Heat capacities of polyethylene and linear fluoropolymers

Kyriakos Loufakis and Bernhard Wunderlich
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, USA
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Heat capacities at constant pressure, C_p, and at constant volume C_v, were calculated with the help of normal mode frequency spectra and compared to experimental data for crystalline or semicrystalline polyethylene, poly(vinyl fluoride), poly(vinylidene fluoride), polytrifluooroethylene and poly(tetrafluoroethylene). A calculation scheme using a Tarasov function for $2N$ skeletal vibrational modes and an approximation of the residual $7N$ normal modes from known data on polyethylene and polytetrafluoroethylene is developed for all homologous, linear fluoropolymers. N is the number of carbon backbone atoms of the repeating unit. Calculations can be carried out over the whole temperature range 0 K to melting. For the two theta temperatures and the constant A_0 used for C_v to C_p conversion, fluorine-concentration dependent curves are given. The relations are expected to hold also for copolymers and blends of intermediate fluorine contents. Recommended experimental (data bank) heat capacities agree to $\pm 2.5\%$ with the calculations.

(Keywords: crystalline; fluoropolymers; glassy; heat capacity; polyethylene; poly(tetrafluoroethylene); poly(trifluoroethylene); poly(vinyl fluoride); poly(vinylidene fluoride); vibration spectrum)

INTRODUCTION

The linking of heat capacities of solid linear macromolecules to their vibrational spectrum[1] has been of long standing interest at ATHAS, our laboratory for *A*dvanced *TH*ermal *A*nalysi*S*[2]. Recently a complete critical analysis of all measured heat capacities of linear macromolecules has been published in form of a data bank[3]. Using this data bank we will make an effort to interpret heat capacities, develop predicitive capabilities, and explore the limits of our understanding of the theory of heat capacities of linear macromolecules. Work has already been completed for polypropylene[4], polytetrafluoroethylene[5], polyethylene[6], and aliphatic polyoxides[6].

In this paper we want to make use of the data on polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) to come up with a discussion of heat capacities of polyethylenes of all degrees of fluorination. Full vibrational frequency data for both head to head and head to tail poly(vinylidene fluoride) (PVF2) as well as for the prior discussed PE and PTFE are available. For poly(vinyl fluoride) (PVF) the group vibrations can be approximated using Raman and i.r. information in conjunction with the known spectrum of poly(vinyl chloride) (PVC). For poly(trifluoroethylene) (PVF3) no such information is available. For all five polymers some, or complete heat capacities as functions of temperature are known to check and augment the calculations.

In brief, the vibrational frequency spectrum is separated into group and skeletal vibrations[7,8]. The group vibrations were found to be largely independent of structure in the vicinity of the given group, i.e. they couple only to a limitied degree to the structure as a whole. Since these vibrations are usually of higher frequency, the frequency assignment need not be too precise to give satisfactory heat capacity result. The skeletal vibrations, in contrast, reach into the low frequency range of acoustic vibrations. Their calculation is based on knowledge of inter- and intramolecular forces and has as yet not reached sufficient precision to match experimental heat capacity results, and are best approximated by a Tarasov two-parameter frequency distribution fitted to experimental heat capacities. The low temperature fit (0–10 K) yields the θ_3-parameter which is largely involved in low frequency, intermolecular vibrations, the intermediate temperature fit (40–200 K) yields the θ_1-parameter which is related largely to the intramolecular chain vibrations. The computer programs for the various heat capacity to θ-temperature inversion and θ-temperature to heat capacity calculations have been described earlier[8,9].

All frequencies are expressed in terms of θ-temperatures in kelvin, where $\theta = h\nu/k$ where h is Planck's constant, k, Boltzmann's constant, and ν, the frequency in hertz. (To change from Hz to K multiply by a factor of 4.799×10^{-11}, to change from wave numbers in cm^{-1} to K multiply by a factor of 1.4388).

POLYETHYLENE AND POLY(TETRAFLUOROETHYLENE)

The heat capacity of PE has been matched within experimental accuracy to the vibrational frequency spectrum. A full discussion was given earlier[6]. The same was done for PTFE[5]. *Table 1* lists the θ-temperatures used for these heat capacity calculations with the computer program described earlier[9]. It will be shown below that appropriate averages of these θ-temperatures can be formed to approximate the heat capacities of all other fluorinated polyethylenes. *Figure 1* illustrates a comparison of the cumulative frequency spectra of PE and PTFE. The group vibrations of PTFE are shifted to much lower frequency, mainly due to the higher mass of the fluorine.

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Table 1 Vibration frequencies in K for crystalline polyethylene and poly(tetrafluoroethylene)[a]

Vibration mode	N	Polyethylene[b]	Polytetrafluoroethylene[c]	
			N	
Skeletal				
Accordion and torsion	2.00	$\theta_3 = 158$ $\theta_1 = 519$	2.00	$\theta_3 = 54$ $\theta_1 = 250$
Group				
Asymmetrical stretching	1.00	4148.1	0.20	2084.8
			0.67	2071.9–1798.5
			0.13	1807.1
Symmetrical stretching	1.00	4097.7	0.17	1653.2
			0.83	1660.4–1040.2
Bending	1.00	2074.7	0.13	553.9
			0.87	553.9– 407.2
Wagging	0.35	1976.6	0.20	828.7
	0.65	1976.6–1698.3	0.20	966.9–906.4
			0.60	966.9–844.6
Twisting	0.52	1874.3	0.23	423.0
	0.48	1874.3–1689.6	0.77	415.8– 273.4
C–C-stretch	0.34	1637.5–1377.6	0.53	1984.1–1670.4
	0.31	1525.4	0.47	1768.3–1670.4
	0.35	1525.4–1377.6		
Rocking	0.04	1494.1	0.27	1086.3
	0.59	1494.1–1038.0	0.73	746.7– 441.7
	0.37	1079.1		

[a] Calculated per mole of CH_2– or CF_2–. θ_3 and θ_1 are the maximum frequencies of a Tarasov treatment, used to approximate the skeletal vibrations. Single frequencies (θ_E) are to be converted with Einstein functions to heat capacities. Ranges correspond to approximately linear portions of the frequency dispersion curve and are converted to a box-type distribution function (θ_U and θ_L). For detailed functions for the calculations of heat capacity from θ_E, θ_U and θ_L see ref. 9

[b] Frequency curve as critically evaluated by Barnes, J. and Fanconi, B. *J. Phys. Chem. Ref. Data* 1978, **7**, 309

[c] Frequency curve as calculated by Hannon, M. J., Boerio, F. J. and Koenig, J. L. *J. Chem. Phys.* 1969, **50**, 2829

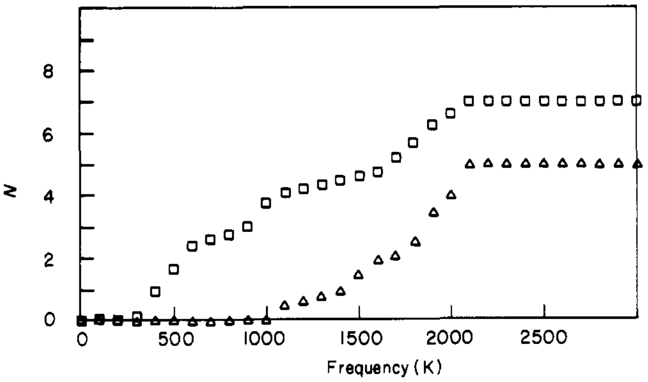

Figure 1 Cumulative spectra of the group vibrations of polyethylene (△) and polytetrafluoroethylene (□). The two C–H-stretching vibrations of polyethylene occur outside the range of the graph (see *Table 1*). Normalized to 1 backbone atom (2 skeletal and 7 group vibrations). Abscissa frequency in K

POLY(VINYLIDENE FLUORIDE)

The vibrational spectrum of crystals of poly(vinylidene fluoride) (PVF2) has been calculated for both the head to tail and the head to head configurations[10–14]. *Table 2* contains a listing of their group vibrations. The dispersion curves were broken into linear segments, approximated by box-distributions, characterized by their upper and lower θ-temperatures (θ_U and θ_L), and horizontal segments, approximated by average single frequencies (Einstein terms θ_E). The cumulative frequency spectra are shown in *Figure 2*. The corresponding heat capacities are compared in *Figure 3* (curve A). Above 200 K the larger number of low frequency vibrations of the CF_2-twisting mode of the head to tail configuration causes the steep increase in heat capacity difference in *Figure 3*. At 100 K the heat capacity contribution of the group vibrations is, however, so small, that the 75% error in group vibration contribution reduces to 6% error in the total heat capacity. These larger deviations at low temperatures are thus not important for the discussion of heat capacity as a whole, either frequency distribution can be used for the calculation. In addition, some of the discrepancies are compensated for by fitting of the skeletal vibration contributions to the experimental heat capacities.

The next stage in our analysis is a comparison of the calculated head to tail PVF2 frequency spectrum of *Table 2* with the average of the PE and PTFE spectra of *Table 1*. The cumulative spectra are compared in *Figure 4* and the corresponding heat capacities, in curve B of *Figure 3*. Although the differences are somewhat larger than in the head-to-tail head-to-head comparison, the error, when calculated in percent of total heat capacity, is less than ±5%, which is the usual precision expected for a heat capacity addition scheme.

With reasonable approximations of the group vibrations, θ_1 and θ_3-values for the Tarasov function of skeletal vibrations were computed next by fitting to the experimental heat capacities, as outlined in refs. 8 and 9 (THETA3 and THETA-TAR-EB programs). *Table 3* shows the results. Based on the lowest temperature heat capacities, a Debye θ-temperature (θ_D) of 114.2 K was derived. The value of θ_D decreases continuously and reached this constant value only at about 3 K. The values chosen for further calculations were $\theta_1 = 346 \pm 5$ K and $\theta_3 = 65.6 \pm 0.5$ K for both configurations which cover the data from about 18 to about 180 K. This is an improvement over the preliminary data which were derived without subtraction of the group vibrations[8] and gave a θ_1 of 330 ± 23 K and a θ_3 of 73 ± 3 K and a θ_D of 120 K for the fitting range of 25 to 80 K. Using the average PE+PTFE spectrum of *Table 1* for the group vibration subtraction leads to a somewhat poorer fit at higher temperature, but it will be shown below that these data are still acceptable for heat capacity calculations.

Table 2 Group vibration frequencies in K for crystalline poly(vinylidene fluoride)[a]

Vibration mode	N	Head to tail	N	Head to head
CH_2 asymmetrical stretching	1.00	4358	1.00	4300.6
			1.00	4294.8
CH_2 symmetrical stretching	1.00	4288	1.00	4281.9
			1.00	4271.8
CH_2 bending	0.12	2047	1.00	2109.3 2117.9
	0.25	2047 2114	0.60	2061.8–2073.3
	0.13	2114	0.25	1938.1–2061.8
	0.25	2003 2114	0.15	1938.1
	0.25	2003		
CH_2 wagging	0.48	2009	1.00	1905.0 1979.8
	0.11	1986 2009	0.07	1917.9
	0.11	1986	0.08	1917.9–1935.2
	0.20	1904 1986	0.21	1935.2–2058.9
	0.10	1878 1904	0.26	2058.9–2081.9
			0.38	2058.9
CH_2 twisting	0.67	1384–1414	0.64	1493.5
	0.33	1332–1384	0.36	1493.5–1519.4
			1.00	1356.8
CH_2– rocking	0.38	1151–1187	1.00	1271.9
	0.25	1151	0.50	1520.8–1533.8
	0.37	1151–1177	0.50	1520.8–1525.1
CF_2– asymmetrical stretching	0.40	1850–1978	1.00	1900.7
	0.15	1978–1986	0.33	1791.3–1828.7
	0.10	1952–1986	0.34	1828.7
	0.25	1764–1952	0.33	1791.3–1828.7
	0.10	1732–1764		
CF_2– symmetrical stretching	0.10	1701–1727	0.52	1710.7–1860.4
	0.25	1727–1895	0.48	1682.0–1860.4
	0.10	1895–1928	0.52	1651.7–1690.6
	0.13	1914–1928	0.48	1670.4–1690.6
	0.32	1760–1914		
	0.10	1727–1760		
CF_2– bending	0.06	731	1.00	848.9
	0.16	731– 772	0.40	733.8
	0.65	772–1167	0.32	733.8– 755.4
	0.13	1167 1209	0.28	748.2
CF_2– wagging	0.09	676	0.31	946.7– 981.3
	0.44	676– 717	0.69	946.7–1066.2
	0.37	717– 780	0.25	440.3
	0.10	780	0.54	440.3– 519.4
			0.21	519.4
CF_2– twisting	0.21	377	0.67	543.9– 624.4
	0.29	377– 432	0.33	543.9
	0.41	432– 574	0.36	461.9
	0.09	574	0.64	461.9– 506.5
CF_2– rocking	0.62	575– 637	0.52	733.8– 756.8
	0.38	575	0.48	733.8 774.1
			0.50	543.9– 558.3
			0.50	558.3– 624.4
C–C– asymmetrical stretching	0.13	1532	0.20	1479.1–1493.5
	0.44	1532–1591	0.80	1493.5
	0.43	1568–1591	1.00	1395.6
C–C– symmetrical stretching	0.90	1217–1265	0.80	1202.3–1389.9
	0.10	1265	0.20	1202.8
			0.43	1151.0–1202.8
			0.57	1226.6 1151.0

[a] Calculated per mole of(CH_2–CF_2–) for the head to tail, and per mole of(CH_2–CF_2–CF_2–CH_2–) for the head to head polymer. Single frequencies (θ_E) are to be converted with Einstein functions to heat capacities and correspond to an average over a narrow range of frequencies. Ranges of frequency correspond to approximately linear portions of the frequency dispersion curve and are converted to a box-type distribution function (θ_U and θ_L). For detailed functions for the calculation of heat capacities from θ_E, θ_U and θ_L see ref. 9. Frequency dispersion as calculated in refs. 13 and 14

The θ-values were next converted to heat capacities C_v in the standard intervals of the data bank (see *Table 5*, below) and plotted together with the experimental values of C_p in *Figure 5*. The computation program CVTOT was used for this calculation[9].

The final step of the computation was the conversion of the C_v-values to C_p. To do so, we used the Nernst–Lindemann equation

$$C_p - C_v = A_o C_p^2 (T/T_m) \quad (1)$$

with a value of A_o of 0.937×10^{-3} K mol J^{-1} and a T_m of 483 K. The A_o-value is taken from a compilation of data based on experimental results on compressibility and expansivity, fitted to the Nernst–Lindemann equation[15]. A plot of the differences between experimental and calculated heat capacities C_p is shown in *Figure 6*. With the exception of the 5–10 K temperature range (in which the deviations are 10–15%, but absolute C_p's are small), the typical difference between experimental and calculated values is less than ±2.5%. At higher temperatures (above 200 K), the deviations become somewhat larger, but in this temperature range the glass

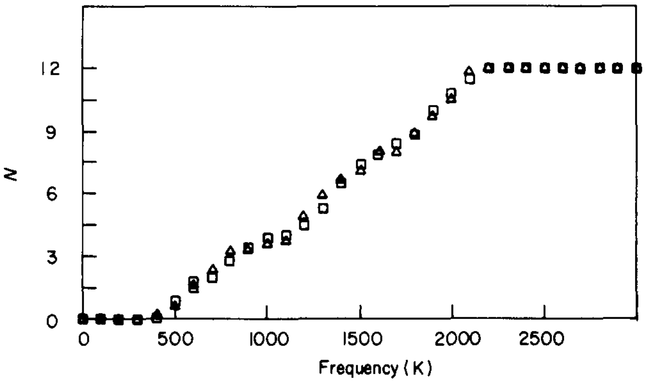

Figure 2 Cumulative group vibration frequency spectra of head to head (□) and head to tail (△) poly(vinylidene fluoride). The two CH-stretching vibrations of the CH_2– group occur outside the range of the graph (see *Table 2*). Normalized to one repeating unit CH_2–CF_2– (4 skeletal and 14 group vibrations). Abscissa frequency in K

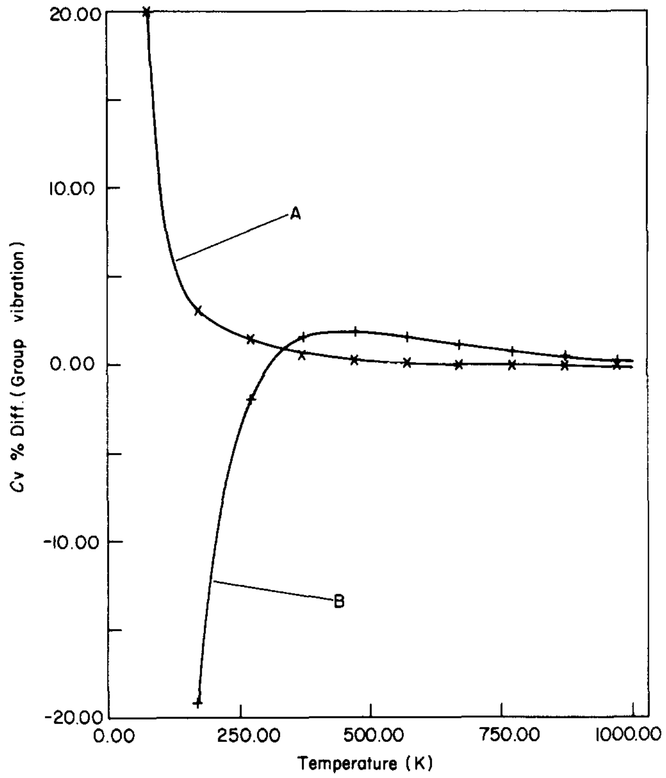

Figure 3 Comparison of heat capacity contributions of group vibrations of poly(vinylidene fluoride). Curve A: C_V (head to tail) – C_V (head to head). Curve B: C_V (PVF_2 head to tail) – C_V (PE + PTFE)

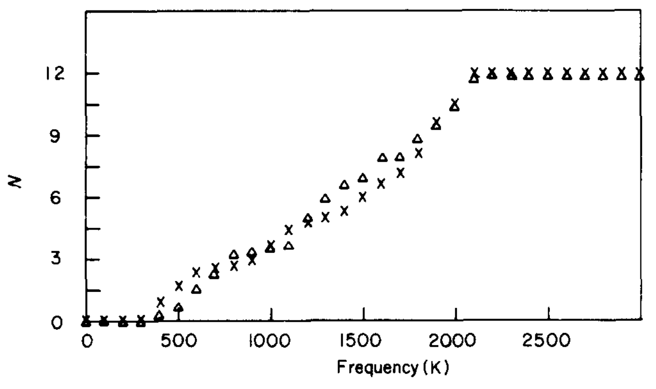

Figure 4 Cumulative group vibration frequency spectra of the polyethylene-polytetrafluoroethylene average (×) and poly(vinylidene fluoride) (△) head to tail calculation. The two CH– stretching vibrations of the CH_2-group occur outside the range of the graph (see *Tables 1* and *2*). Normalized to one repeating unit CH_2–CF_2– (4 skeletal and 14 group vibrations). Abscissa frequency in K

transition is approached (about 233 K) and since all experimental data are based on semicrystalline data, such positive deviation is expected.

POLY(VINYL FLUORIDE)

The derivation of a suitable frequency spectrum for poly(vinyl fluoride) (PVF) to compute the heat capacity contributions of the group vibrations is somewhat more involved since no dispersion curves have been published. We derived an approximation by adjusting the known frequency spectrum of (PVC)[16] according to the frequency ratios of the experimental i.r. and Raman frequencies[17] which are known for both the chloride and fluoride. The nine normal stretching and bending modes of CH_2– and CH– are practically identical for PVC and PVF. The two C–C stretching modes change close to the ratio of their inverse square root reduced masses. The C–F stretching mode is much higher in frequency than could

Table 3 Tarasov theta-temperatures for poly(vinylidene fluoride) using various ranges of fit[a]

Group vibrations	θ_1	θ_3	Temperature range (K)
1. Average of PE and	346.8± 6	66.5±0.5	18–40
PTFE (see	379.9±30	62.8±3	16–130
Table 1)	385.5±29	62.3±3	14–180
2. Head to tail	346.0± 5	65.6±0.5	18–40
	344.5± 9	65.8±1	18–130
	347.0±13	65.5±1.2	16–180
3. Head to head	345.9± 5	65.6±0.5	18–40
	344.5± 6	65.4±0.6	18–70
	342.5±17	66.0±1.6	16–130

[a] All calculations based on four skeletal vibration per CH_2–CF_2– repeating unit using a Debye theta temperature of 114.2 K fitted at 3 K

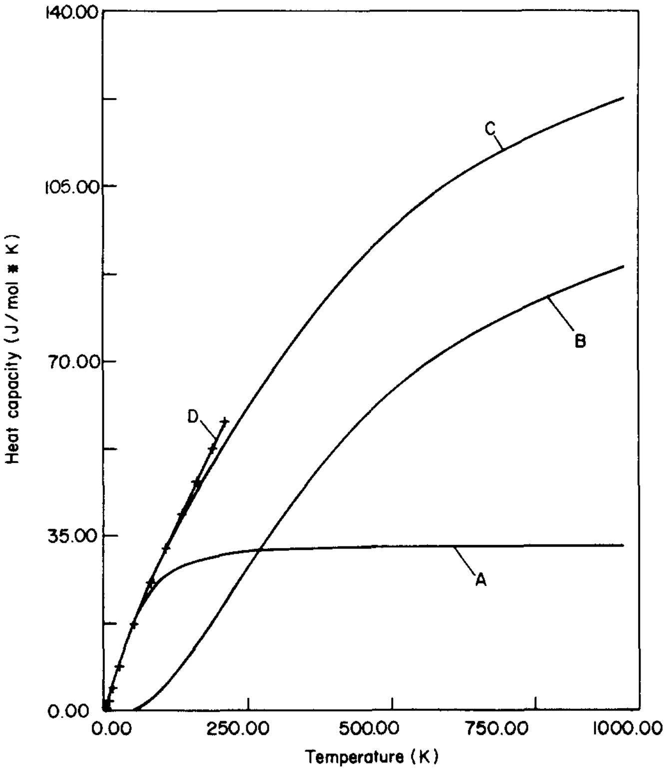

Figure 5 Heat capacity of poly(vinylidene fluoride). Calculated curves of C_V. Curve A: skeletal vibration contribution, Tarasov treatment ($\theta_3 = 65.6$ K, $\theta_1 = 346$ K). Curve B: group vibrations contribution head to tail, *Table 2*). Curve C: sum of curves A and B. Curve D: experimental data of the ATHAS data bank of C_p

be derived from the reduced mass, indicative of the higher binding energy of C–F (force constant). The two C–F bending modes are, in turn, not much different from those in C–Cl, their frequencies are, however, so low that they couple largely with the skeletal modes, which may obscure the effect of the lower mass, shorter bond length, and stronger bonding in C–F. In *Table 4* this approximate frequency spectrum is listed.

In *Figure 7* a comparison of this frequency spectrum with two averages is given. One comparison shown by the symbol (×) was obtained by adding the polyethylene spectrum of *Table 1* for 3/2 chain atoms to the PTFE spectrum of *Table 1* for 1/2 chain atom. The other comparison shown by the symbol (+) was obtained by adding the polyethylene spectrum of *Table 1* for 1 chain atom to the head to tail PVF2 spectrum of *Table 2* for 1 chain atom. The differences of the heat capacity contributions of these two averages to the spectrum of *Table 4* are shown in *Figure 8*. The agreement between the three spectra is, as expected, not as good as in the poly(vinylidene fluoride) case because of the difference in structure. The group vibrations of CH_2–CF_2– are better approximated by CH_2–+CF_2–, than CHF– is approximated by 1/2 CH_2–+1/2 CF_2–. The 2 to 5% lower heat capacity in the 1000 to 500 K range is caused by the lower frequencies for the C–H and C–F bending vibrations of CH_2–CHF– in the 1500 K range. The large maximum of curve A in *Figure 8* can be linked to the lower frequency limit of the CF_2 twisting vibrations in PTFE relative to PVF2 and PVF. Below 250 K, where the error reaches more than 10%, the absolute contribution of the group vibrations to the heat capacity is again small enough so

Table 4 Group vibration frequencies in K for crystalline poly(vinyl fluoride)[a]

Vibration mode	N	Frequency
CH stretching	1	4284.7
CH_2 asymmetrical stretch	1	4258.8
CH_2 symmetrical stretch	1	4189.8
CH_2 bending	1	2020.1
CH_2 wagging	0.34	2053.2
	0.16	2038.8–2053.2
	0.5	1951.0–2038.8
CH_2 twisting	0.5	1870.4–1907.8
	0.2	1863.2–1870.4
	0.3	1863.2–1907.8
CH_2 rocking	0.11	1404.3–1415.8
	0.39	1286.3–1404.3
	0.17	1204.3–1217.2
	0.33	1217.2–1286.3
CH bending	0.29	1808.6
	0.21	1784.1–1808.6
	0.27	1735.2–1784.1
	0.23	1709.3–1735.2
CH wagging	0.5	1682.0–1693.5
	0.5	1670.4–1682.0
CF stretching	0.5	1561.1–1582.7
	0.16	1553.9–1568.3
	0.12	1539.5–1553.9
	0.22	1561.1–1568.9
CF bending	0.28	810.0– 834.5
	0.12	818.7– 834.5
	0.10	768.3– 818.7
	0.29	503.6– 768.3
	0.21	503.6
CF wagging	0.09	648.9– 664.7
	0.24	546.7– 648.9
	0.17	518.0– 546.7
	0.12	493.5– 518.0
	0.09	456.1– 493.5
	0.29	440.3– 456.1
C–C asymmetrical stretch	0.79	1812.9–1856.1
	0.21	1856.1
C–C symmetrical stretch	0.08	1697.8–1705.0
	0.25	1625.8–1697.8
	0.17	1597.1–1625.8
	0.08	1644.5–1650.3
	0.29	1597.1–1644.5
	0.13	1597.1

[a] Calculated per mole of (CH_2–CHF–). Single frequencies (θ_E) are to be converted with Einstein functions to heat capacities and correspond to an average over a narrow range of frequencies. Ranges of frequency correspond to approximately linear portions of the frequency dispersion curves and are converted to a box type distribution function (θ_U and θ_L). For detailed functions for the calculation of heat capacities for θ_E, θ_U and θ_L see ref. 9

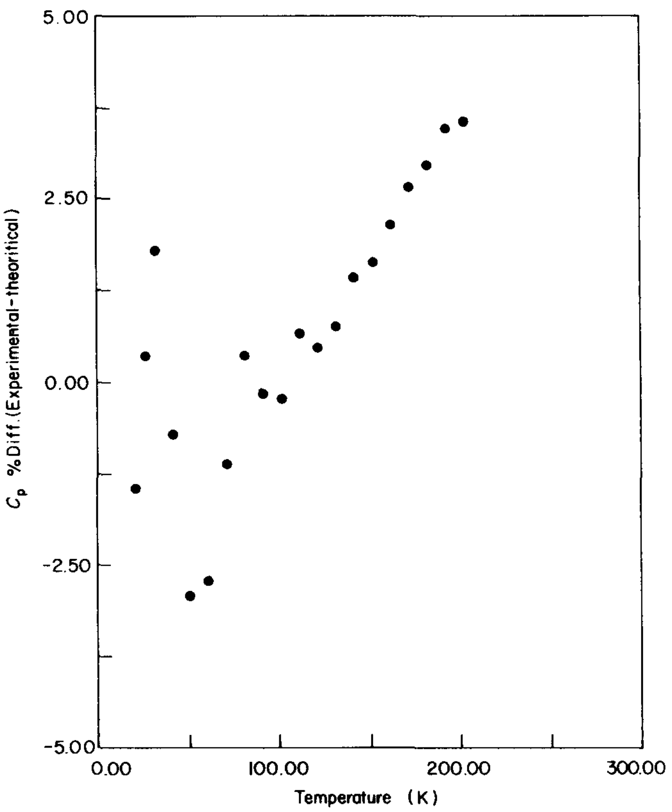

Figure 6 Heat capacity difference C_p (experimental)—C_p (calculated) of poly(vinylidene fluoride) in % as a function of temperature. See *Figure 5* for calculation parameters, $A_0 = 0.937 \times 10^{-3}$ K mol J^{-1}, $T_m = 482$ in equation (1)

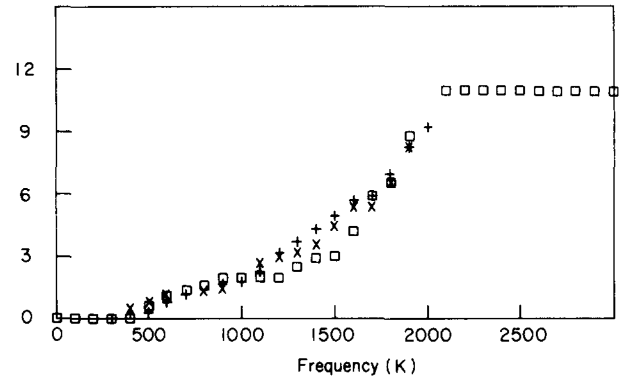

Figure 7 Cumulative group frequency spectra for poly(vinyl fluoride). The three CH– stretching vibrations of the CH_2 and the CH– groups occur outside the range of the graph (see *Table 4*). (□): spectrum of *Table 4*; (×): average of 3/2 polyethylene and 1/2 polytetrafluoroethylene; (+): Average of polyethylene and poly(vinylidene fluoride). Normalized to one repeating unit CH_2–CHF– (4 skeletal and 14 group vibrations)

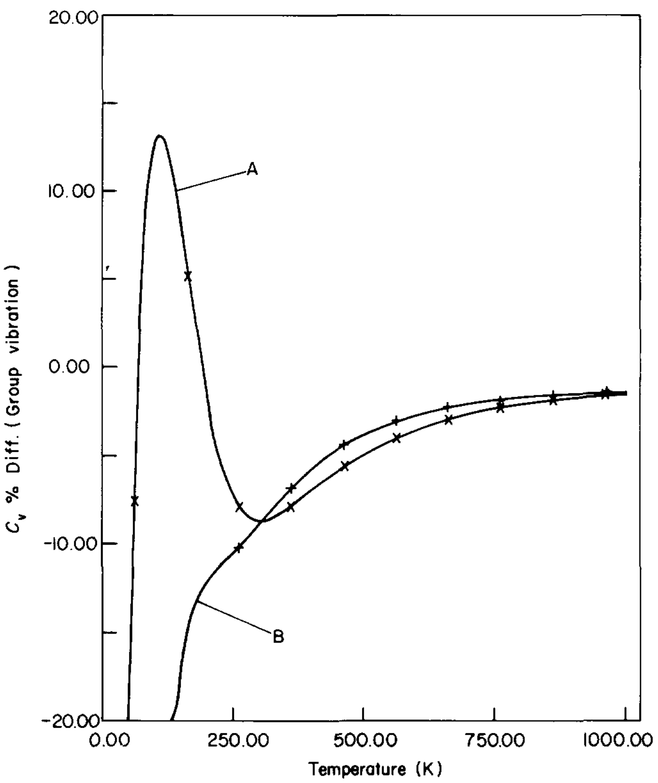

Figure 8 Comparison of poly(vinyl fluoride) Curve A: C_v (PVF)−C_v (3/2PE+1/2PTFE); Curve B: C_v (PVF)−C_v (PE+PVF2)

that the error in total heat capacity is not serious. In addition, some of these deviations will be compensated by the fit of the contribution of the skeletal vibrations to the experimental data adjusted by the group vibration contributions.

The experimental heat capacities of the data bank[3] were now treated as in the PVF2 case, above. θ_D had to be estimated using the argument of Lee and Choy[18] ($\theta_D = 170$ K) based on sound velocity measurements since the heat capacity measurements reach only down to 80 K. Assuming the various models, θ_3 and θ_1-values of 105 and 440 K were derived fitting the Tarasov equation to the measured heat capacities reduced by the group vibration contributions. These values agree well with the earlier data of Lee and Choy[18] ($\theta_3 = 110$ K, $\theta_1 = 430$ K).

All three approximations of the frequency spectrum gave approximately the same fit of the experimental heat capacity. The computed data of C_v are given in *Table 5*, below, and are plotted in *Figure 9* (CVTOT program). The C_v to C_p conversion was made using equation (1) with a value[19] of 1.00×10^{-3} K mol J^{-1} and a T_m of 503 K. *Figure 10* shows the percent deviation of the experiment from the calculation. Over practically the whole range of measurement the deviation is less than ±2.5%. Above 200 K the approach to the glass transition (314 K) makes, again, the experimental heat capacity increase above the calculated values.

Table 5 Calculated heat capacity at constant volume in J/(K mol of repeating unit)

	PTFE[a]	PVF3[b]	PVF2[c]	PVF[d]	PE[e]
θ_1 (K)	250	315	346	440	519
θ_3 (K)	54	56	66	105	158
A_0(K mol J^{-1})	4.86 E−3	4.86E−3	3.75E−3	3.00E−3	4.86E−3
m_F	1.000	0.750	0.500	0.250	0.000
T (K)					
1	0.3555E−2	0.2624E−2	0.1741E−2	0.5343E−2	0.2000E−3
2	0.2844E−1	0.2099E−1	0.1392E−1	0.4274E−2	0.1600E−2
3	0.9598E−1	0.7083E−1	0.4700E−1	0.1442E−1	0.5401E−2
4	0.2271	0.1677	0.1114	0.3419E−1	0.1280E−1
5	0.4392	0.3250	0.2171	0.6678E−1	0.2500E−1
10	0.2578E+1	0.1967E+1	0.1470E+1	0.5266	0.2000
20	0.7880E+1	0.6190E+1	0.5325E+1	0.3017E+1	0.1482E+1
30	0.1262E+2	0.1003E+2	0.8932E+1	0.6098E+1	0.3824E+1
40	0.1695E+2	0.1367E+2	0.1227E+2	0.9022E+1	0.6446E+1
50	0.2096E+2	0.1721E+2	0.1542E+2	0.1177E+2	0.8998E+1
60	0.2479E+2	0.2065E+2	0.1834E+2	0.1441E+2	0.1140E+2
70	0.2853E+2	0.2397E+2	0.2107E+2	0.1693E+2	0.1363E+2
80	0.3221E+2	0.2718E+2	0.2362E+2	0.1933E+2	0.1567E+2
90	0.3583E+2	0.3026E+2	0.2603E+2	0.2160E+2	0.1753E+2
100	0.3935E+2	0.3322E+2	0.2831E+2	0.2372E+2	0.1920E+2
110	0.4276E+2	0.3605E+2	0.3049E+2	0.2570E+2	0.2070E+2
120	0.4604E+2	0.3876E+2	0.3259E+2	0.2753E+2	0.2205E+2
130	0.4919E+2	0.4135E+2	0.3462E+2	0.2924E+2	0.2329E+2
140	0.5220E+2	0.4383E+2	0.3659E+2	0.3082E+2	0.2443E+2
150	0.5507E+2	0.4622E+2	0.3851E+2	0.3231E+2	0.2551E+2
160	0.5782E+2	0.4851E+2	0.4038E+2	0.3371E+2	0.2654E+2
170	0.6045E+2	0.5073E+2	0.4222E+2	0.3505E+2	0.2754E+2
180	0.6296E+2	0.5288E+2	0.4403E+2	0.3634E+2	0.2854E+2
190	0.6537E+2	0.5497E+2	0.4582E+2	0.3760E+2	0.2954E+2
200	0.6768E+2	0.5700E+2	0.4759E+2	0.3884E+2	0.3055E+2
210	0.6990E+2	0.5898E+2	0.4934E+2	0.4007E+2	0.3159E+2
220	0.7203E+2	0.6093E+2	0.5107E+2	0.4130E+2	0.3266E+2
230	0.7410E+2	0.6283E+2	0.5279E+2	0.4253E+2	0.3376E+2
240	0.7610E+2	0.6470E+2	0.5450E+2	0.4378E+2	0.3489E+2
250	0.7803E+2	0.6654E+2	0.5619E+2	0.4505E+2	0.3505E+2

Table 5 (Continued)

	PTFE[a]	PVF3[b]	PVF2[c]	PVF[d]	PE[e]
θ_1 (K)	250	315	346	440	519
θ_3 (K)	54	56	66	105	158
A_0 (K mol J^{-1})	4.86E−3	4.86E−3	3.75E−3	3.00E−3	4.86E−3
m_F	1.000	0.750	0.500	0.250	0.000
260	0.7991E+2	0.6834E+2	0.5787E+2	0.4633E+2	0.3724E+2
270	0.8173E+2	0.7012E+2	0.5954E+2	0.4763E+2	0.3847E+2
280	0.8350E+2	0.7186E+2	0.6118E+2	0.4894E+2	0.3972E+2
290	0.8522E+2	0.7358E+2	0.6281E+2	0.5027E+2	0.4100E+2
300	0.8690E+2	0.7527E+2	0.6442E+2	0.5161E+2	0.4229E+2
310	0.8853E+2	0.7693E+2	0.6601E+2	0.5297E+2	0.4361E+2
320	0.9012E+2	0.7856E+2	0.6758E+2	0.5433E+2	0.4494E+2
330	0.9166E+2	0.8016E+2	0.6913E+2	0.5569E+2	0.4628E+2
340	0.9317E+2	0.8174E+2	0.7064E+2	0.5706E+2	0.4762E+2
350	0.9464E+2	0.8328E+2	0.7214E+2	0.5842E+2	0.4897E+2
360	0.9607E+2	0.8479E+2	0.7360E+2	0.5979E+2	0.5032E+2
370	0.9746E+2	0.8627E+2	0.7504E+2	0.6114E+2	0.5167E+2
380	0.9881E+2	0.8772E+2	0.7646E+2	0.6249E+2	0.5301E+2
390	0.1001E+3	0.8914E+2	0.7784E+2	0.6383E+2	0.5435E+2
400	0.1014E+3	0.9053E+2	0.7919E+2	0.6515E+2	0.5568E+2
410	0.1026E+3	0.9188E+2	0.8051E+2	0.6646E+2	0.5699E+2
420	0.1039E+3	0.9321E+2	0.8181E+2	0.6776E+2	0.5830E+2
430	0.1050E+3	0.9450E+2	0.8308E+2	0.6904E+2	0.5959E+2
440	0.1062E+3	0.9576E+2	0.8431E+2	0.7030E+2	0.6087E+2
450	0.1073E+3	0.9699E+2	0.8552E+2	0.7154E+2	0.6213E+2
460	0.1084E+3	0.9819E+2	0.8670E+2	0.7277E+2	0.6337E+2
470	0.1094E+3	0.9936E+2	0.8785E+2	0.7397E+2	0.6460E+2
480	0.1104E+3	0.1005E+3	0.8897E+2	0.7515E+2	0.6581E+2
490	0.1114E+3	0.1016E+3	0.9007E+2	0.7632E+2	0.6701E+2
500	0.1124E+3	0.1027E+3	0.9114E+2	0.7746E+2	0.6818E+2
510	0.1133E+3	0.1038E+3	0.9218E+2	0.7858E+2	0.6934E+2
520	0.1142E+3	0.1048E+3	0.9320E+2	0.7968E+2	0.7084E+2
530	0.1151E+3	0.1058E+3	0.9419E+2	0.8076E+2	0.7160E+2
540	0.1159E+3	0.1068E+3	0.9516E+2	0.8183E+2	0.7270E+2
550	0.1167E+3	0.1077E+3	0.9610E+2	0.8287E+2	0.7379E+2
560	0.1175E+3	0.1086E+3	0.9702E+2	0.8389E+2	0.7485E+2
570	0.1183E+3	0.1095E+3	0.9792E+2	0.8489E+2	0.7590E+2
580	0.1190E+3	0.1104E+3	0.9880E+2	0.8587E+2	0.7694E+2
590	0.1197E+3	0.1113E+3	0.9966E+2	0.8683E+2	0.7795E+2
600	0.1206E+3	0.1121E+3	0.1005E+3	0.8778E+2	0.7895E+2

[a] Poly(tetrafluoroethylene), 2 chain atoms
[b] Pol(trifluoroethylene)
[c] Poly(vinylidene fluoride)
[d] Poly(vinyl fluoride)
[e] Polyethylene, 2 chain atoms

POLYTRIFLUOROETHYLENE

PVF3 is the test for the additivity suggested in this treatment. No detailed vibration analysis, nor i.r. or Raman data interpretations are available. The data bank lists heat capacities from 25–304 K, the glass transition temperature. Using the group vibration spectrum of PTFE (*Table 1*) for 1 chain atom and head to tail PVF2 (*Table 2*) for 1 chain atom as an approximation, θ_3 and θ_1 values were found as before ($\theta_3 = 56$ K, $\theta_1 = 315$ K). The value of θ_3 is identical to the one derived earlier by Lee and Choy[18] from sound velocity data. *Figure 11* shows the various contributions to C_v and their fit to the experimental data. *Table 5* shows all C_v values in the standard steps of the data bank. The difference between calculation and experiment is shown in *Figure 12*. The heat capacity at constant pressure for this comparison was calculated using the universal value for A_0 of equation (1) (0.972×10^{-3} K mol J^{-1}). Again, the deviation over most of the temperature range is not more than ±2.5%. A somewhat larger deviation in the 25–50 K temperature range was suggested already by Lee and Choy to be due to experimental error[18].

DISCUSSION

The direct comparison of the cumulative frequency spectra of the head to tail and head to head configurations of PVF2 in *Figure 2* shows only minor differences. The heat capacity difference derived from these group vibrations of the two geometric isomers is, at temperatures above 250 K, even less significant (curve A, *Figure 3*). Similar observations have been made before for the changes of heat capacities with conformation; glasses and crystals have above 50 K commonly close to the same heat capacity. This is best documented by the results of the data bank[2,3]. The larger deviations in C_p caused by the group vibrations at lower temperature are not significant for the overall heat capacity contribution since the skeletal vibration contribution is overwhelming at low

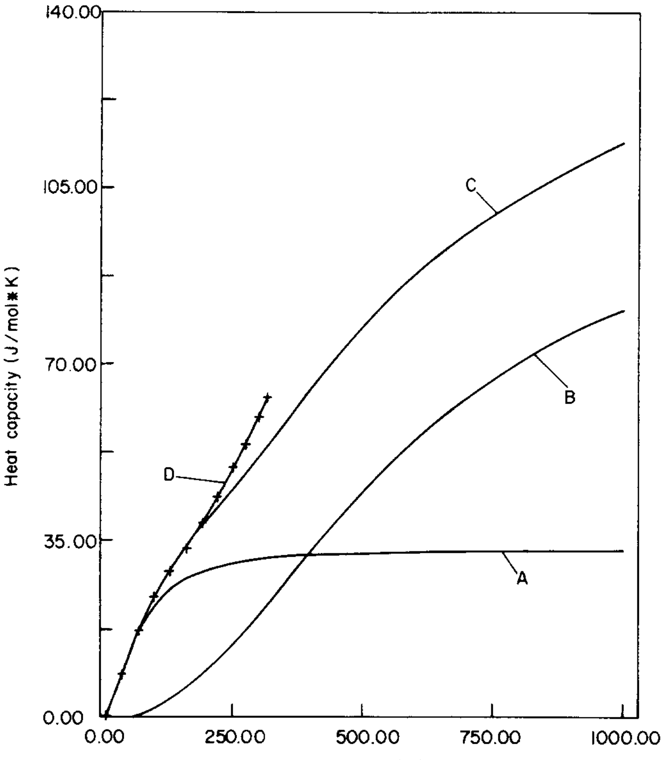

Figure 9 Heat capacity of poly(vinyl fluoride). Calculated curves of C_v. Curve A: skeletal vibration contribution. Tarasov treatment ($\theta_3=105$ K, $\theta_1=440$ K). Curve B: group vibration contribution (as given in *Table 4*). Curve C: sum of curves A and B. Curve D: experimental data of the ATHAS data bank of C_p

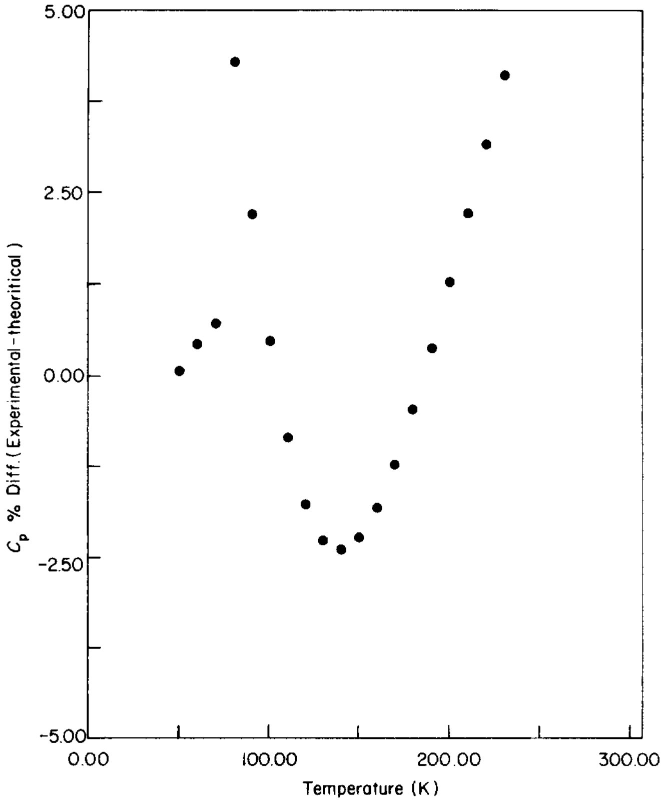

Figure 10 Heat capacity difference C_p (experimental) – C_p (calculated) of poly(vinyl fluoride) in % as a function of temperature. $A_0=1.00\times10^{-3}$ K mol J^{-1}, $T_m=503$ K in equation 1

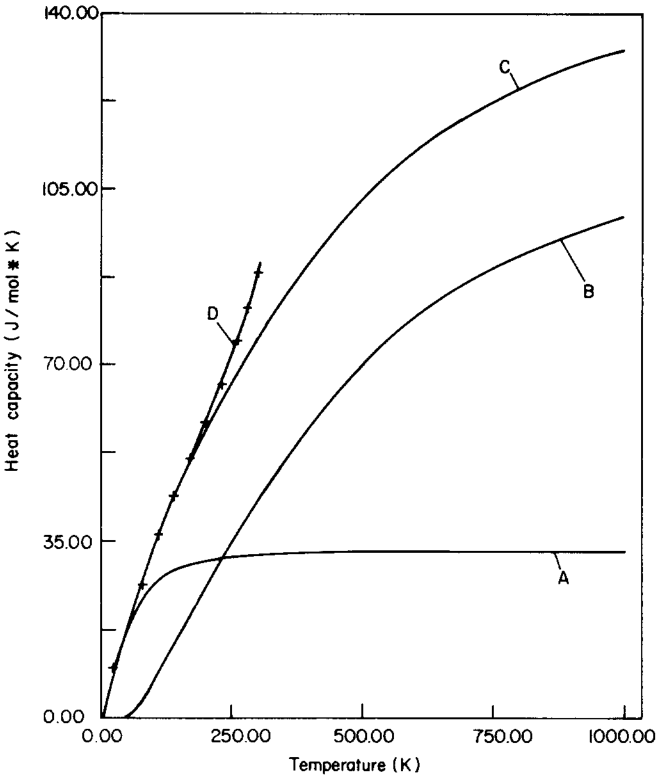

Figure 11 Heat capacity of polytrifluoroethylene. Calculated curves of C_v. Curve A: skeletal vibration contribution, Tarasov treatment ($\theta_3=56$ K, $\theta_1=315$ K). Curve B: group vibration contribution (appropriate average of data of *Table 1*). Curve C: sum of curves A and B. Curve D: experimental data of the ATHAS data bank of C_p

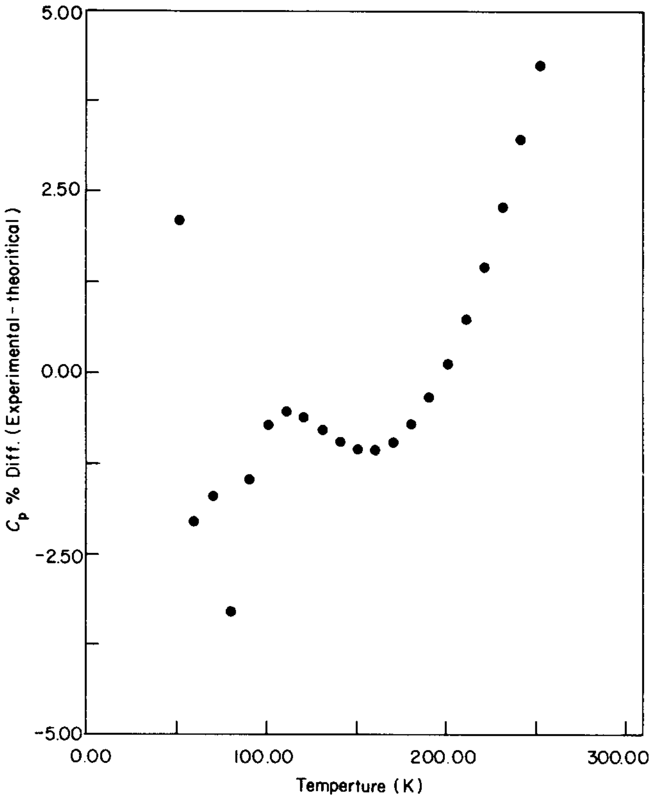

Figure 12 Heat capacity difference C_p (experimental) – C_p (calculated) polytrifluoroethylene in % as a function of temperature. $A_0=0.972\times10^{-3}$ K mol J^{-1} (universal value). $T_m=468$ K in equation 1

Table 6 Constants for heat capacities of fluoropolymers

Polymer	θ_1 (K)	θ_3 (K)	M	$\theta_1 \times M^{1/2}$	$A_0 \times 10^3$	$A'_0 \times 10^{3\,b}$
Polyethylene	519	158[c]	28	2752	4.86	2.43
Poly(vinyl fluoride)	440	105	46	2984	3.00	1.00
Poly(vinylidene fluoride)	346	66	64	2768	3.75	0.937
Polytrifluoroethylene	315	56	82	2852	(4.86)	(0.972)
Polytetrafluoroethylene	250	54	100	2500	4.86	0.810

[a] Per heavy atom, i.e. 2 for CH_2CH_2– and 6 for CF_2–CF_2–

[b] Per repeating unit of two chain atoms in K mol J^{-1}

[c] Value extrapolated to 100% crystallinity. Amorphous polyethylene has a θ_3 of 80 K. All other values of θ_3 are semicrystalline polymers, with PTFE being highest in crystallinity

temperature (see *Figures 5, 9* and *11*) and reduces the error (compare *Figures 6, 10* and *12*).

The comparison of the various approximations of cumulative frequency spectra by the use of the PE and PTFE spectra in *Figure 1* and PVF2 spectrum in *Figure 4* show that there are significant differences in terms of frequency (*Figures 4* and 7). The major determining factors of frequencies, mass, M, and force constant, F, are even in simple vibrations not linearly additive, but involve $\sqrt{F/M}$. For the more complicated, coupled systems discussed here, there are no simple predictions possible. The more different the molecular structure, the poorer is the averaged spectrum. The error in approximating CHF– by the average of CH_2 and CF_2 is much larger than the error in approximating CH_2–CF_2 by the average of CH_2–CH_2 and CF_2–CF_2 (compare *Figures 4* and 7). In terms of heat capacities the discrepancies in the cumulative group vibration spectrum are serious only in the temperature range below 200 K (see *Figures 3* and *8*). In this temperature region the total heat capacity is, however, dominated by the skeletal vibrations as shown in *Figures 5, 9* and *11*. The overall error in using the rather crude frequency approximations is thus acceptable (compare *Figures 6* and *10* with *Figure 12*).

The increasing sensitivity of heat capacity to changes in the frequency at low temperature is also a major factor in the discussion of the Tarasov θ_1 and θ_3 temperatures. *Table 6* contains a listing of all θ_1 and θ_3 temperatures. The intramolecular skeletal vibrations are dominant for θ_1. Column 5 of *Table 6* indicates that the θ_1 values are close to proportional to the inverse square root of mass, an observation made earlier[8,18,20]. The influence of substitution on the force constants of the C–C backbone bond seems minor. Similarly, changes in crystallinity have only little influence on θ_1.

Effects of the changes in macromolecular structure on θ_3 are not as easily assessed. The cohesive energy density decreases from 8.4 kJ mol^{-1} for polyethylene to 6.7 kJ mol^{-1} for PTFE[21], in line with a decreasing θ_3, but the decrease is not continuous through the intermediate degrees of fluorination (according to the usual calculation schemes[21]). The influence of the mass alone also does not give a full explanation in the trend of θ_3. The influence of crystallinity, which changes θ_3 of PE almost by a factor of two, is a most likely parameter important for the remaining variation. Unfortunately the samples for low temperature heat capacity measurements were not well characterized relative to crystallinity. The low temperature heat capacities up to about 50 K are thus the least understood and in need of further experimental input.

A final remark concerns the glass transitions of the partially crystalline polymers. In all cases (including PE[22] and PTFE[23]) is there a small increase in heat capacity some 60 or more kelvin below T_g (see *Figures 6, 10* and *12*). Some of this increase is perhaps the result of an imperfect C_v to C_p conversion (see *Figures 5, 9* and *11*), but it seems likely that all these macromolecules have a glass transition reaching to much lower temperature than previously assumed.

ADDITION SCHEME

Because of the overall trend in heat capacity of fluorinated PE's, it may be possible to calculate intermediate degrees of fluorination by empirical interpolation of the data in *Table 5* and the corresponding data of PE[2,6] and PTFE[5]. A major discussion of this type of empirical addition scheme is being developed in our laboratory for all carbon-backbone polymers. For the fluorinated PE's a more precise prediction scheme can be developed similar to the prior scheme for polyoxides[6]. In this addition scheme we make use of the above documented approximate additivity of group vibrations using the data of PE and PTFE in *Table 1*. The skeletal heat capacity contribution is next found by fitting θ_3 and θ_1 values of *Table 6* in K into the following functions of m, the mole fraction of fluorine replacing hydrogen:

$$\theta_3(m) = 150.63m^2 - 253.43m + 157.95 \qquad (2)$$

$$\theta_1(m) = 106.29m^2 - 372.29m + 520.49 \qquad (3)$$

The standard deviation of equation (2) is ±2.4 K and of equation (3), ±11 K. With these values C_v for any concentration of fluorine can be approximated. Also, the heat capacity can be extended beyond the glass transition which is of importance for the discussion of the thermal properties of partially crystalline macromolecules, an ongoing project in our laboratory. Besides for homopolymers and copolymers, one would expect that this calculation scheme would also be applicable to blends.

To convert C_v to C_p, equation (1) is to be used. The measurement-based values of A_0 have again been fitted into a quadratic equation:

$$A_0(m) = [3.48m^2 - 4.95m + 2.32] \times 10^{-3} \qquad (4)$$

Equation (4) leads to data in K mol J^{-1} for each two chain-atom repeating unit with a standard deviation of $\pm 0.27 \times 10^{-3}$ K mol J^{-1}.

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REFERENCES

1 Wunderlich, B. *J. Chem. Phys.* 1962, **37**, 1207

2 Gaur, U. and Wunderlich, B. *Am. Chem. Soc. Symp. Ser.* **197**, 355; Provder, T. (Ed.) *Am. Chem. Soc.*, Washington, DC, USA, 1982

3 Gaur, U., Shu, H.-C., Mehta, A., Lau, S.-F., Wunderlich, B. B. and Wunderlich, B. *J. Phys. Chem. Ref. Data* 1981, **10**, 89, 119, 1001, 1051; 1982, **11**, 313, 1065; 1983, **12**, 29, 65, 91

4 Grebowicz, J., Lau, S.-F. and Wunderlich, B. *J. Polym. Sci., Polym. Symp.* 1984, **71**, 19

5 Lau, S. F. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 379

6 Grebowicz, J., Suzuki, H. and Wunderlich, B. *Polymer* 1985, **26**, 561

7 Baur, H. and Wunderlich, B. *Adv. Polymer Sci.* 1970, **7**, 151

8 Cheban, Yu. V., Lau, S.-F. and Wunderlich, B. *Colloid Polym. Sci.* 1982, **260**, 9

9 Lau, S.-F. and Wunderlich, B. *J. Thermal Analysis* 1983, **28**, 59

10 Bachmann, M. A. and Koenig, J. L. *J. Chem. Phys.* 1981, **74**, 5896

11 Enomoto, S., Kawai, Y. and Sugita, M. *J. Polym. Sci., Part A2*, 1968, **6**, 861

12 Cessac, G. L. and Curro, J. G. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 695

13 Tashiro, K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1981, **14**, 1757

14 Kobayashi, M., Tashiro, K. and Tadokoro, H. *Macromolecules* 1975, **8**, 158

15 Grebowicz, J. and Wunderlich, B. *J. Thermal Analysis* 1985, **30**, 229

16 Rubcic, A. and Zerbi, G. *Macromolecules* 1974, **7**, 754

17 Koenig, J. L. and Mannion, J. J. *J. Polym. Sci., Part A2* 1966, **4**, 401

18 Lee, W. K. and Choy, C. L. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 619

19 Choy, C. L. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1263

20 Wunderlich, B. and Jones, L. D. *J. Macromol. Sci.* 1969, **B3**, 67

21 Van Krevelen, D. W. and Hoftyzer, P. J. 'Properties of Polymers', Elsevier, Amsterdam, 1972

22 Gaur, U. and Wunderlich, B. *Macromolecules* 1980, **13**, 445

23 Lau, S.-F., Wesson, J. and Wunderlich, B. *Macromolecules* 1984, **17**, 1102