# Heat capacities of solid, branched macromolecules

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Heat capacities at constant pressure and volume for solid, branched macromolecules were calculated from 0 to 1000 K from approximated frequency data and compared, when possible, with experimental data. The polymers analysed were: polyethylene, polypropylene, poly-1-butene, poly-1-pentene, poly-1-hexene, poly-1-heptene, poly-1-octene, polyisobutylene, polyacrylonitrile, poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-butyl methacrylate), poly(methacrylic acid), poly(methyl acrylate), poly(ethyl acrylate), poly(n-butyl acrylate) and poly(octadecyl acrylate). It was found that the group vibrations are strictly additive and that the skeletal vibrations can be fitted to an empirical distribution which reaches the polyethylene spectrum at a side-chain length of about six chain atoms.

**(Keywords: crystalline; glassy; heat capacity; polyacrylonitrile; poly-1-butene; polyethylene; poly(ethyl acrylate); poly(ethyl methacrylate); poly-1-heptene; poly-1-hexene; polyisobutylene; poly(methyl acrylate); poly(methacrylic acid); poly(methyl methacrylate); poly(n-butyl acrylate); poly(n-butyl methacrylate); poly(octadecyl acrylate); poly-1-octene; poly-1-pentene; polypropylene; vibration spectrum)**

## INTRODUCTION

The linking of the vibrational frequency spectra of over 50 linear macromolecules to their heat capacities has been completed recently[1-11]. The basic approach involves the separation of the spectrum into group and skeletal vibrations. The group vibrations are largely independent of the macromolecule into which a given group, such as $-CH_3$, $-C_6H_5$, $-CH_2-O-$ etc., is included. From normal mode calculations on isolated macromolecules or low molecular weight analogues, the group frequency distributions are sufficiently well known so that their heat capacity contribution can be computed without recourse to heat capacity measurements. The skeletal vibrations, in turn, are for linear macromolecules sufficiently well approximated by a Tarasov function that needs only two fitting parameters $\theta_3$ and $\theta_1$[12,13]. The parameter $\theta_3$ is obtained by fitting the heat capacity in the 0 to 50 K temperature region to a quadratic vibration–frequency distribution function, as originally proposed by Debye. It is a measure of the intermolecularly coupled vibrations. The parameter $\theta_1$ is obtained by fitting the heat capacity in the 100 to 300 K temperature region to a constant vibration frequency distribution function. The parameter $\theta_1$ is a measure of the intramolecularly coupled vibrations.

In these earlier studies it was observed that the Tarasov function worked best for strictly linear macromolecules. Even for molecules like poly(ethylene terephthalate) corrections were necessary to account for the phenylene rings included in the backbone. Similarly, polystyrene[8], which has a larger mass in the side-chain than in the main chain, needed the skeletal vibrations of the phenyl group to be corrected for. In the present paper a larger series of branched hydrocarbon, methacrylic and acrylic polymers are analysed to find the influence of increasingly long side-chains on this treatment of heat capacities.

The computations follow the previously established procedure[1-11]. The experimental data are taken from the ATHAS data bank[14], which contains all published heat capacities, critically evaluated up to 1980. If needed, an update is performed. First, the experimental heat capacity at constant pressure $C_p$ is converted to $C_v$, the heat capacity at constant volume, used for all computations. Since compressibility and expansivity data are not available over the full temperature ranges for any of the analysed materials, this conversion is carried out using the Nernst–Lindemann equation:

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

where the constant $A_0$ is either fitted to the limited experimental information, or set equal to the universal constant $5.11 \times 10^{-3}$ K mol/J.[15] The mole in the $A_0$ constant refers to one mole of heavy atoms (C, O and N in our cases) and not one mole of repeating unit. $T_m^\circ$ is an approximation of the equilibrium melting temperature in kelvin. After this, the heat capacity contributions of the group vibrations are subtracted from $C_v$ to establish the experimental, skeletal heat capacity (at low temperature this is a minor correction). The remaining skeletal heat capacity is fitted to the Tarasov function $T(\theta_1/T, \theta_3/T)$. With the group vibrations and $\theta_1$ and $\theta_3$ established, the heat capacity can be calculated[16] at the fixed data bank intervals from 0 to 1000 K and an error discussion performed. (Intervals of 0.1 K from 0 to 1.0 K, 0.2 K to 2.0 K, 1 K to 10 K, 2 K to 20 K, 5 K to 30 K and 10 K to 1000 K.)

All frequencies in this paper are, for convenience, expressed in kelvin ($1\,K = 0.695\,cm^{-1} = 2.08 \cdot 10^{-10}$ Hz; $h\nu/k = \theta$). The detailed computer programs for the needed inversions and information on the Einstein, Debye and Tarasov functions are given elsewhere[13,16]. Note that in all these discussions only the two parameters, $\theta_1$ and $\theta_3$, are fitted to the experimental heat capacities and it will be shown that even these may in many cases be predictable.

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## POLYETHYLENE

Polyethylene (PE) is the basic polymer for all discussions. Its heat capacity has been measured in various temperature ranges over 100 times[14]. The group vibrations in *Table 1*[17] are coupled with $\theta_3$ values of 158 K for completely crystalline and 80 K for glassy PE, and $\theta_1$ values of 519 K (independent of crystallinity). The calculated data fit the experiment over the range from 0 to 450 K with an average and RMS deviation of 1.6 ± 4.9 %. This deviation range is somewhat above the experimental uncertainty and caused by larger deviations in the 300–375 K and 400–450 K temperature regions. It may be connected with experimental problems in separation of crystallinity effects and introduction of defects or premelting in the respective two temperature regions. The computed heat capacity is included in the summary graphs of *Figures 4*, *7* and *11*, below.

**Table 1** Group vibration frequencies in K ($h\nu/k$)

| Approx. vibrational mode | $N$ | Frequency (K) | Footnote |
|---|---|---|---|
| A. $CH_2$– (Polyethylene) | | | |
| Asymm. stretching | 1.00 | 4148 | *a* |
| Symm. stretching | 1.00 | 4098 | *a* |
| Bending | 1.00 | 2075 | *a* |
| Wagging | 0.35 | 1977 | *a* |
| | 0.65 | 1977–1698 | *a* |
| Twisting | 0.52 | 1874 | *a* |
| | 0.48 | 1874–1690 | *a* |
| C–C stretching | 0.34 | 1638–1378 | *a* |
| | 0.31 | 1525 | *a* |
| | 0.35 | 1525–1378 | *a* |
| Rocking | 0.04 | 1494 | *a* |
| | 0.59 | 1494–1038 | *a* |
| | 0.37 | 1079 | *a* |
| B. $CH_2$–$CHCH_3$– (Polypropylene) | | | |
| $CH_3$ asymm. stretching | 1.00 | 4262 | *b* |
| $CH_3$ asymm. stretching | 1.00 | 4259 | *b* |
| $CH_2$ asymm. stretching | 1.00 | 4213 | *b* |
| CH stretching | 1.00 | 4181 | *b* |
| $CH_3$ symm. stretching | 1.00 | 4147 | *b* |
| $CH_2$ symm. stretching | 1.00 | 4085 | *b* |
| $CH_3$ asymm. bending | 1.00 | 2107 | *b* |
| $CH_3$ asymm. bending | 1.00 | 2101 | *b* |
| $CH_2$ bending | 1.00 | 2094 | *b* |
| $CH_3$ symm. bending | 0.25 | 1987 | *b* |
| | 0.38 | 1987–1973 | *b* |
| | 0.37 | 1973 | *b* |
| CH bending | 0.42 | 1973–1963 | *b* |
| | 0.58 | 1966 | *b* |
| CH bending | 0.64 | 1944 | *b* |
| | 0.28 | 1944–1916 | *b* |
| | 0.08 | 1916 | *b* |
| $CH_2$ wagging | 0.18 | 1876 | *b* |
| | 0.43 | 1876–1842 | *b* |
| | 0.39 | 1846 | *b* |
| $CH_2$ twisting | 0.33 | 1791–1722 | *b* |
| ($CH_3$-rocking) | 0.55 | 1722–1695 | *b* |
| | 0.12 | 1695 | *b* |
| C–C chain stretching | 0.16 | 1685 | *b* |
| | 0.84 | 1685–1650 | *b* |
| C–$CH_3$ stretching | 0.44 | 1614–1568 | *b* |
| | 0.56 | 1614–1534 | *b* |
| $CH_3$ rocking | 0.55 | 1521–1453 | *b* |
| ($CH_2$ wagging) | 0.45 | 1453 | *b* |
| $CH_3$ rocking | 0.65 | 1393–1361 | *b* |
| (C–C chain stretching) | 0.21 | 1361–1333 | *b* |
| | 0.14 | 1336 | *b* |
| $CH_2$ rocking | 0.52 | 1295–1222 | *b* |
| | 0.48 | 1289 | *b* |
| $CH_2$ bending | 1.00 | 2094 | *b* |
| $CH_3$ symm. bending | 0.25 | 1987 | *b* |
| | 0.38 | 1987–1973 | *b* |
| | 0.37 | 1973 | *b* |
| CH bending | 0.42 | 1973–1963 | *b* |
| | 0.58 | 1966 | *b* |
| CH bending | 0.64 | 1944 | *b* |
| | 0.28 | 1944–1916 | *b* |
| | 0.08 | 1916 | *b* |
| $CH_2$ wagging | 0.18 | 1876 | *b* |
| | 0.43 | 1876–1842 | *b* |
| | 0.39 | 1846 | *b* |
| $CH_2$ twisting | 0.33 | 1791–1722 | *b* |
| ($CH_3$ rocking) | 0.55 | 1722–1695 | *b* |
| | 0.12 | 1695 | *b* |
| C–C chain stretching | 0.16 | 1685 | *b* |
| | 0.84 | 1685–1650 | *b* |
| C–$CH_3$ stretching | 0.44 | 1614–1568 | *b* |
| | 0.56 | 1614–1534 | *b* |
| $CH_3$ rocking | 0.55 | 1521–1453 | *b* |
| ($CH_2$ wagging) | 0.45 | 1453 | *b* |
| $CH_3$ rocking | 0.65 | 1393–1361 | *b* |
| (C–C chain stretching) | 0.21 | 1361–1333 | *b* |
| | 0.14 | 1336 | |
| $CH_2$ rocking | 0.52 | 1295–1222 | *b* |
| | 0.48 | 1289 | *b* |
| C–C chain stretching | 0.17 | 1197 | *b* |
| | 0.55 | 1198–1167 | *b* |
| | 0.28 | 1167 | *b* |
| C. CO–O–(ester) | | | |
| C–COO stretching | 1.00 | 1215 | *c* |
| C=O stretching | 1.00 | 2530 | *c* |
| C–O stretching | 1.00 | 1800 | *c* |
| C=O in-plane bending | 1.00 | 980 | *c* |
| C=O out-of-plane bending | 1.00 | 840 | *c* |
| D. CO–O–H (acid) | | | |
| C–COO stretching | 1.00 | 1151 | *d* |
| C=O stretching | 1.00 | 2459 | *d* |
| C–O stretching | 1.00 | 1816 | *d* |
| O–H stretching | 1.00 | 5093 | *d* |
| O–H in-plane bending | 1.00 | 2122 | *e* |
| O–H out-of-plane bending | 1.00 | 1345 | *e* |
| C=O in-plane bending | 1.00 | 980 | *c* |
| C=O out-of-plane bending | 1.00 | 840 | *c* |
| *E.* $C\equiv N$ (nitrile) | | | |
| $C\equiv N$ stretching | 1.00 | 3219 | *f* |
| C–CN stretching | 1.00 | 1119 | *f* |
| C–CN wagging | 1.00 | 100–373 | *f* |
| $C\equiv N$ wagging | 1.00 | 90–200 | *f* |
| *F.* O–C (hetero-chain structures) | | | |
| stretching | 0.22 | 1385 | *c* |
| | 0.11 | 1632 | *c* |
| | 0.67 | 1632–1385 | *c* |
| *G.* $CH_2$–$CR_1R_2$ (double substituted structures) | | | |
| stretching | 1.00 | 1164–1680 | *g* |

[a] From normal mode calculation of polyethylene, ref. 17

[b] From normal mode calulation of polypropylene, ref. 18

[c] From discussion of polyesters, ref. 7

[d] From i.r. and Raman spectra, refs. 31, 32 and 33

[e] From carboxylic acid data, ref. 34

[f] From i.r. and Raman spectra of polyacrylonitrile, ref. 37

[g] From polypropylene, ref. 3

## POLYPROPYLENE

Measurements and calculations of the heat capacity of polypropylene (PP) have been detailed earlier[3]. It was found that the heat capacity is described best by using seven skeletal vibrations and the 20 group vibrations listed in *Table 1*. The group vibrations in *Table 1* are somewhat more detailed than those used before[3]; they are based on an isolated-chain, normal-mode calculation[18]. All heat capacity calculations were repeated with the new group vibrations, but hardly any changes resulted. Over the whole temperature range the new, calculated heat capacities agreed to better than ±0.25% with the prior, calculated ones[3]. A comparative plot of the cumulative group vibrational spectra of PP and PE shows that for the purpose of heat capacity calculation the group vibrations of PP can even be approximated by those of PE plus a single block of four vibrations of constant density (box distribution) between 1178 and 1900 K including mainly two $CH_3$ rocking and two C–C stretching vibrations. To this, the five rather narrow frequency range CH–$CH_3$ hydrogen bending vibrations at about 2015 K and the four equally narrow hydrogen stretching vibrations at about 4212 K need to be added (the third, symmetrical $CH_3$ rocking vibration at about 300 K (torsional) is included in the skeletal vibrations).

The heat capacity of crystalline PP leads to a $\theta_3$ of 91 K, that of amorphous PP to a $\theta_3$ of 78 K. The corresponding $\theta_1$ is 714 K for crystalline PP and 633 K for amorphous PP. The $\theta_3$ values of PP are close to $\theta_3$ of amorphous PE, which may be reasonable, considering the more open helical PP structure. The higher $\theta_1$ of PP than for PE cannot be deduced from the calculated isolated chain vibrations. Plots of the integral skeletal vibrations, as obtained by Barnes and Frankoni[17] for PE and by Zerbi and Piseri[18] for PP, show no significant differences. Both fluctuate about a straight line reaching from zero to about 800 K, i.e. both should have similar $\theta_1$ values, in contrast to the experiment.

## POLY-1-BUTENE

Low-temperature heat capacities of poly-1-butene (PB) are available only for one semicrystalline sample ($w^c = 0.44$) down to 22 K [14]. By comparison with PE and PP one expects nine skeletal vibrations and 27 group vibrations.

The group vibrations were analysed by Holland-Moritz and Sausen[19] using i.r. and Raman information. Their results agree well with a frequency spectrum made up of the PE and PP vibrations of *Table 1*. Subtracting the group-vibration heat capacity, the skeletal heat capacity up to 160 K was well represented by a $\theta_1$ value of 618 ± 12 K and $\theta_3$ of 93.1 ± 1.1 K. Using these $\theta_1$ and $\theta_3$ values, the group vibrations of *Table 1* for PE and PP and the universal $A_0$ value in equation (1), the calculated $C_p$ matches the measurements to −0.2 ± 1.5% up to 200 K (average and RMS errors).

*Figure 1* shows the computed heat capacities at constant volume and the experimental, data bank heat capacity at constant pressure. The differences between experiment and calculation are shown in *Figure 2*.

## POLY-1-PENTENE, POLY-1-HEXENE, POLY-1-HEPTENE AND POLY-1-OCTENE

Of these polymers the data bank[14] offers heat capacities for amorphous and semicrystalline poly-1-pentene (PPEN), but only from 200 to 230 K ($T_g = 233$ K), and for

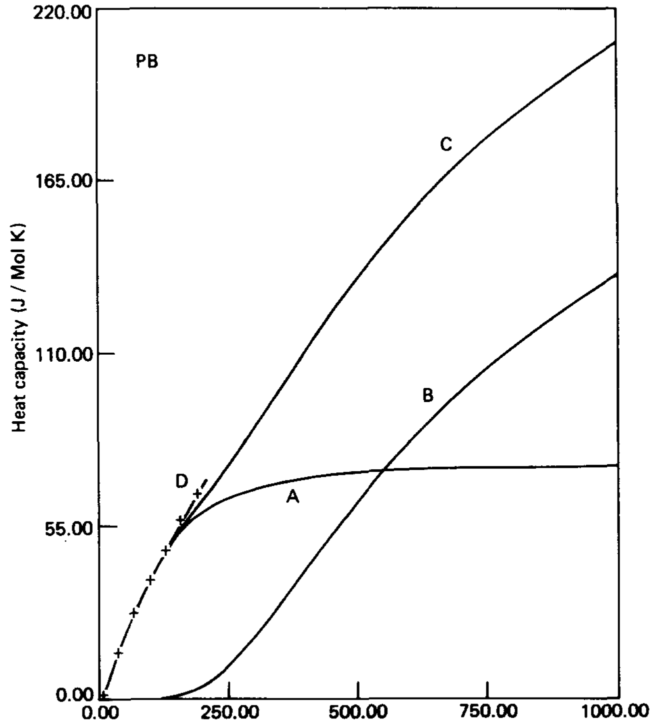

**Figure 1** Heat capacity of poly-1-butene, PB. Calculated curves of $C_V$. Curve A: skeletal vibration contribution, Tarasov treatment ($\theta_3 = 93.1$ K, $\theta_1 = 618$ K, N = 9). Curve B: group vibration contribution, for frequencies see *Table 1* PE + PP. Curve C: sum of curves A and B. Curve D: experimental $C_p$ as given in the data bank[14]

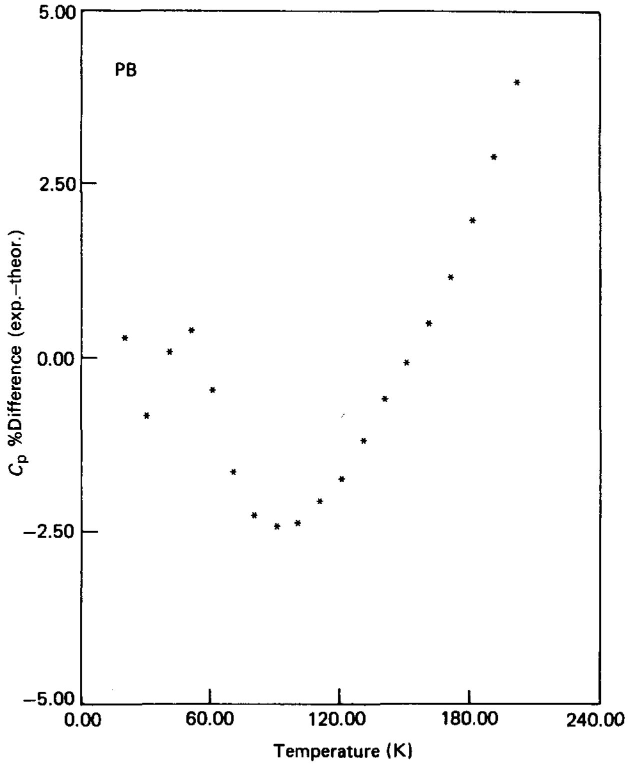

**Figure 2** Heat capacity difference $C_p$(experimental) − $C_p$(calculated) of poly-1-butene, PB, in % as a function of temperature. See *Figure 1* for calculation parameters, $A_0 = 5.11 \times 10^{-3}$ K mol/J, $T_m^\circ = 411$ K in equation (1)

amorphous poly-1-hexene (PH) from 20 to 220 K ($T_g = 233$ K).

The skeletal vibrations of the polymers are 11, 13, 15 and 17, respectively. The group vibrations were constructed using the appropriate number of sets of PE group vibrations (2, 3, 4 and 5, respectively) and that of PP. The experimental heat capacities were reproduced best with a $\theta_1$ of 580 K for PPEN and $562.6 \pm 23$ K (from 20 to 150 K) for PH. The low temperature data of PH permit a setting of $\theta_3 = 85.5$ K ($\pm 1.4$ K from 20 to 150 K). The group vibrations are in good accord with the discussion of the poly(alkyl ethylene)s by Holland-Moritz and Sausen[20]. The difference of the experimental and calculated heat capacities are shown in *Figure 3*.

With the $\theta_1$ values of PE, PP, PB, PPEN and PH established, those of poly-1-heptene (PHEP) and poly-1-octene (PO) were extrapolated to be 555 K and 550 K, respectively. Similarly the $\theta_3$-values of PPEN, PHEP and PO were guessed at on the basis of the other polymers to be about 95 K for all three polymers. The computed heat capacities of all branched polyethyelenes are compared in *Figure 4*.

## POLY(METHYL METHACRYLATE)

The series of polyacrylates and polymethacrylates described next can be derived from the branched polyethylenes by inclusion of an ester group CO–O– in the side chain. Aliphatic polyesters have been discussed earlier[7], and it will be shown that there exists little difference in the influence of an ester group on heat capacity in the main- or side-chain. *Tables 2* and *3* list the types of group vibrations and number of skeletal vibrations for all further analysed polymers.

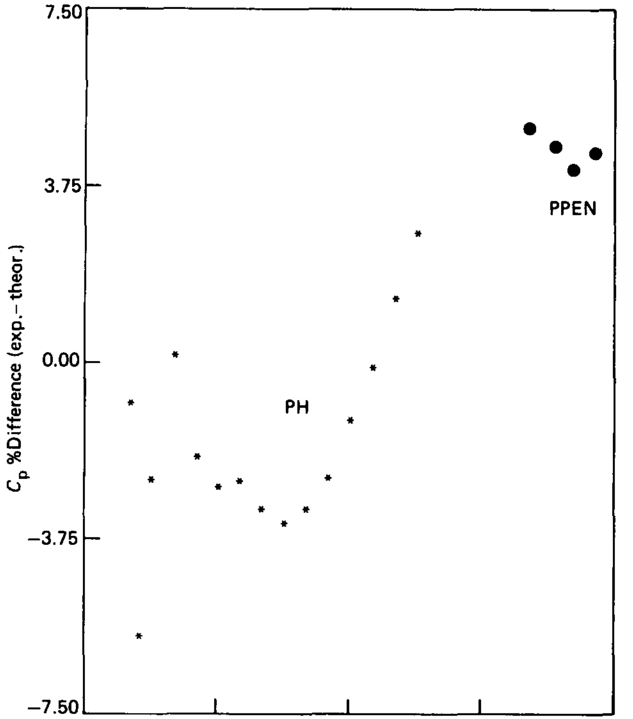

**Figure 3** Heat capacity difference $C_p$(experimental) − $C_p$(calculated) of poly-1-pentene, PPEN, and poly-1-hexene, PH, in % as a function of temperature. (●) PPEN, (•) PH. Calculation parameters see text, universal $A_0$ for equation (1). $T_m^o = 403$ K and 303 K, respectively

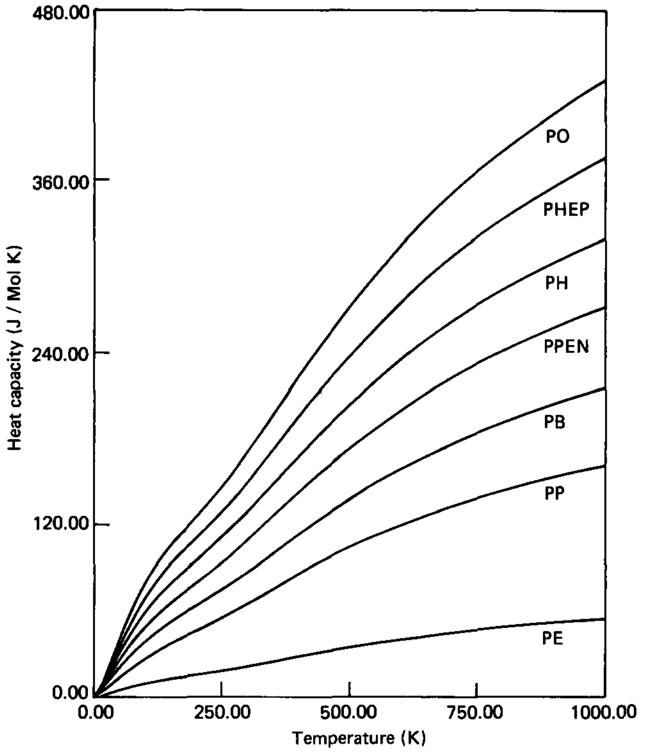

**Figure 4** Heat capacity at constant volume of polyethylene, PE; polypropylene, PP; poly-1-butene, PB; poly-1-pentene, PPEN; poly-1-hexene, PH; poly-1-heptene, PHEP; and poly-1-octene, PO. For calculation parameters see text

The first member of this series is PMMA. Its heat capacity was well described in the data bank (1980)[14]. Since 1980, however, the earlier measurements of O'Reilly *et al.*[21] between 80 K and the glass transition temperature (378 K) have been published and were included in the ATHAS data bank (1986). As in the prior treatment[14] the new results were fitted into spline functions and listed together with the earlier tabulations[14] from 80 K to the glass transition in the ATHAS standard temperature intervals. As justified before[14], Sochava and Trapeznikova's data and Rabinovich and Lebedev's data from 190 to 300 K, as well as Pavlinov *et al.*'s data from 290 to 360 K were excluded in the further analysis because of larger deviations. The new data point of O'Reilly *et al.* at 230 K is also apparently in error (too high) and is omitted. All other data were then averaged at each temperature. These average data were further smoothed by curve fitting from 60 to 200 K into the equation

$$C_p = \exp[0.126487(\ln T)^3 - 1.92094(\ln T)^2 + 10.4986 \ln T - 15.9170] \text{ J/mol K} \qquad (2)$$

with a root mean-square (RMS) deviation of ±0.4%. The data from 150 to 370 K were curve fitted into the equation

$$C_p = \exp[0.0494295(\ln T)^3 - 0.736510(\ln T)^2 + 4.43689 \ln T - 5.58777] \text{ J/mol K} \qquad (3)$$

with a RMS deviation of ±0.3%. The new recommended data (1986) were obtained from equation (2) over the temperature range from 60 to 200 K, and from equation (3) over the temperature range from 210 to 370 K. The data from 0.2 to 50 K were not changed from the recommended data (1980). The new $C_p$ data were used to

**Table 2** Number of vibrational modes of methacrylate polymers and polyisobutylene

| Approximate mode | PMMA[a] | PEMA[b] | PNBMA[c] | PMAA[d] | PIB[e] |
|---|---|---|---|---|---|
| A. $CH_2$ | | | | | |
| $CH_2$ asym. stretch | 1 | 2 | 4 | 1 | 1 |
| $CH_2$ sym. stretch | 1 | 2 | 4 | 1 | 1 |
| $CH_2$ bend | 1 | 2 | 4 | 1 | 1 |
| $CH_2$ wag | 1 | 2 | 4 | 1 | 1 |
| $CH_2$ twist | 1 | 2 | 4 | 1 | 1 |
| $CH_2$ rock | 1 | 2 | 4 | 1 | 1 |
| C–C stretch (PP) | 1 | 1 | 1 | 1 | 1 |
| $CH_2$–O stretch | | 1 | 1 | | |
| C–C stretch (PE) | | | 2 | | |
| B. $CH_3$ | | | | | |
| $CH_3$ asym. stretch | 2 | 2 | 2 | 1 | 2 |
| $CH_3$ asym. stretch | 2 | 2 | 2 | 1 | 2 |
| $CH_3$ sym. stretch | 2 | 2 | 2 | 1 | 2 |
| $CH_3$ asym. deformation | 2 | 2 | 2 | 1 | 2 |
| $CH_3$ asym. deformation | 2 | 2 | 2 | 1 | 2 |
| $CH_3$ sym. deformation | 2 | 2 | 2 | 1 | 2 |
| $CH_3$ rock | 4 | 4 | 4 | 2 | 4 |
| $CH_3$–C stretch | 1 | 2 | 2 | 1 | 2 |
| $CH_3$–O stretch | 1 | | | | |
| C. COO | | | | | |
| C–COO stretch | 1 | 1 | 1 | – | – |
| C=O stretch | 1 | 1 | 1 | – | – |
| C–O stretch | 1 | 1 | 1 | – | – |
| C=O in plane bend | 1 | 1 | 1 | – | – |
| C=O out of plane bend | 1 | 1 | 1 | – | – |
| D. COOH | | | | | |
| C–COOH stretch | | | | 1 | |
| C=O stretch | | | | 1 | |
| C–O stretch | | | | 1 | |
| O–H stretch | | | | 1 | |
| O–H in plane bend | | | | 1 | |
| out of plane bend | | | | 1 | |
| C=O in plane bend | | | | 1 | |
| out of plane bend | | | | 1 | |
| E. $C(R_1R_2)$ | | | | | |
| C–C stretch (PP) | 1 | 1 | 1 | 1 | 1 |
| F. Skeletal vibrations | 14 | 16 | 20 | 11 | 10 |
| Total | 45 | 54 | 72 | 36 | 36 |

[a] PMMA: poly(methyl methacrylate)
[b] PEMA: poly(ethyl methacrylate)
[c] PNBMA: poly(*N*-butyl methacrylate)
[d] PMMA: poly(methacrylic acid)
[e] PIB: polyisobutylene

**Table 3** Number of vibrational modes of acrylate polymers and polyacrylonitrile

| Approximation mode | PMA[a] | PEA[b] | PNBA[c] | PODA[d] | PAN[e] |
|---|---|---|---|---|---|
| A. $CH_2$ | | | | | |
| $CH_2$ asym. stretch | 1 | 2 | 4 | 18 | 1 |
| $CH_2$ sym. stretch | 1 | 2 | 4 | 18 | 1 |
| $CH_2$ bend | 1 | 2 | 4 | 18 | 1 |
| $CH_2$ wag | 1 | 2 | 4 | 18 | 1 |
| $CH_2$ twist | 1 | 2 | 4 | 18 | 1 |
| $CH_2$ rock | 1 | 2 | 4 | 18 | 1 |
| C–C stretch (PP) | 1 | 1 | 1 | 1 | 1 |
| $CH_2$–O stretch | | 1 | 1 | 1 | |
| C–C stretch (PE) | | | 2 | 16 | |
| B. $CH_3$ | | | | | |
| $CH_3$ asym. stretch | 1 | 1 | 1 | 1 | |
| $CH_3$ asym. stretch | 1 | 1 | 1 | 1 | |
| $CH_3$ sym. stretch | 1 | 1 | 1 | 1 | |
| $CH_3$ asym. deformation | 1 | 1 | 1 | 1 | |
| $CH_3$ asym. deformation | 1 | 1 | 1 | 1 | |
| $CH_3$ sym. deformation | 1 | 1 | 1 | 1 | |
| $CH_3$ rock | 2 | 2 | 2 | 2 | |
| $CH_3$–C stretch | | 1 | 1 | 1 | |
| $CH_3$–O stretch | 1 | | | | |
| C. CH | | | | | |
| C–H stretch | 1 | 1 | 1 | 1 | 1 |
| C–H bend | 2 | 2 | 2 | 2 | 2 |
| C–C stretch (PP) | 1 | 1 | 1 | 1 | 1 |
| D. COO | | | | | |
| C–COO stretch | 1 | 1 | 1 | 1 | |
| C=O stretch | 1 | 1 | 1 | 1 | |
| C–O stretch | 1 | 1 | 1 | 1 | |
| C=O in plane bend | 1 | 1 | 1 | 1 | |
| C=O out of plane bend | 1 | 1 | 1 | 1 | |
| E. CN | | | | | |
| C≡N stretch | | | | | 1 |
| C–CN stretch | | | | | 1 |
| C–CN wag | | | | | 1 |
| C≡N wag | | | | | 1 |
| F. Skeletal vibrations | 11 | 13 | 17 | 45 | 6 |
| Total | 36 | 45 | 63 | 189 | 21 |

[a] PMA: poly(methyl acrylate)
[b] PEA: poly(ethyl acrylate)
[c] PNBA: poly(n-butyl acrylate)
[d] PODA: poly(octadecyl acrylate)
[e] PAN: polyacrylonitrile

recalculate enthalpy, entropy and free enthalpy from 60 to 370 K. All new, recommended thermodynamic data of PMMA (1986) are listed in *Table 4*.

Although the i.r. and Raman spectra of PMMA have been studied by several authors[22–28], there is no definitive, full assignment of the vibrational spectrum of PMMA. The approximate group vibrations listed in *Table 1*, derived from linear, aliphatic polyesters, are, however, close to the reported experimental i.r. and Raman frequencies of PMMA. For the $CH_2$ group, the deviations of the stretching frequencies are less than 3%, the bending vibrational frequency is almost the same, the upper limit of the wagging box-distribution is close to the experimental PMMA data and the reported rocking frequency lies within the approximate box distribution of *Table 1*. No vibration corresponding to the $CH_2$ twisting mode of polyethylene was observed in the experimental spectrum of PMMA. For the ($\alpha$)$CH_3$ group, the stretching and deformation frequencies are in agreement with the reported data within about 2%, and the reported rocking frequency also lies within the approximated box distribution. For the (O)$CH_3$ group, somewhat higher

**Table 4** Thermodynamic data for amorphous poly(methyl methacrylate)

| $T$ | $C_p$ ($J K^{-1} mol^{-1}$) (recommended) | $C_p$ ($J K^{-1} mol^{-1}$) (calculated) | $\Delta^a$ (%) | $H_T - H_0$ ($J mol^{-1}$) | $S - S_0^a$ ($J K^{-1} mol^{-1}$) |
|---|---|---|---|---|---|
| 0.0 | 0.0 | 0.0 | – | 0.0 | 0.0 |
| 0.2 | 0.0001248 | – | – | 0.0000125 | 0.0000624 |
| 0.3 | 0.0002101 | – | – | 0.0000292 | 0.0001286 |
| 0.4 | 0.0003451 | – | – | 0.0000570 | 0.0002068 |
| 0.5 | 0.0005411 | 0.0004 | 26.1 | 0.0001013 | 0.0003040 |
| 0.6 | 0.0008120 | 0.0006 | 26.1 | 0.0001690 | 0.0004258 |
| 0.7 | 0.001173 | 0.0010 | 14.7 | 0.0002682 | 0.0005772 |
| 0.8 | 0.001641 | 0.0015 | 8.6 | 0.0004089 | 0.0007636 |
| 0.9 | 0.002234 | 0.0022 | 1.5 | 0.0006027 | 0.0009903 |
| 1.0 | 0.002971 | 0.0030 | −0.98 | 0.0008629 | 0.001263 |
| 1.2 | 0.004959 | 0.0052 | −4.9 | 0.001656 | 0.001973 |
| 1.4 | 0.007776 | 0.0082 | −5.5 | 0.002929 | 0.002942 |
| 1.6 | 0.01161 | 0.0123 | −5.9 | 0.004868 | 0.004223 |
| 1.8 | 0.01667 | 0.0175 | −5.0 | 0.007639 | 0.005843 |
| 2.0 | 0.02316 | 0.0240 | −3.6 | 0.01157 | 0.007896 |
| 3.0 | 0.08543 | 0.0810 | 5.2 | 0.06586 | 0.02792 |
| 4.0 | 0.2215 | 0.1920 | 13.3 | 0.2193 | 0.06985 |
| 10.0 | 1.667 | 2.5612 | −53.6 | 5.914 | 0.7391 |
| 20.0 | 7.965 | 9.4246 | −18.3 | 54.12 | 3.5690 |
| 30.0 | 14.67 | 15.8881 | −8.3 | 167.3 | 8.005 |
| 40.0 | 21.38 | 21.9345 | −2.6 | 346.7 | 13.12 |
| 50.0 | 27.67 | 27.7989 | −0.5 | 592 | 18.56 |
| 60.0 | 34.72 | 33.5723 | 3.3 | 906 | 24.26 |
| 70.0 | 40.99 | 39.2701 | 4.2 | 1285 | 30.09 |
| 80.0 | 46.76 | 44.8675 | 4.0 | 1724 | 35.94 |
| 90.0 | 52.12 | 50.3253 | 3.4 | 2219 | 41.77 |
| 100.0 | 57.14 | 55.6082 | 2.7 | 2765 | 47.52 |
| 110.0 | 61.89 | 60.6943 | 1.9 | 3361 | 53.19 |
| 120.0 | 66.43 | 65.5785 | 1.3 | 4002 | 58.77 |
| 130.0 | 70.80 | 70.2693 | 0.75 | 4689 | 64.27 |
| 140.0 | 75.03 | 74.7857 | 0.33 | 5418 | 69.67 |
| 150.0 | 79.16 | 79.1525 | 0.01 | 6189 | 74.99 |
| 160.0 | 83.22 | 83.3973 | −0.21 | 7001 | 80.23 |
| 170.0 | 87.22 | 87.5472 | −0.38 | 7854 | 85.39 |
| 180.0 | 91.19 | 91.6274 | −0.48 | 8746 | 90.49 |
| 190.0 | 95.14 | 95.6604 | −0.55 | 9678 | 95.53 |
| 200.0 | 99.08 | 99.6652 | −0.59 | 10649 | 100.5 |
| 210.0 | 103.1 | 103.6570 | −0.54 | 11660 | 105.4 |
| 220.0 | 107.0 | 107.6490 | −0.61 | 12711 | 110.3 |
| 230.0 | 110.9 | 111.6489 | −0.68 | 13801 | 115.2 |
| 240.0 | 114.9 | 115.6652 | −0.67 | 14930 | 120.0 |
| 250.0 | 118.8 | 119.6994 | −0.76 | 16098 | 124.7 |
| 260.0 | 122.7 | 123.7569 | −0.86 | 17305 | 129.5 |
| 270.0 | 126.6 | 127.8355 | −0.98 | 18551 | 134.2 |
| 273.15 | 127.9 | 129.1456 | – | 18956 | 135.7 |
| 280.0 | 130.5 | 131.9373 | −1.1 | 19837 | 138.9 |
| 290.0 | 134.5 | 136.0598 | −1.2 | 21162 | 143.5 |
| 298.15 | 137.7 | 139.4299 | – | 22274 | 147.3 |
| 300.0 | 138.5 | 140.2011 | −1.2 | 22527 | 148.1 |
| 310.0 | 142.4 | 144.3607 | −1.4 | 23932 | 152.7 |
| 320.0 | 146.4 | 148.5334 | −1.5 | 25376 | 157.3 |
| 330.0 | 150.4 | 152.7187 | −1.5 | 26860 | 161.9 |
| 340.0 | 154.5 | 156.9136 | −1.6 | 28384 | 166.4 |
| 350.0 | 158.5 | 161.1149 | −1.6 | 29949 | 171.0 |
| 360.0 | 162.6 | 165.3230 | −1.7 | 31555 | 175.5 |
| 370.0 | 166.7 | 169.5337 | −1.7 | 33201 | 180.0 |
| 378.0 | 170.0 ($T_g$ glass) | 172.9861 | – | 34285 | 182.5 |
| 378.0 | 202.7 ($T_g$ liquid) | – | – | 34285 | 182.5 |
| 380.0 | 203.2 | – | – | 34691 | 183.5 |
| 390.0 | 205.5 | – | – | 36734 | 188.8 |
| 400.0 | 207.9 | – | – | 38801 | 194.1 |
| 410.0 | 210.3 | – | – | 40892 | 199.2 |
| 430.0 | 215.0 | – | – | 45146 | 209.4 |
| 440.0 | 217.4 | – | – | 47308 | 214.3 |
| 450.0 | 219.8 | – | – | 49494 | 219.2 |
| 460.0 | 222.2 | – | – | 51704 | 224.1 |
| 470.0 | 224.5 | – | – | 53937 | 228.9 |
| 480.0 | 226.9 | – | – | 56194 | 233.7 |
| 490.0 | 229.3 | – | – | 58475 | 238.4 |
| 500.0 | 231.7 | – | – | 60780 | 243.0 |
| 510.0 | 234.0 | – | – | 63109 | 247.6 |
| 520.0 | 236.4 | – | – | 65461 | 252.2 |
| 530.0 | 238.8 | – | – | 67837 | 256.7 |
| 540.0 | 241.1 | – | – | 70236 | 261.2 |
| 550.0 | 243.5 | – | – | 72659 | 265.6 |

[a] $\Delta$ is the deviation of the experimental $C_p$ from the calculated $C_p$, i.e. $[C_p(\text{experimental}) - C_p(\text{calculated})]/C_p(\text{experimental})$

frequencies were observed than for the ($\alpha$)CH$_3$, but the deviations of the frequencies of *Table 1* from the experimental PMMA data are still less than 4%. For the COO– group, the C=O stretching frequency is very close to the experimental PMMA data. The only larger differences (up to 30%) are those of the $\nu_s$(C–CO–O) and the C=O in-plane and out-of-plane bending vibrations. These three vibrations are also known to be sensitive to the environment of the carboxyl group[33,34]. Since no full distributions of these modes are available it is not possible to assess the error introduced by using the frequencies of *Table 1*. These frequencies are, however, low enough that some of the error could be compensated by the experiment-fitted skeletal vibrations.

The three-dimensional Debye-temperature $\theta_D$ of amorphous PMMA was obtained by inversion of the experimental $C_v$ in the temperature range 0.8 to 4 K ($\theta_D = 144.5 \pm 3.2$ K). Below 0.8 K $\theta_D$ decreases with temperature, as is usually found for glassy materials[29]. In the temperature range from 40 K to 250 K $\theta_1$ becomes then $679.5 \pm 16.6$ K. In the same temperature range $\theta_3$ varies little, it is $66.7 \pm 0.8$ K.

For the conversion of $C_p$ to $C_v$ the experimental room temperature value of $A_0$ ($3.43 \times 10^{-3}$ K mol/J)[15] and an estimated $T_m^\circ$ from melting of isotactic PMMA (450 K)[21] were used in equation (1).

For the given group vibrations of *Table 1* and $\theta_1$ and $\theta_3$, above, $C_v$ was calculated from 0 to 1000 K as shown in *Figure 5*. The deviation of the experimental $C_p$ from the calculated $C_p$ is plotted in *Figure 6*. The average and RMS deviations are $-0.32 \pm 2.2$% for the temperature from 30 to 370 K. Relatively larger deviations between 4 and 30 K are likely caused by error in measurement (see data bank discussion). Below 1 K the chosen $\theta_D$ does not represent the data (see above). Above 160 K the calculated $C_p$ gets gradually larger than the experimental (+0.2% at 160 K, +1.7% at 370 K), which may rest with the uncertainty in the $A_0$ value. From the calculated $C_v$ and the experimental $C_p$ a fitted $A_0$ for minimal error was obtained to be $2.58 \times 10^{-3}$ K mol J$^{-1}$, well within the present experimental uncertainty of compressibility and expansivity data[15].

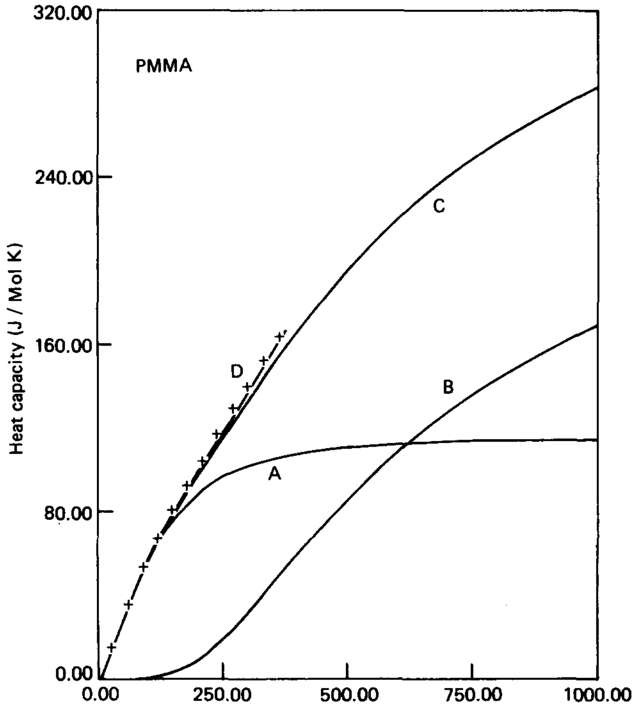

**Figure 5** Heat capacity of poly(methyl methacrylate), PMMA. Calculated curves of $C_V$. Curve A: skeletal vibration contribution, Tarasov treatment ($\theta_3 = 66.7$ K, $\theta_1 = 679.5$ K, N = 14). Curve B: group vibration contribution, for frequencies see *Tables 1* and *2*. Curve C: sum of curves A and B. Curve D: experimental $C_p$ as given in *Table 4*

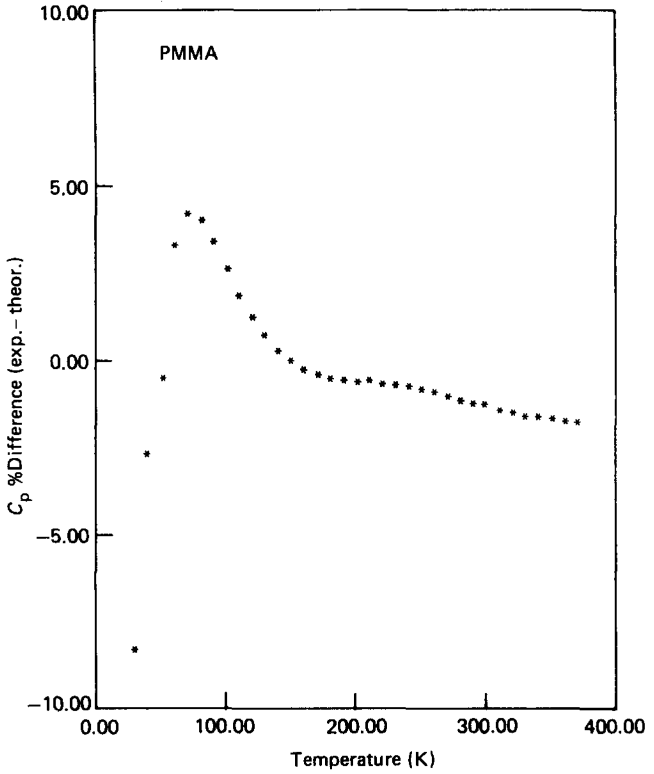

**Figure 6** Heat capacity difference $C_p$(experimental) – $C_p$(calculated) of poly(methyl methacrylate), PMMA, in % as a function of temperature. See *Figure 5* for calculation parameters. $A_0 = 3.43 \times 10^{-3}$ K mol/J; $T_m^\circ = 450$ K in equation (1)

## POLY(ETHYL METHACRYLATE)

There is no experimental $C_p$ below 80 K for poly(ethyl methacrylate) (PEMA), so that the recommended data from 80 to 330 K[14] were used to obtain $\theta_1$ after conversion to $C_v$ and subtraction of the group contributions as listed in *Tables 1* and *2*. In this temperature range $\theta_1 = 622.2 \pm 24.7$ K. With $\theta_1$ established, $\theta_3$ was estimated to be 89.9 K, but at 80 K and higher the contribution of $\theta_3$ to $C_p$ is already almost fully excited, i.e. the $\theta_3$ value may contain a larger error. A second estimate of $\theta_3 = 60$ K was based on the $\theta_3$ values for PMMA and PNBMA. Both $\theta_3$ values were used to calculate $C_p$. The heat capacity is plotted in *Figure 7*. *Figure 8* shows the deviation of the experimental $C_p$ from the calculated $C_p$; the average and RMS deviations are $-0.06 \pm 2.0$% with $\theta_3 = 89.9$ K, and $-0.17 \pm 1.9$% with $\theta_3 \approx 60$ K in the temperature range of 80–330 K.

In the calculation of $C_p$ the same $A_0$ was assumed as for PMMA, and it was assumed that there exists a parallel relation between $T_g$ and $T_m^\circ$ for methacrylate polymers in order to obtain a guess of $T_m^\circ$ of PEMA.

## POLY(n-BUTYL METHACRYLATE)

There are recommended heat capacity data for poly(n-butyl methacrylate) (PNBMA) from 80 to 290 K[14]. The value of $\theta_1$ was found to be 558.9 ± 25.9 K between 80 and 190 K when the universal $A_0$ was used with the group vibrations of *Tables 1* and *2*. All of the lower temperature $\theta_3$ values were averaged and led to $\theta_3 = 58$ K. The calculated heat capacity is plotted in *Figure 7*. *Figure 8* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations are $2.6 \pm 3.6\%$ in the temperature region 80–290 K. With increasing temperature, the calculated $C_p$ gets gradually smaller than the experimental data. It may well be that this is an indication of a broader glass transition, as observed for polyethylene[30].

## POLY(METHACRYLIC ACID)

The i.r. and Raman spectra of poly(methacrylic acid) (PMAA) have been studied by several authors[31–34]. It was found that PMAA has a helical conformation and that there exist intramolecular hydrogen bonds causing some shift in the H vibration frequencies. The vibration modes and frequencies of the –COOH group are listed in *Tables 1* and *2*.

The recommended $C_p$ data[14] begin at 50 K and go up to 300 K. The $\theta_1$ was observed to be quite constant in this temperature range; its average value is 652.5 ± 13.2 K. The value of $\theta_3$ was also quite constant in the temperature range of 50–130 K (106.7 ± 4.2 K). The heat capacity is plotted in *Figure 7*. *Figure 8* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations are $+0.66 \pm 0.42\%$. The recommended data[14] between 10 and 40 K are not based on experiment, but were obtained from curve fitted functions reported in the literature. They also coincide with our calculated $C_p$ well (at 20 K—0.2%, at 30 K—3.4%).

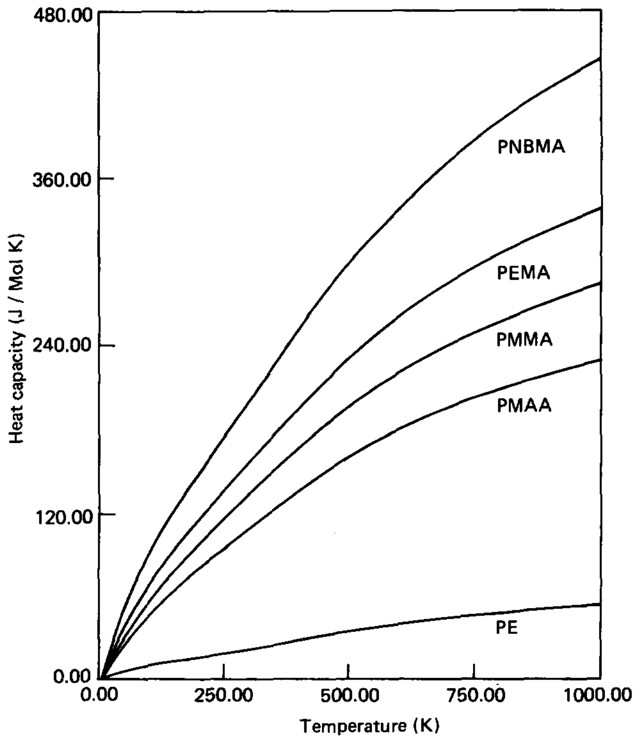

**Figure 7** Heat capacity at constant volume of polyethylene, PE; poly(methyl methacrylate), PMMA; poly(ethyl methacrylate), PEMA; poly(n-butyl methacrylate), PNBMA and poly(methacrylic acid), PMAA. For calculation parameters see text

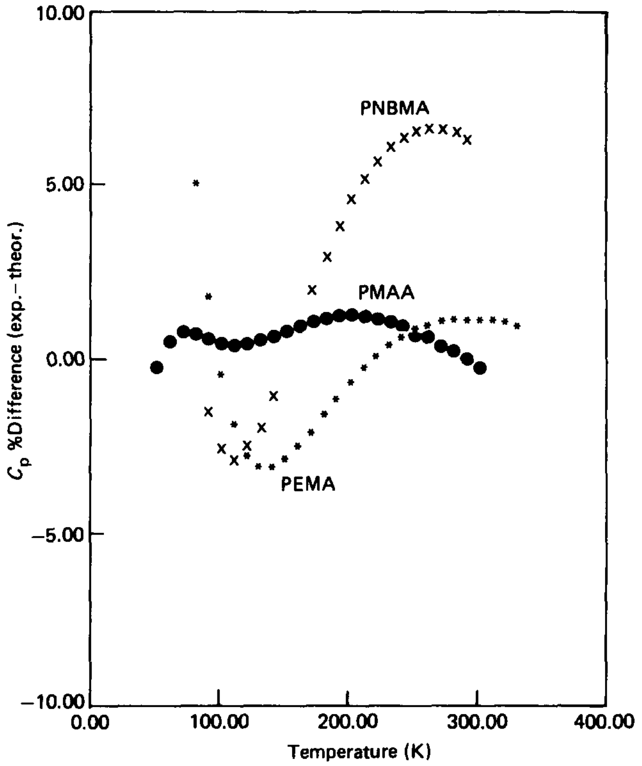

**Figure 8** Heat capacity difference $C_p$(experimental) − $C_p$(calculated) of poly(ethyl methacrylate), PEMA, poly(*n*-butyl metacrylate), PNBMA and poly(methacrylic acid), PMAA. (•) PEMA, (×) PNBMA, (●) PMAA. Assumed $A_0$ and $T_m^\circ$: $3.43 \times 10^{-3}$, $5.11 \times 10^{-3}$ and $3.43 \times 10^{-3}$ K mol/J; 402.4, 348.8 and 596.4 K, respectively

## POLY(METHYL ACRYLATE)

The i.r. spectrum of poly(methyl acrylate) (PMA) has been reported[35], and most of the approximate vibrational frequencies listed in *Table 1* are close to these reported data. Experimental heat capacity data for PMA are available between 50 and 270 K[14] and were used to calculate $\theta_1$ (552 ± 10.4 K in the temperature range from 50 to 180 K). We chose $\theta_3$ at the lowest temperature heat capacity to get highest precision ($\theta_3 = 86.3$ K at 50 K). The calculated heat capacity is plotted in *Figure 9*. *Figure 10* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations are $0.09 \pm 1.8\%$ in the temperature region 50–270 K. The calculated $C_p$ is much larger than the recommended data between 10 and 40 K. In this region the recommended data were based on extrapolations in the literature. The present calculations suggest that these extrapolations are in error and the heat capacities should be replaced by the present, calculated values.

In the heat capacity calculation of acrylate polymers, it was assumed that $T_m^\circ$ equals 3/2 $T_g$. The thus obtained $T_m^\circ$ coincides with an estimate from the melting point of poly(tert-butyl acrylate)[36] based on parallel relations between $T_g$ and $T_m$. The experimental value of $A_0$ for PMMA was taken also for the $C_p$ calculation of PMA and PEA, but the universal $A_0$ was taken for the $C_p$ calculation of PNBA (and also for PNBMA).

## POLY(ETHYL ACRYLATE)

The recommended heat capacity data[14] for poly(ethyl acrylate) (PEA) between 90 and 240 K were used to

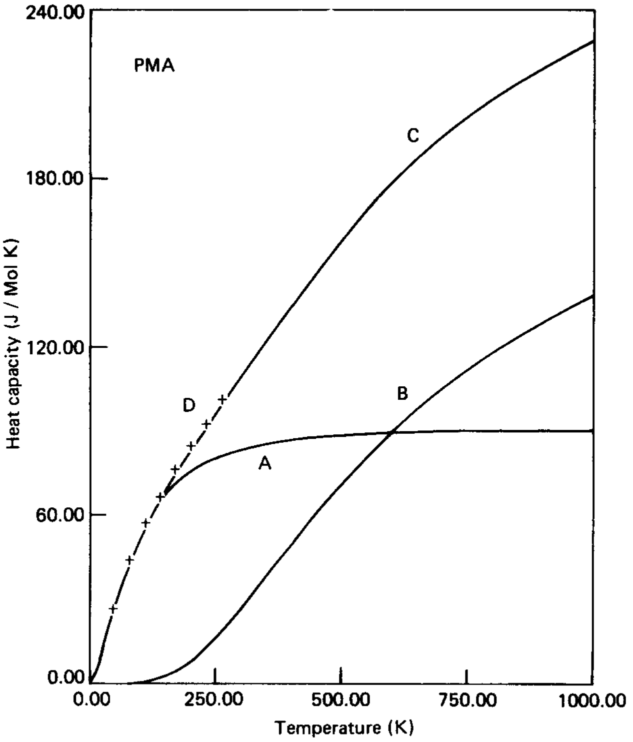

**Figure 9** Heat capacity of poly(methyl acrylate), PMA. Calculated curves of $C_V$. Curve A: skeletal vibration contribution, Tarasov treatment ($\theta_3 = 86.3$ K, $\theta_1 = 552$ K, N = 11). Curve B: group vibration contribution, for frequencies see *Tables 1* and *3*. Curve C: sum of curves A and B. Curve D: experimental $C_p$ as given in the data bank[14]

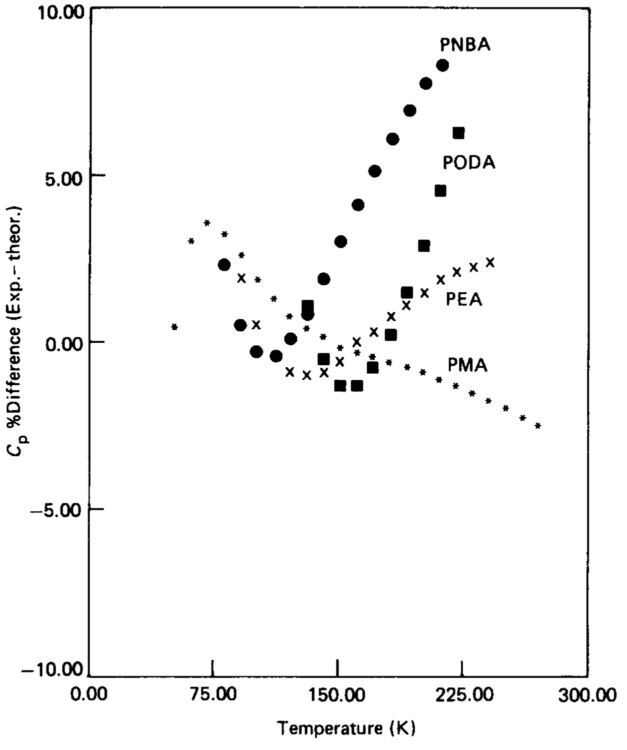

**Figure 10** Heat capacity difference $C_p$(experimental) − $C_p$(calculated) of poly(methyl acrylate), PMA; poly(ethyl acrylate), PEA; poly(n-butyl acrylate), PNBA, and poly(octadecyl acrylate), PODA. (*) PMA, (×) PEA, (●) PNBA and (■) PODA. Assumed $A_0$ and $T_m^\circ$: $3.43 \times 10^{-3}$, $3.43 \times 10^{-3}$, $5.11 \times 10^{-3}$ and $5.11 \times 10^{-3}$ K mol/J; 418.5, 373.5, 313.7 and 352 K, respectively

calculate $\theta_1$ after subtraction of the group vibration contributions (see *Tables 1* and *3*) ($\theta_1 = 543 \pm 13$ K in the temperature region 90–210 K). The value for $\theta_3$ was obtained to be 89.2 K at 100 K. The heat capacity is plotted in *Figure 11*. *Figure 10* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations are $0.67 \pm 1.2\%$.

## POLY(n-BUTYL ACRYLATE)

The recommended heat capacity data for poly(n-butyl acrylate) (PNBA) between 80 and 210 K[14] were used to calculate $\theta_1$. The average $\theta_1$ is $517.5 \pm 8.2$ K in the temperature region 80–140 K. The value for $\theta_3$ is 88.2 K, chosen at 90 K. The heat capacity is plotted in *Figure 11*. *Figure 10* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations are $3.3 \pm 3.1\%$. As found also for PNBMA, the calculated $C_p$ becomes with increasing temperature gradually smaller than the experimental $C_p$. The percentage deviation from experimental data reaches 8.3 % at $T_g$. Again, it suggests a broad glass transition because of the long $CH_2$– sequence in the side chain.

## POLY(OCTADECYL ACRYLATE)

Experimental heat capacity data for poly(octadecyl acrylate) (PODA) are available between 130 and 300 K[42] and were used to calculate $\theta_1$. The average $\theta_1$ is $519.8 \pm 22.8$ K in the temperature region 130–200 K. The value for $\theta_3$ is 84.4 K. The calculated $C_v$ is plotted in *Figure 11*. *Figure 10* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations between 130 and 220 K are $1.2 \pm 2.6\%$. Above 220 K, the calculated $C_p$ becomes gradually smaller than the experimental $C_p$ as the melting temperature is approached (352 K) (250 K: 11.7%, 300 K: 20.8%).

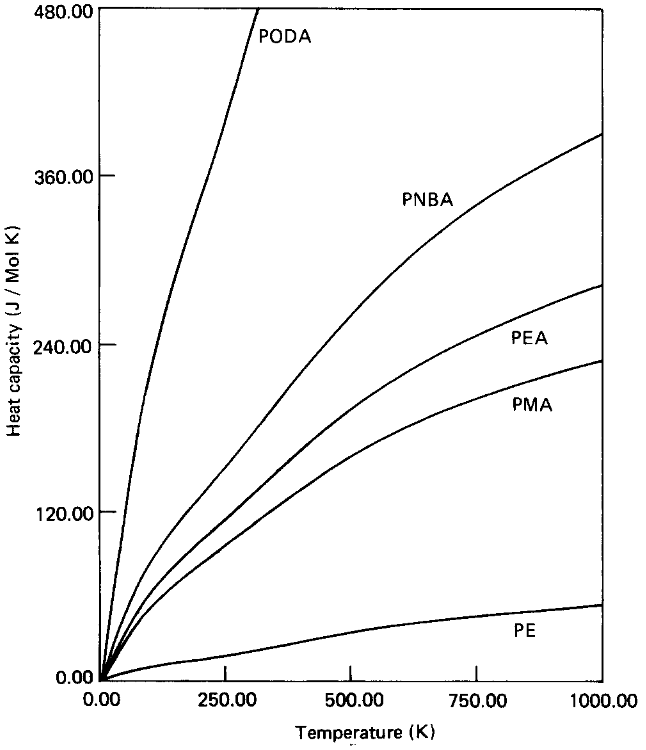

**Figure 11** Heat capacity at constant volume of polyethylene, PE; poly(methyl acrylate), PMA; poly(ethyl acrylate), PEA; poly(n-butyl acrylate), PNBA; and poly(octadecyl acrylate), PODA. For calculation parameters see text

## POLYACRYLONITRILE

I.r. spectroscopic studies[37–41] have been limited by changes in the absorption bands for different thermal histories. According to Krimm[37], there should be six normal vibrational modes of the –CN group: C–CN stretching, C≡N stretching, C–CN bending and wagging, C≡N bending and wagging. Their measured vibrational frequencies are 1119.4 K, 3218.6 K, 765.4 K, 372.6 K, 618.7 K and 182.7 K, respectively. Since each C contributes two skeletal vibrations, only four of the group vibrations are considered in *Table 1*. Meanwhile, the experimental, skeletal heat capacity between 40 and 60 K is higher than expected for six skeletal vibrations (6 R). This means there are some contributions of group vibrations with lower frequencies to the heat capacity. Thus we assume that the C–CN and C≡N bending frequencies (764.4 K, 618.7 K) couple strongly to the skeletal vibrations. Furthermore, C–CN and C≡N wagging frequencies were changed to two box distributions due to the probable broad distribution of these bonds.

The recommended $C_p$[14] between 10 and 50 K were obtained from curve fitted functions, so that only the recommended experimental $C_p$[14] between 60 and 370 K were used to calculate $\theta_1$. The average $\theta_1$ was obtained to be 952 ± 26 K in the temperature range from 70 to 200 K. The lowest $\theta_3$ was 61.9 K at 70 K. The heat capacity is plotted in *Figure 12* and *Figure 13* shows the deviation of the experimental $C_p$ from the calculated $C_p$. The average and RMS deviations are $+0.03 \pm 2.0\%$ over the temperature range from 60 to 370 K.

## POLY(ISOBUTYLENE)

In order to find the relation between $\theta_1$ and macromolecular structure we also calculated the heat capacity of PIB based on the approximate vibrational frequencies listed in *Table 2*. The recommended heat capacity[14] between 20 and 190 K was used to calculate $\theta_1$. The average $\theta_1$ was found to be 850 ± 9.8 K between 120 and 190 K. We chose the lowest $\theta_3$ (102.8 K at 20 K) for all calculations.

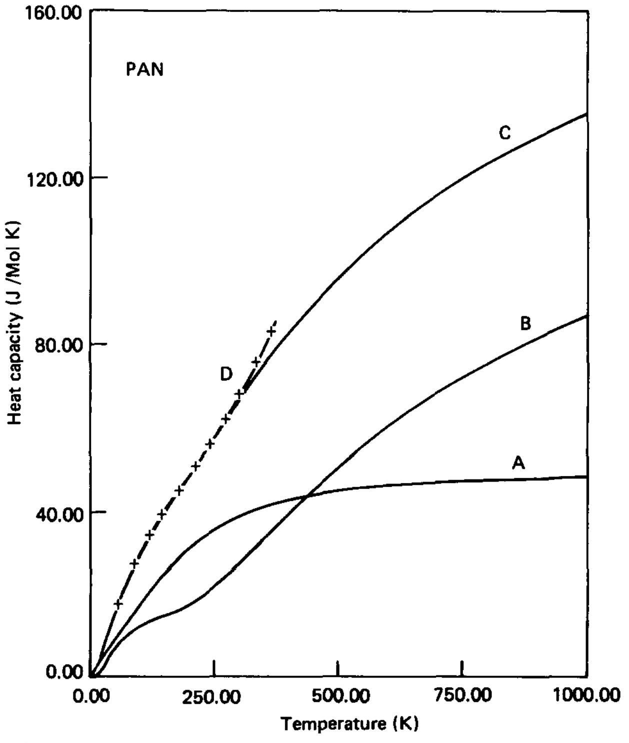

**Figure 12** Heat capacity at constant volume of poly(acrylonitrile). Curve A. skeletal vibration contribution to $C_v$, Tarasov treatment ($\theta_3 = 61.9$ K, $\theta_1 = 952$ K, $N = 6$). Curve B: group vibration contribution to $C_v$, for frequencies see *Tables 1* and *3*. Curve C: sum of curves A and B. Curve D: experimental $C_p$ as given in the data bank[14]

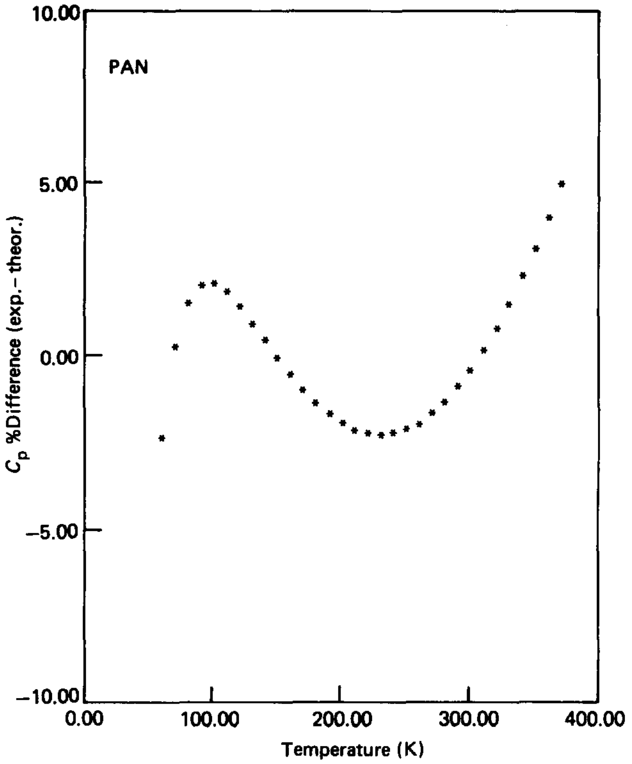

**Figure 13** Heat capacity difference $C_p$(experimental) – $C_p$(calculated) of poly(acrylonitrile), PAN. $A_0 = 3.43 \times 10^{-3}$ K mol J$^{-1}$, $T_m^0 = 613$ K

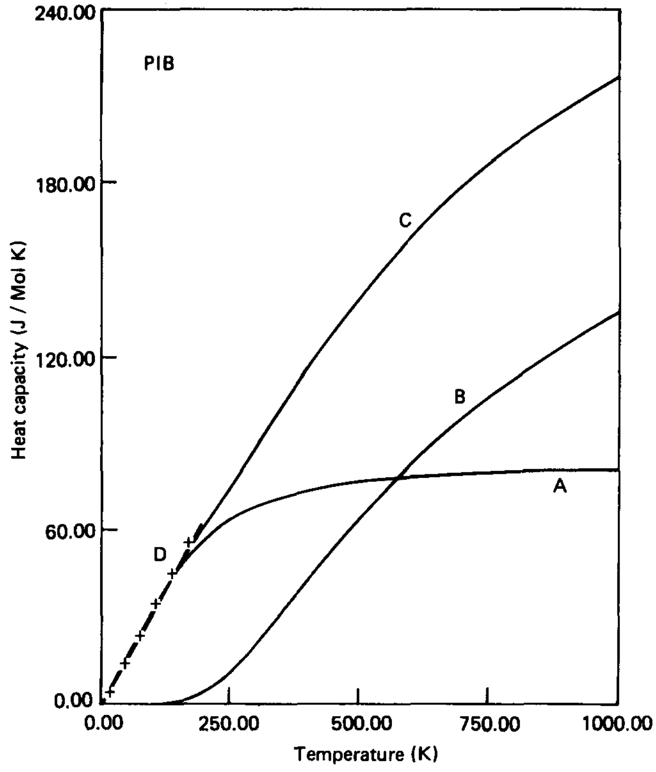

**Figure 14** Heat capacity at constant volume of polyisobutylene, PIB. Curve A: skeletal vibration contribution to $C_v$. Tarasov treatment ($\theta_3 = 102.8$ K, $\theta_1 = 850$ K, $N = 10$). Curve B: group vibration contribution to $C_v$, for frequencies see *Tables 1* and *2*. Curve C: sum of curves A and B. Curve D: experimental $C_p$ as given in the data bank[14]

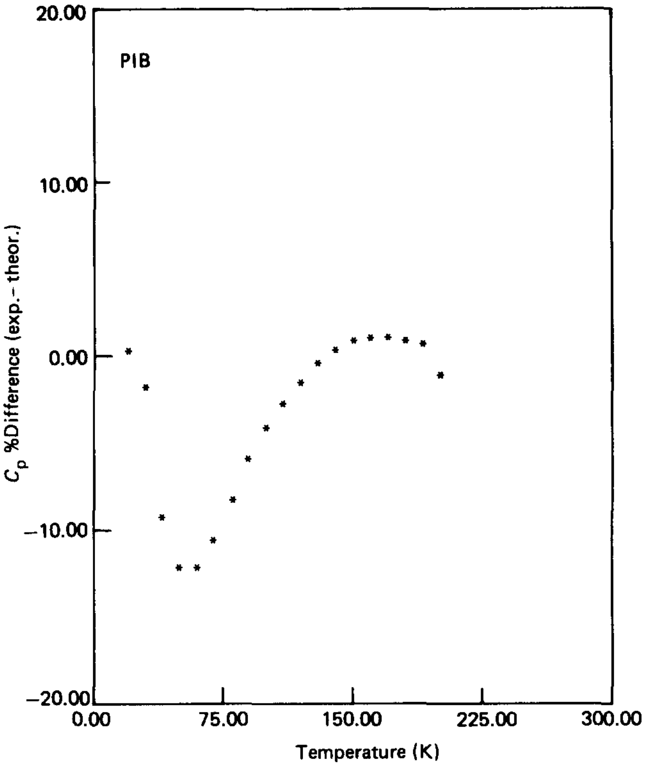

**Figure 15** Heat capacity difference $C_p$(experimental)$-C_p$(calculated) of polyisobutylene, PIB. $A_0 = 5.11 \times 10^{-3}$ K mol J$^{-1}$, $T_m^\circ = 300$ K (estimated)

The heat capacity is plotted in *Figure 14*. *Figure 15* shows the deviation of calculated $C_p$ from experimental $C_p$. The average and RMS deviations are $-3.4 \pm 4.7\%$ in the temperature range of 20–190 K.

The strongly negative error between 50 and 75 K can be linked to the limits of the applicability of the Tarasov equation to backbone chains with alternating masses along the chain as was observed before for poly(vinylidene fluoride)[5] and poly(vinylidene chloride)[6].

## DISCUSSION

The first point to make about the calculated heat capacities of the 17 increasingly branched macromolecules is that they fit the experimental data well (see *Figures 2, 3, 6, 8, 10* and *13*). For polyisobutylene (*Figure 15*) the limit of the application of the Tarasov treatment seems to be reached. It would, however, be a minor effort to devise a better fitting frequency distribution for alternating light and heavy masses since the exact solution for such chain of beads was developed long ago[12].

As in the polymers analysed before[1–11], the group vibrations are for the purpose of computation of heat capacities well represented by additivity of average or representative frequencies derived from normal mode calculations or from i.r. or Raman spectra of the macromolecule, chemically similar macromolecules, or low molecular weight model compounds (see *Table 1*). Effects of the remaining discrepancies are minimized by the fit of the skeletal heat capacities via the Tarasov equation to the experimental, skeletal heat capacities after subtraction of the approximated group vibration contributions. It will thus be possible to have a reasonably short list of group vibration heat capacity contributions to cover virtually all polymers of interest. Initial estimates indicate that 30 sets of group vibrations may be sufficient (see *Table 1* for seven such sets of group vibrations and *Tables 2* and *3* for their use). A computer program to handle the 30 tables of group vibration heat capacities through curve fitted functions is being developed.

The $\theta_3$ and $\theta_1$ parameters of the Tarasov treatment of the analogously treated skeletal vibrations reveal four facts:

(1) In the polyethylene and polypropylene, for which reliable single-chain normal mode frequency distributions are known, the experiment-fitted upper limits of the vibrational spectra ($\theta_1$) do not fit the calculations (see PP results, above). Without this experimental result one would probably have guessed that packing of chains would have a smaller influence on the intramolecular vibration frequencies.

(2) The intermolecular vibration limits $\theta_3$ for amorphous branched polyethylenes and acrylates are all practically the same (80–90 K). Methacrylates and PAN are slightly lower (58–67 K) and poly(methacrylic acid) PMAA and polyisobutylene are slightly higher (107 and 103 K, respectively). The spread is less than that between amorphous and crystalline polyethylene (80–154 K). Structural information suggests that perhaps the higher skeletal mass of the double-branches of methacrylates causes the decrease in $\theta_3$. PMAA would be expected to have a higher $\theta_3$ due to its hydrogen bonding. The high $\theta_3$ of PIB may also be related to the general difficulty of describing alternating-mass chains with a Tarasov equation.

(3) The intramolecular vibration limits $\theta_1$ show a special trend displayed in *Figure 16*. When plotted as the inverse of the repeating unit molar mass, all $\theta_1$ values except PAN fall onto two curves, one for the double branches of PIB and polymethacrylates, and one for the single branches of polyacrylates and branched polyethylenes. The influence of the branching is lost at a side-chain length of above about 6 atoms. Mathematically the two curves can be represented by:

$$\theta_1 = 363 + 1820/\sqrt{M} \quad \text{(in K)} \qquad (4)$$

(branched hydrocarbons or n-alkyl acrylates, $\pm 2\%$)

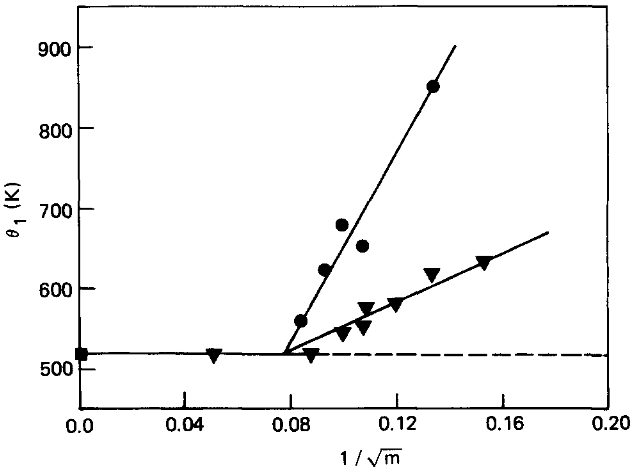

**Figure 16** Tarasov parameter $\theta_1$ for n-alkyl hydrocarbons and n-alkyl acrylates (▼), and PIB, PMMA and n-alkyl methacrylates (●), as a function of the inverse repeating unit mass

and

$$\theta_1 = 95.4 + 5556/\sqrt{M} \quad (\text{in K}) \qquad (5)$$

(PIB, PMAA or n-alkyl methacrylates, ±4%)

where $M$ represents the repeating unit molecular mass.

(4) The ester and carboxyl groups have no special influence on the $\theta_1$ temperature. With group vibrations as listed in *Tables 1–3*, ester and carboxyl groups lead to a $\theta_1$ close to the polyethylene value of 519 K. The same observation was made with ester groups incorporated in the main-chain instead of the side-chain[7]. This is not so for the nitrile group.

Thus this research has led not only to a description of the heat capacities of the 17 macromolecules listed, but it also allows extrapolation to a large number of homologous homopolymers. Furthermore, previous experience has shown that the heat capacities of copolymers and blends can be calculated by adding the heat capacities of the mole fractions of the constituent homopolymers.

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## REFERENCES

1 Wunderlich, B. *J. Chem. Phys.* 1962, **37**, 1207; updated ref. 2 and present paper
2 Grebowicz, J., Suzuki, H. and Wunderlich, B. *Polymer* 1985, **26**, 561
3 Grebowicz, J., Lau, S. F. and Wunderlich, B. *J. Polym. Sci. Polym. Symp.* 1984, **71**, 19
4 Lau, S. F. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 379
5 Loufakis, K. and Wunderlich, B. *Polymer* 1985, **26**, 1875
6 Loufakis, K. and Wunderlich, B. *Polymer* 1986, **27**, 563
7 Lim, S. and Wunderlich, B. *Polymer*, to be published
8 Judovits, L. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.*, to be published
9 Cheng, S. Z. D., Lim, S., Judovits, L. H. and Wunderlich, B. *Polymer* 1987, **28**, 10
10 Grebowicz, J., Aycock, W. and Wunderlich, B. *Polymer* 1986, **27**, 575
11 Xenopoulos, A. and Wunderlich, B., to be submitted
12 Wunderlich, B. and Baur, H. *Adv. Polym. Sci.* 1970, **7**, 151
13 Cheban, Yu. V., Lau, S. F. and Wunderlich, B. *Colloid Polym. Sci.* 1982, **260**, 9
14 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
15 Grebowicz, J. and Wunderlich, B. *J. Thermal Anal.* 1985, **30**, 229
16 Lau, S. F. and Wunderlich, B. *J. Thermal Anal.* 1983, **28**, 59
17 Barnes, J. and Frankoni, B. *J. Phys. Chem. Ref. Data* 1978, **7**, 1309
18 Zerbi, G. and Piseri, L. *J. Chem. Phys.* 1968, **49**, 3840
19 Holland-Moritz, K. and Sausen, E. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1
20 Holland-Moritz, K. and Sausen, E. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 25
21 O'Reilly, J. M., Bair, H. E. and Karasz, F. E. *Macromolecules* 1982, **15**, 1083
22 Dirlikov, S. and Koenig, J. L. *Appl. Spectrosc.* 1979, **33**, 551, 555
23 Schneider, B., Stokr, J. and Schmidt, P. *Polymer* 1979, **20**, 705
24 Willis, H. A., Zichy, V. J. I. and Hendra, P. J. *Polymer* 1969, **10**, 737
25 Nagai, H. *J. Appl. Polym. Sci.* 1963, **7**, 1697
26 Dirlikov, S. and Koenig, J. L. *J. Raman Spectrosc.* 1980, **9**, 150
27 Lipschitz, I. and Gray, J. M. *ACS Polym. Prepr.* 1979, **20**, 503
28 Lipschitz, I. and Gray, J. M. *ACS Polym. Prepr.* 1983, **24**, 133; 1984, **25**, 199
29 See, for example, Perepechko, I., 'Low Temperature Properties of Polymers', Pergamon Press, Oxford, 1980; Pohl, R. O. *Phase Transitions* 1985, **5**, 239
30 Gaur, U. and Wunderlich, B. *Macromolecules* 1980, **13**, 445
31 Belopolskaya, T. V. and Trapeznikova, O. N. *Opt. Spectrosc.* 1966, **20**, 133
32 Leyte, J. C., Zniderweg, L. H. and Vledder, H. J. *Spectrochim. Acta* 1967, **23A**, 1397
33 Koenig, J. L., Angood, A. C., Semen, J. and Lando, J. B. *J. Am. Chem. Soc.* 1969, **91**, 7250
34 Hadzi, D. and Sheppard, N. *Proc. Roy. Soc. Lond.* 1953, **A216**, 247
35 Haken, J. K. and Werner, R. L. *Br. Polym. J.* 1971, **3**, 263
36 Miller, M. L. and Rauhut, C. E. *J. Polym. Sci.* 1959, **38**, 63
37 Ling, C. Y. and Krimm, S. *J. Polym. Sci.* 1958, **31**, 513
38 Yamadera, R., Tadokoro, H. and Murahashi, S. *J. Chem. Phys.* 1964, **41**, 1233
39 Tadokoro, H., Murahashi, S., Yamadera, R. and Kamei, T. *J. Polym. Sci., A* 1963, **1**, 3029
40 Liang, C. Y., Pearson, F. G. and Marchessault, R. H. *Spectrochim. Acta* 1961, **77**, 568
41 Witenhafer, D. E. and Koenig, J. L. *J. Macromol. Sci.–Phys.* 1968, **B2**, 147
42 Cao, M.-Y., to be published