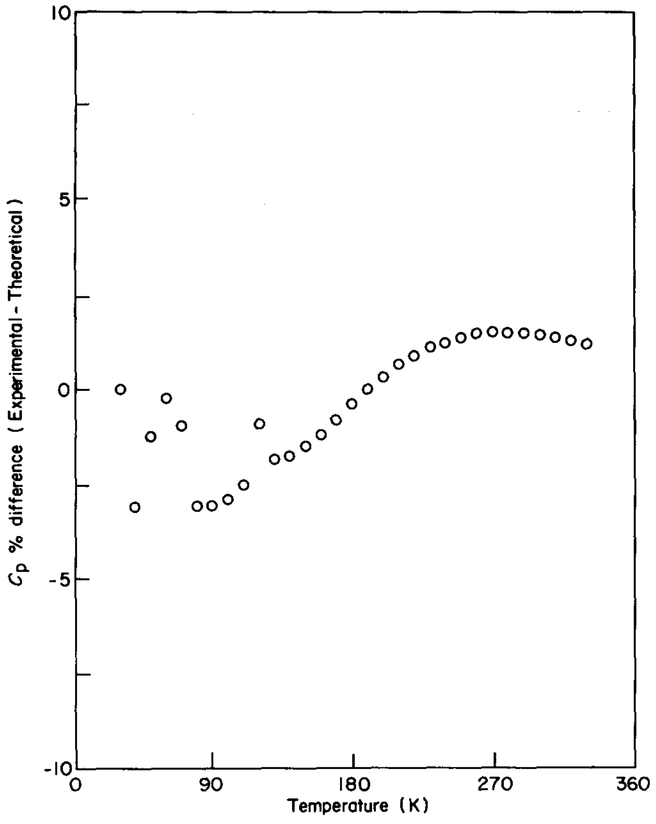


Figure 13 Deviation between calculation and experimental data of PET in the temperature range 30–300 K. Calculation based on the Zannoni and Zerbi dispersion curve

559.6±7 K in temperature range 130–400 K if the Zannoni and Zerbi dispersion curve of the phenylene group is used[24], and it changes to 603.0±16.6 K in the same temperature range when the isolated vibrational frequencies are applied[23]. The average standard deviation for both cases are ±0.3 and ±0.5%, respectively when $\theta_3 = 40$ K is used. They are shown in *Figure 15*. Again, the skeletal and group contributions to C_v and total C_v calculated are shown in *Figure 16* together with the experimental C_p for the better approximation.

DISCUSSION

The heat capacities of solid, high temperature polymers presented here could not be described using the Tarasov approximation, i.e. the Tarasov approximation seems to be limited to strictly linear macromolecules. Even for linear macromolecules one must, in addition, have an approximately even mass distribution along the chain. Alternation in mass along the chain also leads to deviations beyond experimental heat capacity accuracy[4,5]. By comparison with a normal mode calculation for PPP (*Figure 2*) the required correction, a box distribution of two modes of vibrations with frequencies between 60 and 90 K were found, and the excellent agreement between calculation and measurement after fitting at only one or two points (for θ_D or θ_1 and θ_3) (*Figures 4–16*) is strong support for suggesting that this treatment is applicable to many, or all, phenylene containing polymers.

For the evaluation of the remaining group vibrations of phenylene there are two sets of vibrational frequencies: one is from Zannoni and Zerbi's dispersion curve of

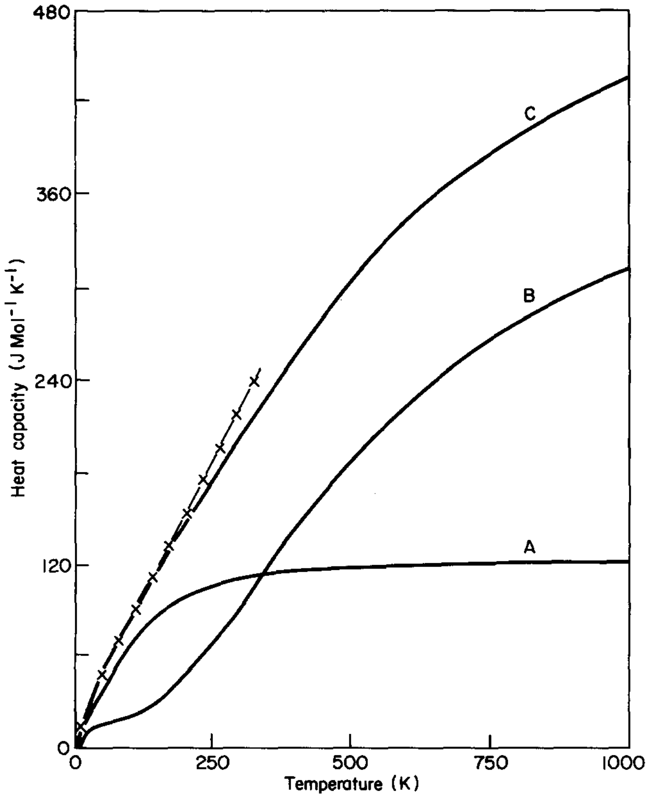


Figure 14 Heat capacity of PET based on the Zannoni and Zerbi dispersion curve. Skeletal contributions to C_v (A), $\theta_1 = 586.4$ K, $\theta_3 = 37.0$ K; group vibrations contribution to C_v (B); total C_v (C); experimental C_p (×)

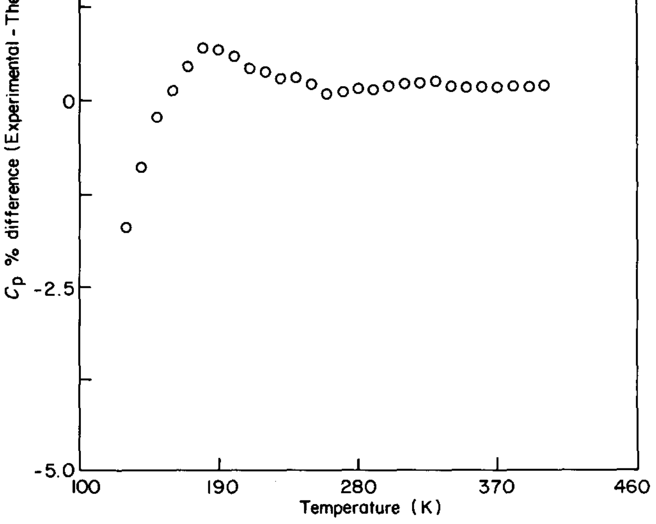


Figure 15 Deviation between calculation and experimental data of PEEK in the temperature range 130–400 K. Calculation based on the Zannoni and Zerbi dispersion curve

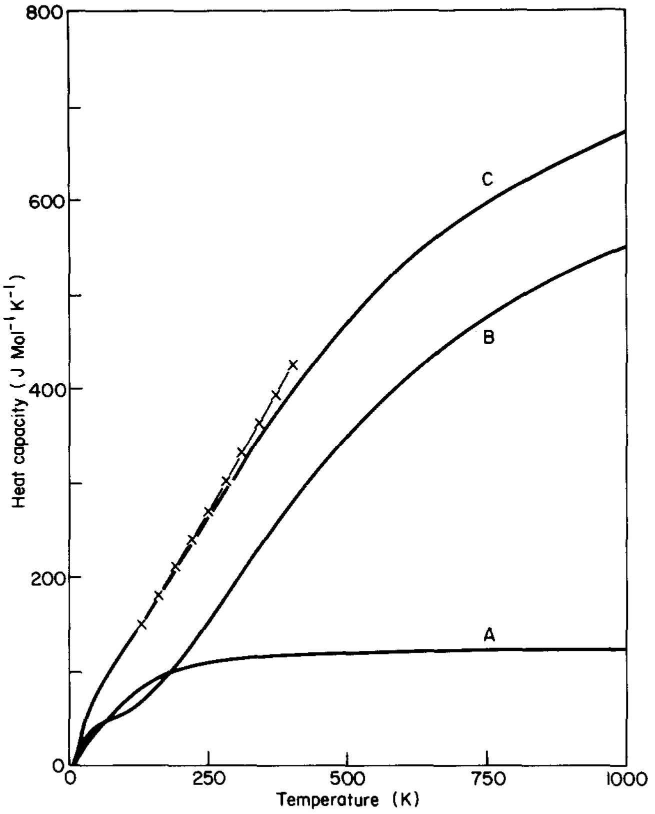


Figure 16 Heat capacity of PEEK based on the Zannoni and Zerbi dispersion curve. Skeletal contribution to C_v (A), $\theta_1 = 559.6$ K, $\theta_3 = 40$ K; group vibration contribution to C_v (B); total C_v (C); experimental C_p (×)

isolated chains of PPP[24], and the other is a set of isolated vibrational frequencies assigned based on low molecular weight model compounds calculated by Pitzer and Scott[23]. As expected, the data of C_p of PPP can be reproduced more accurately when the Zannoni and Zerbi dispersion curve is used than when calculated based on the low molecular weight model compound, isolated vibrational frequencies (0.12% vs. 1.3%). When those two set frequencies were applied to polymers, of which the phenylene group is only a part of the repeating unit, the difference between the two calculations becomes less. This is not only based on the lower fraction of phenylene groups, but also partially due to a more effective compensation of the error in group vibration assignment by the Tarasov fit to the remaining skeletal vibrations.

For the eight polymers, the θ_1 parameter of the Tarasov approximation can be seen in *Table 1*. The value of θ_1 for PPP, which has the highest phenylene group content is 543.7 K, and θ_1 for PET which has the lowest phenylene content is 586.4 K. In between PPP and PET, are PO, PEEK, PPX, PPS, PPO, PC sequentially in weight fraction phenylene. The θ_1 sequence of those eight polymers fits a linear relationship between θ_1 and the square root of f_ϕ as is illustrated in *Figure 17*:

$$\theta_1 = -109.68\ (f_\phi)^{1/2} + 654.93\ (\mathrm{K})\ (\pm 0.4\%) \qquad (3)$$

This expression is close to an inverse square root dependence as one would expect from the common change of frequencies with mass. From the analysis of polymers of varying crystallinity one does not expect a large variation of θ_1 with crystallinity[19].

For θ_3, only data for PC and PET can be derived because no other low temperature (1–10 K) heat capacity data are available. Both, PC and PET, have a θ_3 which is almost identical, close to 40 K (37.0 for PET and 39.9 K for PC). As a first approximation we assume that all other, similar macromolecules have the same θ_3. One expects a strong dependence of θ_3 on crystallinity, i.e. even the PC and PET data correspond below about 30 K only to the amorphous polymer for which experimental heat capacities were available. More low temperature data are needed to establish both θ_3 and its crystallinity dependence.

ADDITION SCHEME

In previous publications[1,5] it has been shown that heat capacities of similar macromolecules may be predicted from an addition scheme of group vibrations and trends in θ_1 and θ_3. Other effects, such as crystal structure, stereo and positional isomerisms, repeating unit sequence in copolymers and mixing of polymers in solution do often not affect the heat capacity contributions significantly. A particular group vibrational frequency in a polymer chain usually exists in a narrow, fixed frequency range and influences other vibrational frequencies very little.

In this paper, all eight polymers contain phenylene groups, and for that group total vibrational modes as well as frequencies have been well-established. The group vibrational modes and frequencies of the other groups are $-CH_2-$, $-CH_3$, $-C(CH_3)_2-$, $-O-$, $-S-$, $-CO-$ and $-COO-$, are also known and listed in *Table 5*. The group vibrational contributions to heat capacity of these groups and phenylene are listed in *Table 6* in the temperature range 10–1000 K based on the present calculation scheme. The remaining skeletal vibration contributions can then easily be established using a value of $\theta_3 = 40$ K and calculating θ_1 from equation (3). The number of skeletal modes is three for each phenylene group and two for each $-C-$ or $-O-$ chain atom. Tables of the 3-dimensional and 1-dimensional Debye-functions are available in the literature[32] or are available through our ATHAS computation centre[9,19]. *Table 7* shows for some temperatures the precision of the addition scheme for the eight polymers analysed.

To parallel the effort of prediction of heat capacity based on consideration of skeletal and group vibrational

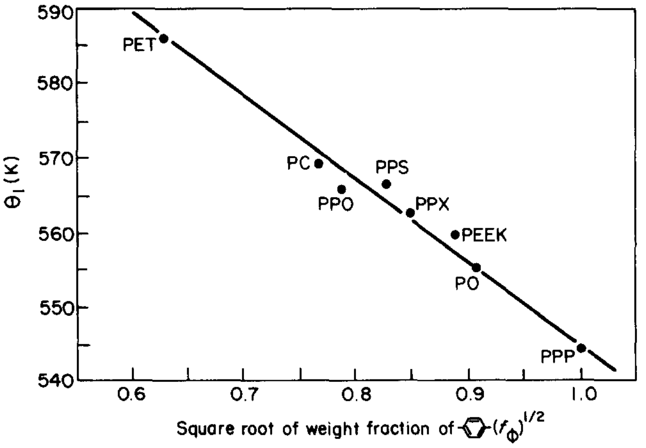
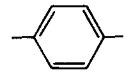


Figure 17 Linear relationship between θ_1 and the square root of the weight fraction of phenylene groups in a repeating unit

Table 5 Number of the group vibrational modes in the repeating units of high melting polymers

Repeating unit	PPP	PO	PPS	PPX	PPO	PET	PC	PEEK
Phenylene	1	1	1	1	1	1	2	3
$-CH_2-$	–	–	–	2	–	2	–	–
$-CH_3-$	–	–	–	–	2	–	–	–
$-C(CH_3)_2-$	–	–	–	–	–	–	1	–
–O–	–	1	–	–	1	–	1	2
–S–	–	–	1	–	–	–	–	–
–CO–	–	–	–	–	–	–	–	1
–COO–	–	–	–	–	–	2	1	–

Table 6 Heat capacity contributions of group vibrational modes in high melting polymers in J K^{-1} mol^{-1}

T (K)		$-CH_2-$	$-CH_3$	$-C(CH_3)_2-$	–O–	–S–	–CO–	–COO–
10	0.62	–	–	–	–	–	–	–
20	5.86	–	–	–	–	–	–	–
40	12.50	–	0.45	0.55	–	–	–	–
50	13.84	–	1.35	1.92	–	–	–	–
60	14.77	–	2.67	3.06	–	–	0.01	0.01
80	16.33	–	5.87	6.65	–	–	0.12	0.12
100	18.27	0.01	8.89	10.64	–	–	0.42	0.42
120	20.81	0.04	11.36	14.78	–	–	0.97	0.97
140	23.93	0.12	13.30	18.91	0.01	0.02	1.74	1.75
150	25.70	0.19	14.11	20.97	0.01	0.02	2.17	2.18
160	27.59	0.29	14.84	23.00	0.01	0.04	2.64	2.67
180	31.70	0.59	16.08	27.02	0.04	0.15	3.64	3.72
200	36.21	1.01	17.15	30.95	0.08	0.20	4.67	4.89
220	41.04	1.59	18.12	34.87	0.15	0.34	5.69	6.11
240	46.10	2.31	19.04	38.81	0.26	0.52	6.70	7.38
250	48.70	2.73	19.51	40.80	0.32	0.62	7.20	8.02
260	51.33	3.17	19.97	42.78	0.39	0.73	7.69	8.67
280	56.64	4.15	20.93	46.78	0.56	0.98	8.66	9.97
300	61.99	5.22	21.92	50.80	0.74	1.23	9.59	11.26
320	67.30	6.37	22.95	54.83	0.96	1.51	10.49	12.53
340	72.55	7.56	24.02	58.83	1.18	1.79	11.37	13.78
350	75.13	8.18	24.56	60.84	1.30	1.94	11.80	14.38
360	77.68	8.80	25.07	62.73	1.52	2.08	12.03	14.98
380	82.68	10.06	26.24	66.76	1.67	2.37	13.05	16.14
400	87.53	11.31	27.37	70.61	1.92	2.65	13.84	17.26
420	92.22	12.56	28.52	74.38	2.16	2.91	14.61	18.33
440	96.72	13.80	29.66	78.07	2.41	3.18	15.36	19.36
460	101.1	14.99	30.80	81.61	2.60	3.38	16.03	20.34
480	105.2	16.21	31.92	85.14	2.89	3.67	16.77	21.27
500	109.2	17.36	33.02	88.48	3.10	3.87	17.39	22.16
520	113.0	18.49	34.11	91.77	3.32	4.10	18.04	23.00
540	116.6	19.61	35.17	94.97	3.58	4.34	18.67	23.80
560	120.1	20.67	36.22	98.02	3.76	4.51	19.24	24.56
580	123.4	21.72	37.24	101.0	3.98	4.72	19.83	25.28
600	126.6	22.71	38.23	103.9	4.15	4.88	20.34	25.97
620	129.7	23.67	39.19	106.6	4.31	5.01	20.81	26.61
640	132.6	24.61	40.14	109.3	4.47	5.16	21.29	27.23
660	135.4	25.52	41.05	111.9	4.63	5.31	21.76	27.81
680	138.1	26.40	41.94	114.4	4.78	5.44	22.19	28.36
700	140.6	27.26	42.81	116.9	4.95	5.59	22.63	28.89
750	146.6	29.26	44.87	122.6	5.24	5.84	23.57	30.09
800	152.0	31.12	46.78	127.9	5.53	6.09	24.42	31.14
850	156.9	32.84	48.55	132.9	5.78	6.30	25.18	32.06
900	161.4	34.41	50.19	137.4	5.97	6.45	25.80	32.87
950	165.4	35.91	51.71	141.7	6.24	6.68	26.47	33.59
1000	169.1	37.28	53.11	145.7	6.44	6.85	27.03	34.23

modes, a purely empirical addition scheme has been developed[33,34]. In this scheme, appropriate contributions of all kinds of chain-groups to the heat capacity have been derived at different temperatures purely from experimental data. This empirical addition scheme is, however, strictly limited to the temperature ranges in which experimental data are available. If compared with our calculated data, the deviation becomes larger, being in the 5%–7% range.

CONCLUSIONS

(1) Heat capacities of eight solid, high melting polymers containing phenylene groups were analysed, based on experimental data below the glass transition temperature and information on vibrational spectra. Heat capacities over the whole temperature range are now available and an addition scheme for the group vibrations permits estimation of heat capacities of related polymers.

Table 7 Calculated heat capacities in J K^{-1} mol^{-1} using the addition scheme of group vibrations listed in *Table 6* and θ_1 from equation (3)

T (K)	C_p (PPP)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)	C_p (PO)[a]	Deviation 1[b] (1%)	Deviation 2[c] (%)
50	21.35	−0.19	–	26.15	0.35	–
100	32.56	−0.09	−0.06	41.85	0.41	–
150	44.37	−0.05	−0.25	56.78	0.26	–
200	57.52	−0.03	−0.21	72.06	0.14	–
250	71.87	−0.01	0.03	88.29	0.09	–
300	86.80	−0.01	−0.12	105.3	0.10	0
350	101.6	0	–	122.5	0.08	−0.08
400	115.9	0	–	139.5	0	–

T (K)	C_p (PPS)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)	C_p (PPX)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)
50	26.03	0.23	–	30.88	0.06	–
100	41.83	0.26	–	50.95	0.14	–
150	57.23	0.16	–	69.10	0.06	–
200	73.50	0.11	–	87.60	0.03	–
250	91.41	0.07	−0.13	108.0	0	−0.90
300	111.0	0	−0.09	130.3	0	–
350	132.3	0.08	–	153.6	0	–
400	155.5	0	–	177.2	0	–

T (K)	C_p (PPO)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)	C_p (PET)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)
50	28.55	−0.35	–	48.86	0.02	1.29
100	59.19	−0.25	−0.54	86.94	0.07	2.99
150	84.65	−0.18	0.57	121.2	0	1.51
200	106.0	−0.19	−0.38	153.7	0	−0.26
250	126.7	−0.31	−0.86	187.1	0	−1.27
300	147.9	−0.54	−0.80	222.2	0	−1.33
350	169.5	−0.82	−0.82	258.8	0	–
400	191.0	−1.14	−1.19	296.6	0	–

T (K)	C_p (PC)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)	C_p (PEEK)[a]	Deviation 1[b] (%)	Deviation 2[c] (%)
50	63.12	0.30	−0.99	78.28	0.12	–
100	112.1	−0.14	2.19	125.6	0.16	–
150	160.3	−0.12	0.94	171.9	0.12	0.35
200	207.7	−0.07	−0.05	220.0	0.18	−0.36
250	256.0	−0.02	−0.31	270.9	0.37	0.18
300	305.7	−0.02	−0.36	323.5	0.57	0.43
350	356.0	0	−0.59	376.1	0.78	0.64
400	405.9	0	−1.26	427.4	0.92	0.78

[a] C_p (PPP) means heat capacity of PPP in the unit of J K^{-1} mol^{-1}. C_p (PO), C_p (PPS), C_p (PPX), C_p (PPO), C_p (PET), C_p (PC) and C_p (PEEK) have the same meaning

[b] Deviation 1 is the deviation between both calculation of heat capacities using the addition scheme of group vibration listed in *Table 6* and θ_1 from equation (3) and calculation described in the section of computation based on experimental data

[c] Deviation 2 is the deviation between calculation of heat capacities using the addition scheme of group vibration listed in *Table 6* and θ_1 from equation (3) and experimental data

(2) The Tarasov approximation for the skeletal vibrations of polymers usually successful for the description of linear macromolecules failed to apply in these polymer containing phenylene groups. The solution to the problem was to add two modes of skeletal vibration for each phenylene group as a fixed box distribution in the frequency range 60–90 K.

(3) Calculations and measurements agree within the limit of typical experimental error (3 ~ 5%).

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