Heat capacities of various solid linear macromolecules

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Heat capacities at constant pressure and constant volume for the solid state are calculated from approximate vibrational spectra and compared with experimental data taken from a critical literature review. A total of 12 macromolecules are discussed: poly(isobutyl acrylate), poly(isobutyl methacrylate), poly(vinyl alcohol), poly(vinyl acetate), polyoxypropylene, poly[oxy-2,2-bis(chloromethyl)trimethylene], poly(vinyl benzoate), poly(vinyl p-ethylbenzoate), poly(vinyl p-isopropylbenzoate), poly(vinyl p-t-butylbenzoate), polycyclopentene and cis-1,4-polyisoprene. The results are compared with prior approximations on about 70 other polymers. For poly(vinyl acetate) new 'recommended data' are presented. The influence of methyl groups on heat capacity is discussed.

INTRODUCTION

Over the last few years we have developed a method to compute heat capacities of linear macromolecules from approximate frequency spectra[1]. For the N skeletal vibrations of a macromolecule, a fit of the experimental heat capacity to a two-parameter (Θ_1 and Θ_3) Tarasov function is attempted. The parameter Θ_1 is characteristic of the upper-frequency limit of the one-dimensional, intramolecular vibrational spectrum. The parameter Θ_3 is the analogous limit of the three-dimensional, intermolecular vibrational spectrum. The frequencies Θ are expressed in kelvin ($1\,K = 0.695\,cm^{-1}$ or $2.08 \times 10^{10}\,Hz$). The remaining group vibrations can be approximated by single or narrow-range frequencies taken from normal-mode calculations of isolated chains, low-molecular-weight analogues, or experimentally identified infra-red or Raman frequencies. The total available body of experimental heat capacities was collected into a critically reviewed data bank[2] and then successively analysed. Polymers were grouped according to their chemical structure to observe regularities in the analysis into polyoxides[3], fluorinated and chlorinated polyethylenes[4], polypropylene[5,6], branched polymers[6], polyesters[7], polyamides[8], polysiloxanes[9] and phenylene-containing polymers[10]. Because of special interests, the polybutadienes[11] and polystyrenes (substituted and crosslinked)[12] were analysed separately. This effort, covering some 70 polymers, left a number of experimental heat capacity data sets without analysis. All these are included in this paper. Their discussion can be taken as a proving ground for the developed analysis system. For the future, we hope within the framework of the new ATHAS organization to provide continuously updated tables of heat capacity data[13].

This major effort on providing an improved basis of thermal analysis has led to a table of residual entropies of over 20 polymers, has enabled us to point out the limits of the two-phase description of semicrystalline polymers by finding a 'rigid amorphous fraction', metastable above the glass transition, and has resolved many questions of mesophase transitions (plastic, liquid and condis crystals)[14]. The present, last set of analyses covers a diverse group of polymers ranging from perfect correspondence of experimental heat capacities with the computation scheme (poly(isobutyl methacrylate), poly(vinyl alcohol), polyoxypropylene, poly[oxy-2,2-bis(chloromethyl)trimethylene] and poly(vinyl benzoate)s, with errors below ±3%) to marginal correspondence (poly(isobutyl acrylate), poly(vinyl acetate), polycyclopentene and cis-1,4-polyisoprene, with errors up to ±5%). Finally, a few, rather complicated, polymers seem to deviate so much from linear macromolecular structure that they could not be fitted into the scheme of computation. These are not described in this paper (poly[carbonylimino(6-hydroxy-1,3-phenylene)methylene(4-hydroxy-1,3-phenylene)iminocarbonyl(-1,3-phenylene], poly(oxy-2,6-diphenyl-1,4-phenylene) and a series of eight polyheteroarylenes, with errors above 5%).

Note that all calculations have been carried to 1000 K, far above the melting temperature, and in most cases even the decomposition temperature. The reason for calculation to this unrealistic limit lies in the possibility of inclusion of some of these groups into high-temperature polymers where they exist at higher temperature in the solid state, and in the possibility of instantaneous heating to high temperatures in laser ablation studies where

Table 1 Number of vibrational modes

Approximate mode	PIBA	PIBMA	PVA	PVAC	PCP	POP	PVB	PVEB	PVIPB	PVTBB	POCMM	PIP
(a) CH$_3$												
CH$_3$ as. stretch	4	6		2		2		2	4	6		2
CH$_3$ sym. stretch	2	3		1		1		1	2	3		1
CH$_3$ as. deformation	4	6		2		2		2	4	6		2
CH$_3$ sym. deformation	2	3		1		1		1	2	3		1
CH$_3$ rock	4	6		2		2		2	4	6		2
CH$_3$–C stretch	2	3		1		1		1	2	3		1
(b) CH$_2$												
CH$_2$ as. stretch	2	2	1	1	3	1	1	2	1	1	2	2
CH$_2$ sym. stretch	2	2	1	1	3	1	1	2	1	1	2	2
CH$_2$ bend	2	2	1	1	3	1	1	2	1	1	2	2
CH$_2$ wag	2	2	1	1	3	1	1	2	1	1	2	2
CH$_2$ twist	2	2	1	1	3	1	1	2	1	1	2	2
CH$_2$ rock	2	2	1	1	3	1	1	2	1	1	2	2
C–C stretch	1		1	1	3	1	1	2	1	1	2	2
(c) CH												
C–H stretch	2	1	1	1	2	1	1	1	2	1		1
C–H bend	4	2	2	2	4	2	2	2	4	2		2
C–C stretch	1		1	1	1		1	1	2	1		1
(d) C (R$_1$,R$_2$)												
C–C stretch	1	3							1			
(e) COO												
C–COO stretch	1	1		1			1	1	1	1		
C=O stretch	1	1		1			1	1	1	1		
C–O stretch	1	1		1			1	1	1	1		
C=O in plane bend	1	1		1			1	1	1	1		
C=O out-of-plane bend	1	1		1			1	1	1	1		
(f) C–O												
C–O stretch	1	1		1	2	1	1	1	1	1	2	
(g) OH												
O–H stretch			1									
O–H bend			2									
C–OH stretch			1									
C–OH bend			2									
(h) C=C												
C=C stretch					1							1
(i) Chain bend												
Polyoxide					1				1			
(j) Chain torsion and bend												
Polyoxide			1				1					
(k) Phenyl												
All vibrational modes						31						
(l) Phenylene												
All vibrational modes of (i) in *Table 2* except 4408, 2161 and 1465 K								28	28	28		
(m) CH$_2$Cl												
CH$_2$ as. stretch											2	
CH$_2$ sym. stretch											2	
CH$_2$ bend											2	
CH$_2$ wag											2	
CH$_2$ twist											2	
CH$_2$ rock											2	
C–CH$_2$Cl stretch											2	
C–Cl stretch											2	
C–Cl bend											2	
(n) Skeletal vibration	18	21	4	11	10	7	10	15	18	21	12	11
Total	**63**	**72**	**21**	**36**	**39**	**30**	**57**	**75**	**84**	**93**	**48**	**39**

Table 2 Group vibration frequencies in kelvin $(h\nu/k)^a$

Approx. vibrational mode	N	Frequency (K)
(a) CH$_2$- (POCMM)		
CH$_2$ as. stretch	1.00	4148
CH$_2$ sym. stretch	1.00	4098
CH$_2$ bend	1.00	2075
CH$_2$ wag	0.65	1698–1977
	0.35	1977
CH$_2$ twist and rock	0.48	1690–1874
	0.52	1874
C–C stretch	0.34	1378–1638
	0.35	1378–1525
	0.31	1525
CH$_2$ rock and twist	0.04	1494
	0.59	1038–1494
	0.37	1079

Approx. vibrational mode	N	Frequency (K)
(b) CH$_2$–CHCH$_3$– (PIBA, PIBMA, POP, POCMM, PVAC, PVA, PVB, PVEB, PVIPB, PVTBB)		
CH$_3$ as. stretch	1.00	4262
CH$_3$ as. stretch	1.00	4259
CH$_3$ as. stretch	1.00	4213
CH stretch	1.00	4181
CH$_3$ sym. stretch	1.00	4147
CH$_2$ sym. stretch	1.00	4085
CH$_3$ as. bend	1.00	2107
CH$_3$ as. bend	1.00	2101
CH$_2$ bend	1.00	2094
CH$_3$ sym. bend	0.25	1987
	0.38	1973–1987
	0.37	1973
CH bend	0.42	1963–1973
	0.58	1966
CH bend	0.64	1944
	0.28	1916–1944
	0.08	1916
CH$_2$ wag	0.18	1876
	0.43	1842–1876
	0.39	1846
CH$_2$ twist	0.33	1722–1791
(CH$_3$ rock)	0.55	1695–1722
	0.12	1695
C–C chain stretch	0.16	1685
	0.84	1650–1685
C–CH$_3$ stretch	0.44	1568–1614
	0.56	1534–1614
CH$_3$ rock (+CH$_2$ wag)	0.55	1453–1521
	0.45	1453
CH$_3$ rock (+C–C chain stretch)	0.65	1361–1393
	0.21	1333–1361
	0.14	1336
CH$_2$ rock	0.52	1222–1295
	0.48	1289
C–C chain stretch	0.17	1197
	0.55	1167–1198
	0.28	1167

Approx. vibrational mode	N	Frequency (K)
(c) CH$_2$Cl– (POCMM)		
C–H as. stretch	1.00	4324
C–H sym. stretch	1.00	4255
CH$_2$ bend	1.00	2079
CH$_2$ wag	1.00	1823
CH$_2$ twist	1.00	1718
CH$_2$ rock	1.00	1264
C–CH$_2$Cl stretch	1.00	1514
C–Cl stretch	1.00	1089
C–Cl bend	1.00	376

Approx. vibrational mode	N	Frequency (K)
(d) CH$_2$–C (R$_1$,R$_2$) (PIBA, PIBMA, PVTBB)		
C–C stretch	1.00	1164–1680

Approx. vibrational mode	N	Frequency (K)
(e) CH$_2$–CH=CH–CH$_2$– (PCP)		
CH stretch	2.00	4347
CH$_2$ as. stretch	2.00	4204
CH$_2$ sym. stretch	2.00	4097
C=C stretch	1.00	2387
CH$_2$ bend	2.00	2078

Table 2—continued

Approx. vibrational mode	N	Frequency (K)
CH$_2$ wag	0.70	1977
	1.30	1698–1977
CH$_2$ twist	0.96	1698–1874
	1.04	1874
CH bend	4.00	1016–1914
C–C stretch	0.93	1525
	1.02	1378–1638
	1.05	1378–1525
CH$_2$ rock	0.08	1494
	1.18	1038–1494
	0.74	1079

Approx. vibrational mode	N	Frequency (K)
(f) –OH (PVA)		
O–H stretch	1.00	4806
O–H bend	1.00	1994
O–H rock	1.00	921
C–OH stretch	1.00	1577
C–OH bend	1.00	691
C–OH rock	1.00	590

Approx. vibrational mode	N	Frequency (K)
(g) CO–O– (PIBA, PIBMA, PVAC, PVB, PVEB, PVIPB, PVTBB)		
C–COO stretch	1.00	1215
C=O stretch	1.00	2530
C–O stretch	1.00	1800
C=O in-plane bend	1.00	980
C=O out-of-plane bend	1.00	840

Approx. vibrational mode	N	Frequency (K)
(h) C–O–C– (PIBA, PIBMA, PVAC, PVB, PVEB, PVIPB, PVTBB, POP, POCMM)		
C–O stretch	0.22	1385
	0.11	1632
	0.67	1385–1632
O–C stretch	1.00	1305

Approx. vibrational mode	N	Frequency (K)
(i) Phenyl (PVB, PVEB, PVIPB, PVTBB)		
C–H stretch	1.00	4408[b]
C–H stretch	1.00	4397
C–H stretch	1.00	4388
C–H stretch	1.00	4378
C–H stretch	1.00	4371
C–C stretch	1.00	2298
C–C stretch	1.00	2281
CCH bend, C–C stretch	1.00	2161[b]
CCH bend	1.00	2074
C–C stretch	1.00	1918
C–C stretch	1.00	1876
CCH bend	1.00	1739
CCH bend	1.00	1682
CCH bend, C–C stretch	1.00	1656
C–C stretch, CCH bend	1.00	1538
CCC bend, C–C stretch	1.00	1502
CCC bend, C–C stretch	1.00	1479
C–H wag	1.00	1465[b]
C–H wag	1.00	1386
C–H wag	1.00	1328
C–H wag	1.00	1232
C–C stretch (C$_6$H$_5$–C)	0.23	1139
	0.32	1112–1139
	0.45	1112–1135
C–H wag, C$_6$H$_5$–C wag	1.00	1097
C–H wag	1.00	1010
CCC bend	1.00	904
CCC bend	0.31	846–862
	0.30	858–862
	0.35	858–902
	0.04	902
Ring mode, coupled to the backbone chain	0.42	771–791
	0.32	771–800
	0.26	815
CCC bend (C$_6$H$_5$–C)	0.31	633
	0.32	633–728
	0.37	728
C–C torsion	1.00	584

Table 2—*continued*

Approx. vibrational mode	N	Frequency (K)
CCC rock (C_6H_5–C)	0.16	435–451
	0.39	451–546
	0.45	546
Ring mode, coupled to the backbone chain C–C torsion	1.00	348

(j) CH=CCH₃–CH₂–CH₂ (PIP)

Approx. vibrational mode	N	Frequency (K)
CH stretch	1.00	4338.0
CH₃ as. stretch	2.00	4266.0
CH₂ as. stretch	1.00	4205.6
CH₂ as. stretch	1.00	4192.7
CH₃ sym. stretch	1.00	4138.0
CH₂ sym. stretch	1.00	4094.8
CH₂ sym. stretch	1.00	4089.1
C=C stretch	1.00	2384.1
CH₃ as. bend	0.18	2109.3
	0.66	2109.3–2282.2
	0.16	2282.2
CH₃ as. bend	1.00	2103.5
CH₂ bend	1.00	2100.6
CH₂ bend	1.00	2092.0
CH₃ sym. bend (+C–C= stretch)	1.00	2005.7
CH₂ wag + twist (+C–C= stretch)	0.79	1915.0–2005.7
	0.21	2005.7
CH₂ twist	1.00	1890.6–1915.0
CH₂ wag + twist (+C–C= stretch)	0.60	1871.9
	0.23	1842.4–1871.9
	0.17	1842.4
CH₂ wag + twist (+C–C= stretch)	1.00	1812.9
CH₂ wag +=CH bend (*ip*)	0.43	1748.1–1789.7
	0.57	1766.8–1789.7
CH₂ wag	0.52	1604.3–1624.3
	0.48	1624.3
C–CH₃ stretch	0.17	1564.0
	0.48	1488.9–1564.0
	0.16	1488.9
	0.19	1488.9–1541.5
CH₃ rock	1.00	1486.3
C–C stretch	0.80	1413.8–1451.3
	0.20	1451.3
CH₃ rock + CH₂ rock (+C–C– stretch)	0.10	1410.7
	0.23	1383.7–1410.7
	0.50	1383.7–1421.3
	0.17	1421.3
CH₂ rock + CH₃ rock (+C–C– stretch)	0.24	1376.1
	0.53	1326.5–1376.1
	0.23	1326.5
CH bend (*op*)	0.50	1240.8–1275.4
	0.50	1244.5
CH₂ rock	1.00	1141.5
CH₂ rock (+C–C stretch)	0.50	1067.9–1090.4
	0.19	1090.4
	0.31	1052.8–1090.4

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a Sources of the listed approximate frequency ranges:
(a) From normal-mode calculation of polyethylene summarized in ref. 3
(b) From normal-mode calculation of polypropylene analysed in refs 5 and 6
(c) From i.r. spectrum published in ref. 19
(d) Approximated from polypropylene in refs 5 and 6
(e) From i.r. and Raman spectra as evaluated in ref. 11
(f) Extracted from i.r. spectrum as given in ref. 16
(g) See ref. 7
(h) See ref. 3
(i) From normal-mode calculation of polystyrene and model compounds as used in ref. 12
(j) From normal-mode calculation of *trans*-1,4-poly(2-methylbutadiene) as described in ref. 20
b Frequences omitted for phenylene group (PVEB, PVIPB, PVTBB)

thermal data are needed for highly superheated structures.

RESULTS

Poly(isobutyl acrylate) and poly(isobutyl methacrylate)

Poly(isobutyl acrylate) (PIBA) and poly(isobutyl methacrylate) (PIBMA) belong to the series of polyacrylates and polymethacrylates analysed before[6]. The same approximations used to calculate the heat capacity for this earlier series of polymers is followed. The types of group vibrations and number of skeletal modes are listed in *Table 1* for all polymers analysed in this paper. The approximate group vibrational frequencies used for computation are listed in *Table 2*.

The recommended heat capacity data[2] below the glass transition temperature (249 K) for PIBA consist of only a few points in the temperature region 220–240 K. They were initially used to calculate Θ_1, but resulted in a low average Θ_1, of 452.6 ± 34.1 K, with a small, but constantly increasing, error. This was taken as an indication that the experiments are still too close to the glass transition. Clearly, lower-temperature heat capacity measurements must be made for this polymer to settle discussions of Θ_1 and Θ_3. Since all acrylates showed, however, a continuous change in Θ_1 with chemical structure (equation (4) in ref. 6), we could estimate that Θ_1 should be 523.8 K. Similarly, Θ_3 can be assumed to be 90 K, similar to poly(n-butyl acrylate) (88.2 K). The heat capacity computed thus, without use of experimental data, is plotted in *Figure 1*. *Figure 2* shows the difference from experiment for the few data points. The average and
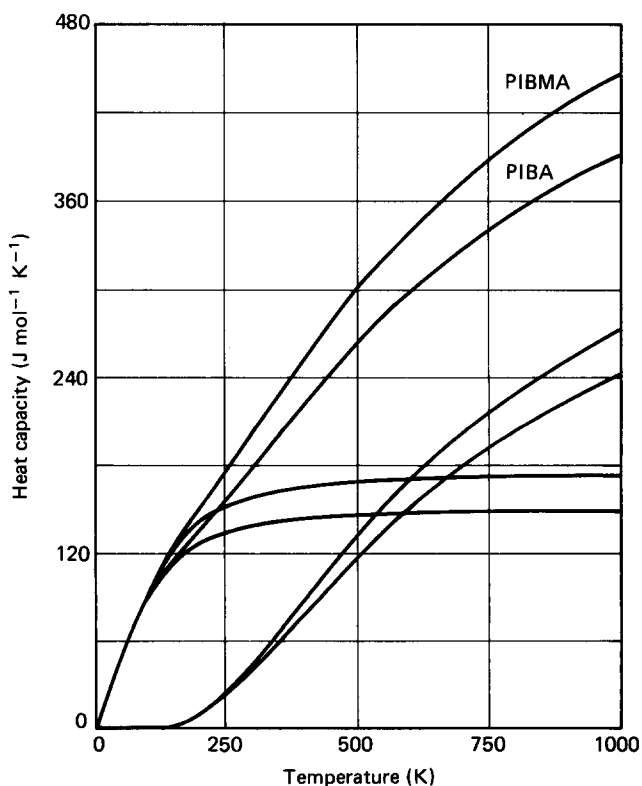

Figure 1 Computed heat capacities at constant volume of solid PIBA and PIBMA: upper curves, total heat capacities; lower curves, group vibration contributions; intermediate curves, skeletal vibration contributions
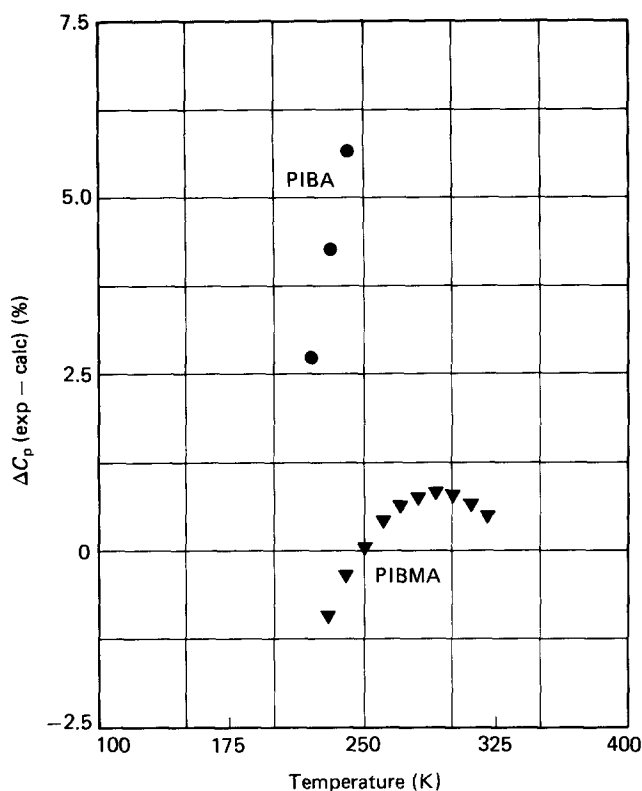
Figure 2 Error plot for *Figure 1*, recalculated into heat capacity at constant pressure using equation (1)

r.m.s. errors are $4.2 \pm 1.5\%$. The universal value of A_0, 5.11×10^{-4} K mol J^{-1}, was assumed for computation of C_p, the heat capacity at constant pressure, since no expansivity or compressibility data are available. The melting temperature was approximated as $3/2$ times the glass transition temperature in the Nernst–Lindemann expression[15]:

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

For atactic PIBMA the glass transition temperature is 326 K, sufficiently high to use available experiments from 230 to 320 K for the evaluation of Θ_1. The average of Θ_1 over this temperature range is 594.9 ± 13.3 K. The value of Θ_3, again, has to be a guess. In comparison with poly(n-butyl methacrylate) (58 K), Θ_3 was chosen to be 60 K for the computation. *Figures 1* and *2* show the results and *Tables 1* and *2* summarize the group vibrations used for the calculations. The average and r.m.s. deviation from the experiment are $0.3 \pm 0.6\%$. PIBMA is thus one of the polymers that fits the computation scheme very well.

As for PIBA, the universal A_0 was used in equation (1) and $T_m{}^\circ$ was assumed to be at $(3/2)T_g$. The Θ_1 derived from the experimental heat capacity fits the straight-line relation between Θ_1 and $(1/M)^{1/2}$ derived for other methacrylates (equation (4) of ref. 6).

Poly(vinyl alcohol)

Poly(vinyl alcohol) (PVA) has a well analysed infra-red spectrum[16]. The vibrational frequencies for O–H stretching, bending and rocking and analogous C–OH modes are listed in *Table 2* together with the C–H and C–C vibrations taken from the polyethylene spectrum.

Recommended heat capacity data[2] are available from 60 to 300 K. These were used to compute Θ_1 to be $494.8 \pm$

21.1 K ($N = 4$) in the temperature range from 70 to 230 K. An attempt to fit Θ_3 at the lowest temperature range for experimental data led to an estimate of 119.1 K. *Figures 3* and *4* show the results using the universal A_0 and an estimated $T_m{}^\circ$ of 520 K in equation (1). The average and r.m.s. deviations are $2.4 \pm 3.9\%$.

The data fit well enough to include PVA into the group of macromolecules with good correspondence between experiment and computation. The somewhat larger error may be connected with the experimental data originating from a poorly characterized sample[2]. Above 260 K the experimental data deviate more from the calculation (see *Figure 4*). Presumably one approaches the glass transition, reported to occur at 358 K.

The intramolecular structure of PVA (side-chain mass 17 g mol^{-1}), after proper accounting for the group vibrations, is similar to polypropylene[5] (side-chain mass 15 g mol^{-1}) and poly(vinyl fluoride)[4] (side-chain mass 19 g mol^{-1}). When calculating Θ_1 for all three polymers for four skeletal modes, indeed, three similar Θ_1 values result: 495, 448 and 440 K, respectively. This supports the observations that the heat capacity due to skeletal vibrations of carbon-backbone polymers are largely only mass-dependent after accounting for the group vibrations. For Θ_3, similarly, values of 119, 87 and 105 K, respectively, were needed to account for the measured heat capacities. Not enough information on crystallinity and intermolecular forces is available for those three polymers to consider the variation in Θ_3.
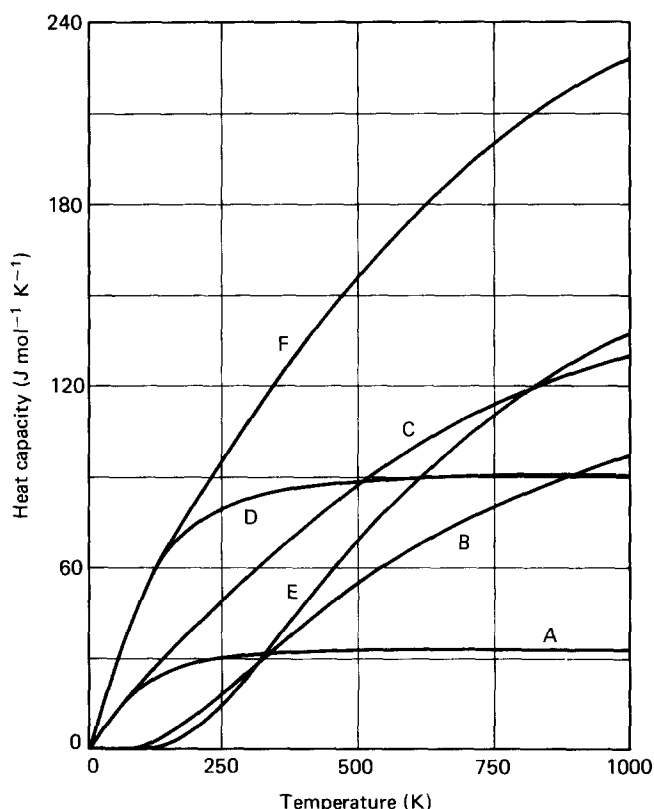

Figure 3 Computed heat capacities at constant volume of solid PVA and PVAC: curves A, B, C and D, E, F represent the skeletal vibration contributions, group vibrations and total heat capacities of PVA and PVAC, respectively
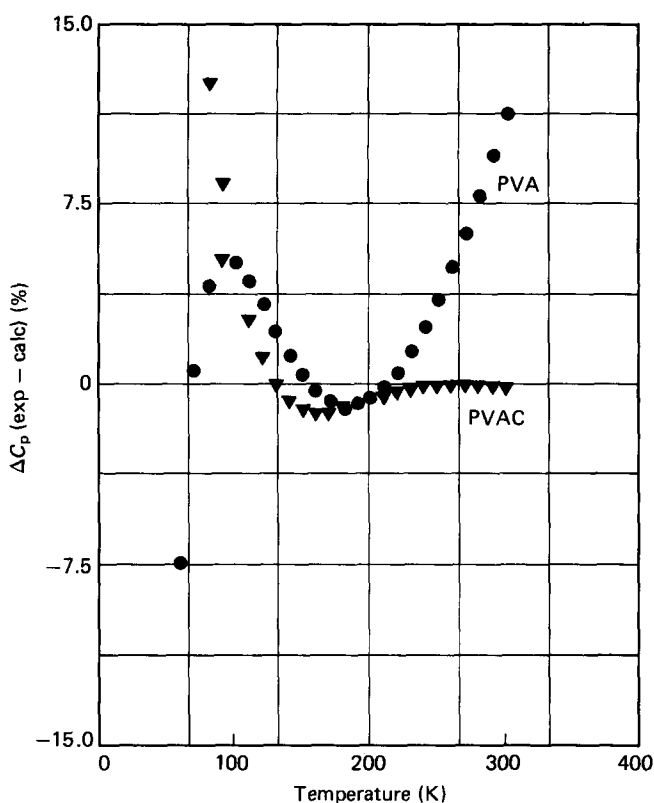
Figure 4 Error plot for *Figure 3*, recalculated into heat capacity at constant pressure using equation (1)

Poly(vinyl acetate)

The poly(vinyl acetate) (PVAC) group vibrations, listed in *Tables 1* and *2*, correspond closely to the reported, assigned infra-red vibrations[17]. Experimental heat capacities are available[2] between 80 and 300 K. It is of interest to note that PVAC is an isomer of poly(methyl acrylate). Structurally the two polymers differ only by a reversal of the carboxylate group. Such changes do not influence the assignment of approximate group vibrations.

In transcribing the heat capacity data in ref. 2, an error occurred, however, in setting the zero of the published graph. The corrected data are shown in *Table 3*. With these and a Θ_3 chosen in accord with poly(methyl acrylate) to be 86.3 K, the data shown in *Figures 3* and *4* were obtained. The two isomers, PVAC and poly(methyl acrylate), have Θ_1 parameters of 581.0 ± 30.3 and 552 K, respectively, with 11 skeletal vibrations. The average and r.m.s. deviation of the corrected experimental data from the calculation are $0.85 \pm 3.4\%$. As with many of the other polymers, an experiment-based Θ_3 value would be of interest to discuss intermolecular force differences, but requires C_p data in the 10–80 K temperature range. The glass transition of PVAC is 304 K ($\Delta C_p = 46.7$ J K^{-1} mol^{-1}) compared to 279 K ($\Delta C_p = 42.3$ J K^{-1} mol^{-1}) for poly(methyl acrylate).

Both isomers fit the relationship for Θ_1 established for branched polymers[6] well. It is also of interest to note that the change in heat capacity at T_g corresponds to four mobile 'beads' freezing according to the semiempirical scheme developed some time ago[18]. Both main chain and side chain account for approximately two beads, each when using the average of about 11 J K^{-1} mol^{-1} as ΔC_p per mole of beads. This should be an indication that the

main chain and side chain contribute and freeze similarly at the glass transition temperature.

Polyoxypropylene and poly[oxy-2,2-bis(chloromethyl)trimethylene]

Polyoxypropylene (POP) and poly[oxy-2,2-bis(chloromethyl)trimethylene] (POCMM), also known under the tradename Penton (Hercules Co.), are substituted members of the polyoxide series of macromolecules analysed earlier[3]. The group vibrations in *Tables 1* and *2* were chosen accordingly. For POP recommended data between 80 and 190 K for glass and semicrystalline samples were used to calculate Θ_1 (493.9 ± 12.7 K) for $N = 7$ skeletal vibrations. At 90 K a Θ_3 value of 111.9 K can be estimated. The results are displayed in *Figures 5* and *6*. The calculated C_p matches the experimental C_p to $0.58 \pm 1.0\%$ (average and r.m.s. error) in a very good correspondence. The universal constant A_0 and a T_m° of 368 K were used in $C_p - C_v$ calculations of equation (1).

Table 3 Recommended heat capacity data for amorphous poly(vinyl acetate)[a]

T (K)	Heat capacity (J K^{-1} mol^{-1})
80.0	46.47
90.0	49.44
100.0	52.41
110.0	55.38
120.0	58.36
130.0	61.33
140.0	64.30
150.0	67.27
160.0	70.25
170.0	73.22
180.0	76.19
190.0	79.16
200.0	82.14
210.0	85.11
220.0	88.08
230.0	91.05
240.0	94.03
250.0	97.00
260.0	99.97
270.0	102.9
273.15	103.9
280.0	105.9
290.0	108.9
300.0	111.9
304.0 (T_g)	113.0
304.0 (T_g)	159.4
310.0	159.6
320.0	160.3
330.0	160.9
340.0	161.5
350.0	162.1
360.0	162.7
370.0	163.3

[a] This table contains more significant figures than are justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation. It replaces the recommended (1980) data table 39 (*J. Phys. Chem. Ref. Data*, 1983, **12**, 57)

Heat capacity in the solid state (80–304 K):

$$C_p = 0.297224T + 22.6873 \ (\pm 0.6\%)$$

Heat capacity in the liquid state (304–370 K):

$$C_p = 0.0617442T + 140.497 \ (\pm 0.1\%)$$

Data from Shieman, M. S., Rabinovich, I. B. and Ovchinnikov, Y. V. *Vysokomol. Soedin. (A)* 1972, **14**, 377
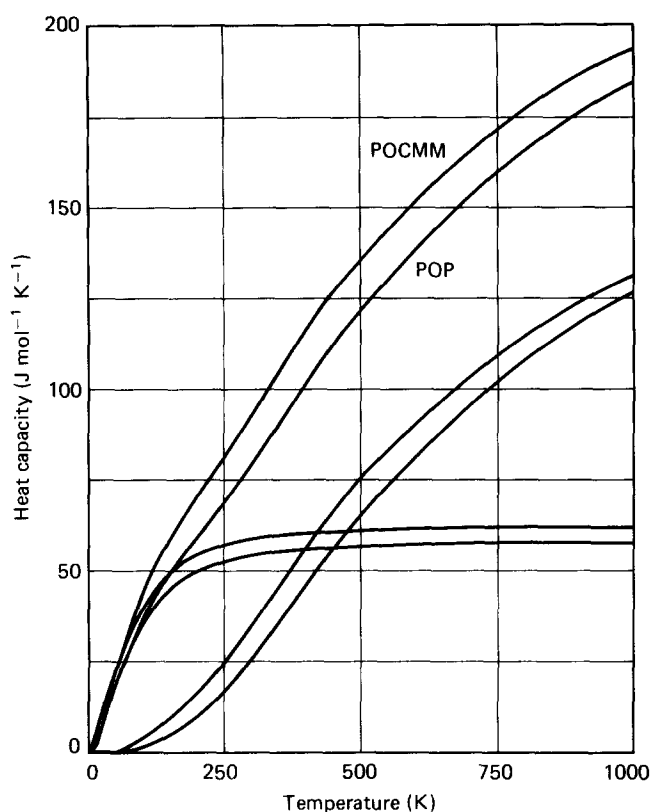
Figure 5 Computed heat capacities at constant volume of solid POP and POCMM: upper curves, total heat capacities; lower curves, group vibration contributions; intermediate curves, skeletal vibration contributions

A comparison of the Θ_1 values of polyethylene ($\Theta_1 = 519$ K, $N = 4$)[3] and polypropylene ($\Theta_1 = 714$ K, $N = 7$)[5] with polyoxyethylene ($\Theta_1 = 353$ K, $N = 4$)[3] and POP ($\Theta_1 = 494$ K, $N = 7$) shows similar effects on the introduction of the $-CH_3$. For both sets of polymers the ratio of the Θ_1 temperatures is 1.4. The change in Θ_1 is not caused by the increase in repeat-unit mass, as suggested for the PVA case. A larger-mass repeat unit would lead to a reduction of Θ_1 on substitution, rather than an increase. The increase in Θ_1 on substitution is the result of the more or less arbitrary addition of the two $HC-CH_3$ bending (555–830 K) and one torsional vibration (296 K)[5] to the skeletal vibrations. Recalculating the heat capacities for $N = 4$ would for both substituted polymers lead to the expected decrease in Θ_1 (refs 3 and 5).

POCMM has additional, low-frequency group vibrations due to the substitution of H by Cl. These frequencies were approximated by the known data for 1,1-dichloroethane[19] and are listed in *Tables 1* and *2*. The experimental heat capacity of a semicrystalline sample led to recommended data between 10 and 270 K (ref. 2). With 12 skeletal vibrations the following parameters were determined: $\Theta_1 = 462.7 \pm 41.9$ K and $\Theta_3 = 43.9$ K. The results are shown in *Figures 5* and *6*. Although the variation in Θ_1 is rather high, the experimental heat capacities are reproduced well. The average and r.m.s. deviations are $-0.15 \pm 2.4\%$ in the temperature region from 70 to 270 K. A_0 was given a value of 0.0014 K mol^{-1} J^{-1}, instead of the universal 0.00511 K mol J^{-1}, and was used as a third fitting parameter, with T_m in equation (1) estimated to be $3T_g/2 = 417$ K.

Poly(vinyl benzoate)s

Four different poly(vinyl benzoate)s were analysed: poly(vinyl benzoate) (PVB), poly(vinyl *p*-ethylbenzoate) (PVEB), poly(vinyl *p*-isopropylbenzoate) (PVIPB) and poly(vinyl *p*-t-butylbenzoate) (PVTBB). The group vibrations were approximated making using of prior analyses of polystyrene, polyesters, vinyl polymers and branch groups. The vibration types, their frequencies and the appropriate references are given in *Tables 1* and *2*. All of the heat capacity measurements were done starting from 190 K, using X-ray amorphous polymers with glass transition temperatures ranging from 330 to 394 K (ref. 2). The results are shown in *Figures 7* and *8*. To get the best fit of the heat capacities, A_0 needed to be treated as a third fitting parameter. The three parameters N, Θ_1 and A_0 for PVB, PVEB, PVIPB and PVTBB were: 10, 540.9 ± 63.8 K, 2.0×10^{-4} K mol J^{-1}; 15, 411.1 ± 16.1 K, 2.0×10^{-4} K mol J^{-1}; 18, 566.9 ± 42.9 K, 1.0×10^{-4} K mol J^{-1}; and 21, 512.4 ± 11.0 K, 2.0×10^{-4} K mol J^{-1}, respectively. With these parameters the heat capacities could be computed up to the glass transitions with average and r.m.s. errors of $0.75 \pm 1.4\%$, $0.24 \pm 0.41\%$, $0.64 \pm 1.2\%$ and $0.18 \pm 0.4\%$ for PVB, PVEB, PVIPB and PVTBB, respectively. To have an estimate of the low-temperature heat capacity, a Θ_3 of 50 K was assumed, the value found experimentally for polystyrene $(48 K)[12]$, which is also close to that for many other polymers with benzene rings in their structure[10].

Although excellent correspondence of experiment and calculation was possible for the poly(vinyl benzoate)s, it is not possible to discuss the obtained Θ_1 values further. The large increase in skeletal modes that had to be fitted to experimental data due to lack of information on
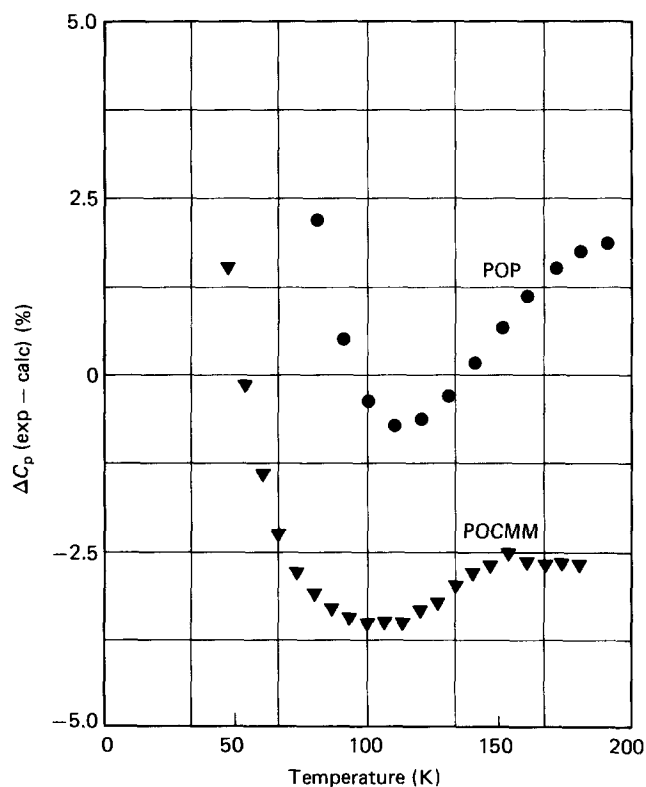

Figure 6 Error plot for *Figure 5*, recalculated into heat capacity at constant pressure using equation (1)
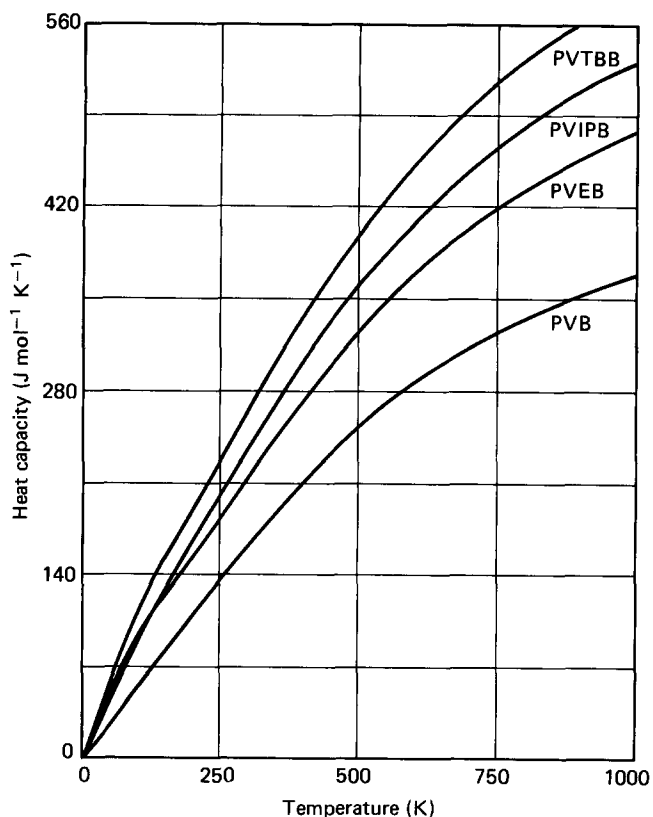
Figure 7 Computed heat capacities at constant volume of solid PVB, PVEB, PVIPB and PVTBB
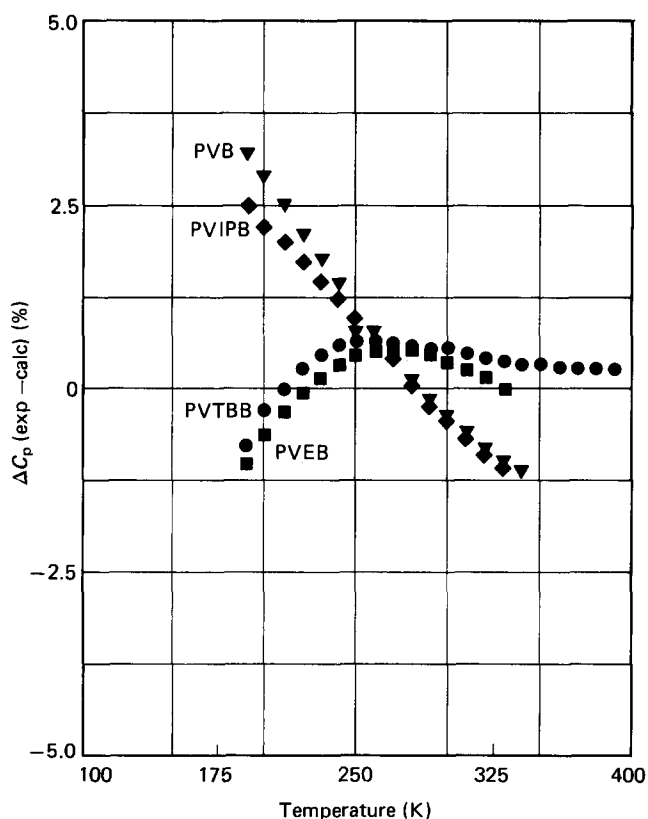

Figure 8 Error plot for *Figure 7*, recalculated into heat capacity at constant pressure using equation (1)

normal-mode frequencies of substituted phenylene groups prohibited the extraction of quantitative information. Lower-temperature heat capacities (20–190 K), expansivity, compressibility, as well as more precise

vibrational data are needed to progress in the discussion of the heat capacity of the poly(vinyl benzoate)s.

Polycyclopentene and cis-1,4-polyisoprene

Polycyclopentene (PCP) and *cis*-1,4-polyisoprene (PIP) (also *cis*-1,4-poly(2-methylbutadiene) or natural rubber) have as main characteristics a double bond in the backbone chain and are thus related to the prior analysed polybutadienes[11]. The group vibration frequencies of PCP were derived by addition of a CH_2- group to the main chain of polybutadiene (see *Tables 1* and *2*). For polyisoprene a normal-mode calculation for the *trans* isomer is available[20]. Since there are only small changes in the group vibrations in going from the *trans* to the *cis* isomer, these were taken also for the computation of the heat capacity contribution of the *cis* isomer (see *Tables 1* and *2*).

For solid PCP, which has a glass transition temperature of 173 K, recommended heat capacity data are available between 10 and 170 K; for PIP, with a T_g of 200 K, the data range is from 2 to 190 K (ref. 2). *Figures 9* and *10* give the computation results for the two polymers.

For PCP, Θ_1 is 547.7 ± 33.9 K and Θ_3 is 153.9 ± 4.8 K ($N = 10$), fitted over the temperature range from 40 to 170 K. The average and r.m.s. errors between 20 and 170 K are $-0.19 \pm 4.6\%$ (see *Figure 10*). For PIP, Θ_1 is 646.9 ± 33.0 K and Θ_3 is 58.3 ± 1.5 K ($N = 11$), fitted over the data range from 7 to 190 K. The average and r.m.s. errors between 7 and 190 K are $0.9 \pm 3.7\%$. For both polymers, equation (1) was used to convert C_p to C_v with estimated melting temperatures of 260 and 301.2 K, respectively.
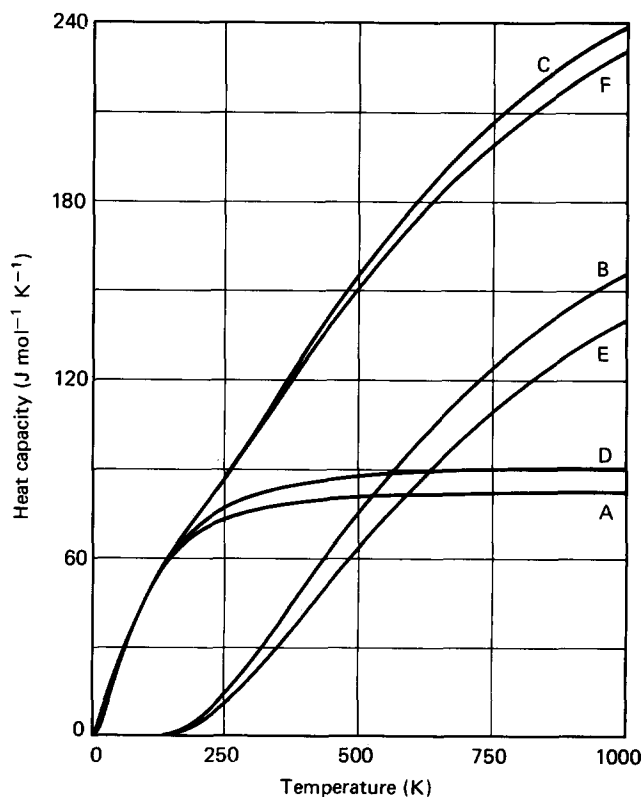

Figure 9 Computed heat capacities at constant volume of solid PCP and PIP: curves A, B, C and D, E, F represent the skeletal vibration contributions, group vibration contributions and total heat capacities of PCP and PIP, respectively

The errors are for both in the category of marginal correspondence. *Figure 10* shows a systematic deviation, indicative of poorer fit of the Tarasov approximation. A similar deviation was also observed for the 1,4-polybutadienes (*cis* and *trans*)[11].

A comparison of the Θ_1 temperatures of polyethylene, *cis*- and *trans*-1,4-polybutadiene and PCP shows the sequence 519, 589, 599 and 564 K, respectively, in parallel with the stiffer, double-bond-containing backbone. For PIP a similar increase in Θ_1 is observed in going from polybutadiene to polyisoprene (594 to 650 K) as in going
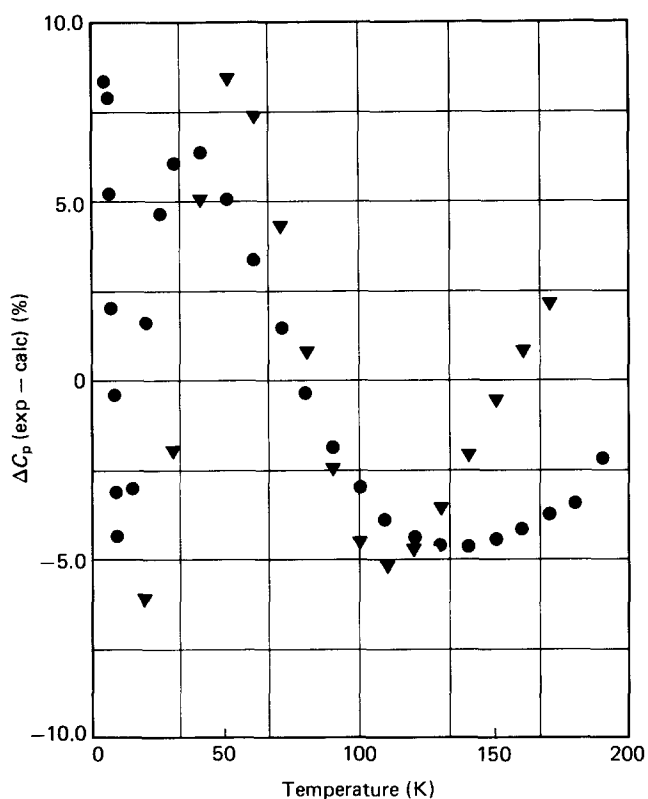
from polyethylene to polypropylene (519 to 633 K). As in the polypropylene case, the increase in Θ_1 is largely due to computation procedure, i.e. the inclusion of three $C-CH_3$ vibration modes in the skeletal vibrations[6].

GENERAL DISCUSSION AND CONCLUSIONS

The analysis of this diverse group of solid linear macromolecules shows the success of the developed method of approximate vibrational spectra and its limitations. There are no problems in using i.r. and Raman data for evaluation of the group vibrations. Best are full normal-mode calculations, but, as a comparison of similar modes in *Table 2* reveals, changes from molecule to molecule are too small to affect the computed heat capacities significantly. It may thus be possible to derive average frequencies for the listed frequencies in *Table 1*.

The skeletal vibrations are represented well by the two-parameter Tarasov equation as long as the molecule is strictly linear and the mass distribution and force constants do not vary significantly along the chain. Branching of chains, alternating heavy masses and inclusion of double bonds may need special discussion, but, with appropriate corrections, permits similar treatments for related compounds. A more detailed discussion of the problems of approximation of skeletal vibrations is given in ref. 21. In the macromolecules presented here, branches could be related to analogous, prior analysed vinyl, acrylic and methacrylic polymers[6] by adjusting the intramolecular skeletal vibration frequency spectrum through Θ_1. The effect of changes in mass were well represented by the usual $(1/M)^{1/2}$ dependence[4].

Missing data on low-temperature heat capacity (10–200 K) hinder further advance in the discussion of intermolecular forces. Similarly, using the universal equation (1) for the estimation of heat capacity at constant volume limits a more precise discussion of effects such as pre-glass-transition increase of heat capacity, anharmonicity effects on heat capacity, and changes in vibration frequencies with temperature. Extensive $p-v-T$

Figure 10 Error plot for *Figure 9*, recalculated into heat capacity at constant pressure using equation (1): ▼, PCP; ●, PIP

Table 4 Methyl-group contributions to the heat capacity $(J\ K^{-1}\ mol^{-1})$ of poly(vinyl benzoate)s[a]

Group	Temperature (K)							
	50	100	150	200	250	300	350	400
–CH₃	4.2	10.2	15.2	18.6	21.2	23.7	26.2	28.9
PVB (calc)	25.5	54.3	81.6	108.4	136.0	164.0	191.7	218.1
PVB (exp)	—	—	—	111.6	137.5	163.4	184.1	—
PVMB (calc)	29.7	64.5	96.8	127.0	157.2	187.7	217.9	247.0
PVEB (exp)	—	—	—	152.9	185.8	218.8	—	—
PVEB (calc)	33.9	74.7	112.0	145.6	178.4	211.4	244.1	275.9
Error (%)	—	—	—	5.0	4.1	3.5	—	—
PVIPB (exp)	—	—	—	168.3	202.5	236.7	—	—
PVIPB (calc)	38.1	84.9	127.2	164.2	199.6	235.1	270.3	304.8
Error	—	—	—	2.5	1.4	0.7	—	—
PVTBB (exp)	—	—	—	190.0	232.0	273.1	314.2	—
PVTBB (calc)	42.3	95.1	142.4	182.8	220.8	258.8	296.5	333.7
Error (%)	—	—	—	4.4	5.1	5.5	6.0	—

[a] Group vibration contribution $(-CH_3)-(-H)$ computed from model compound frequencies for polystyrene and poly(p-methylstyrene) of ref. 12
Frequencies: $C-CH_3$ stretch, 1755 K; $C-H$ stretch, 4137 and 4264 K; $C-H$ bend, 2114, 2109 and 1979 K; $C-CH_3$ bend, 446 and 515 K; and $C-CH_3$ torsion, 151 K
Experimental data from ref. 2

data extrapolated to fully amorphous and crystalline samples would permit progress in this area. In the meantime, A_0 often needs to be used as a third adjustable parameter.

Many of the presently and earlier described macromolecules can be related through the substitution of a –H by a –CH_3. The method of analysis used up to now involved subtraction of the three –H group vibration contributions (one C–H stretching and two bending frequencies), adding of the –CH_3 group vibrations (C–CH_3 stretching, three C–H stretching and five C–H bending frequencies) and increasing the skeletal vibrations by three (two C–CH_3 bending and one C–CH_3 torsional frequency). Removing the –CH_3 further from the backbone chain, as in the poly(vinyl benzoate)s for example, one may question this procedure since the –CH_3 skeletal vibrations are most likely decoupled from the skeleton, as proven for p-substituted polystyrenes[12]. This may be the reason for the added adjustment of A_0 needed in the poly(vinyl benzoate) computations.

Table 4 shows that computation of a group vibration contribution to heat capacity for –CH_3 substituting –H can be used to estimate the heat capacity of PVMB (poly(vinyl p-methylbenzoate)), PVEB, PVIPB and PVTBB by adding the proper heat capacity contribution once, twice, three times and four times to the calculated PVB heat capacity. The combined average and r.m.s. error is $3.8 \pm 1.8\%$, close to the expected experimental error.

With the series of polyimides and polyacrylates mentioned in the 'Introduction', whose heat capacities are reviewed in paper IX of ref. 2, a group of polymers is reached with structures too far from linear to be analysed by the present method. It may be of interest to develop a similar method using two-dimensional approximations of the skeletal vibration spectrum. It was shown before that such a method is applicable to layer-like inorganic crystals[22].

ACKNOWLEDGEMENT

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