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HEAT CAPACITIES OF LINEAR MACROMOLECULES

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Abstract - Adiabatic and differential scanning calorimetry can both make important contributions to the measurement of heat capacities. All heat capacities of linear macromolecules have been collected, computer stored and evaluated. Together with information on glass transitions and equilibrium melting data, the heat capacities are used to derive an overall understanding of the thermal property. Prediction schemes of solid and liquid heat capacities, the increase of heat capacities at the glass transition temperature, and the temperatures of melting are analyzed.

INTRODUCTION

Heat capacities are reasonably well understood [1]. In the solid state, only vibrational contributions need to be considered. For linear macromolecules, it is sufficient to use the harmonic oscillator approximation. All linear macromolecules have, furthermore, a similar backbone structure, permitting easy analysis of the vibrational frequency spectrum in terms of chemical structure. For such discussion, the overall frequency spectrum is divided into skeletal vibrations and group vibrations.

For an approximate discussion of the skeletal vibrations, the molecule is considered to consist of a chain of structureless beads of the given formula weight. The intramolecular vibrations of the skeleton can now easily be estimated. For many carbon backbone macromolecules, geometry and force constants are the same. A change in mass is the only remaining variable. It changes the vibrational frequency proportional to $1/\sqrt{\text{mass}}$. The intermolecular skeletal vibrations, in turn, are usually few and affect heat capacities only up to about 50 K. Often it is possible to approximate the intermolecular skeletal vibrations with a three-dimensional Debye function [2] and the higher frequency intramolecular skeletal vibrations can be averaged into a one-dimensional Debye function as suggested by Tarasov [3].

The group vibrations spread usually over narrow frequency ranges and their heat capacity contribution can be approximated by Einstein functions [4] at average frequencies.

In this way all but the contributions of the intermolecular skeletal vibrations to the heat capacity are additive according to the chemical structure. An earlier suggested additivity scheme [5] is to be tested with new data and extended to other backbones.

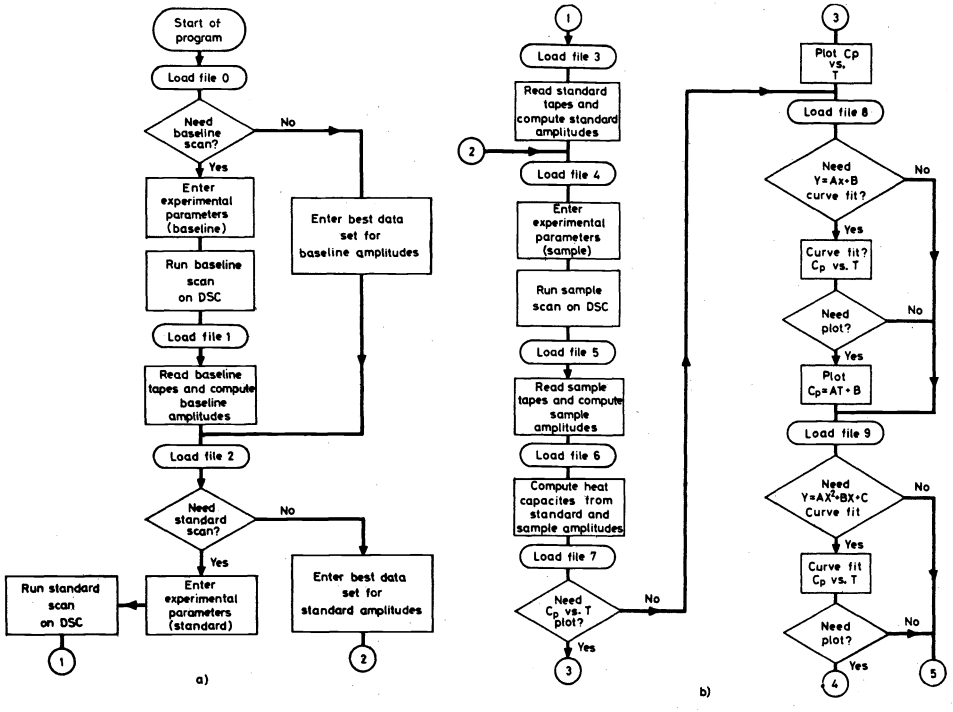
Additivity of the heat capacity of liquids is more difficult to assess. The major additional contribution to the vibrational heat capacity is the potential energy, describable by a hole theory [6]. Such contributions are only partially based on intramolecular effects and as a result, additivity of liquid heat capacities is still a subject of discussion. It will be shown that the old "bead model" needs extension for different size "beads".

For many years heat capacity data of high precision were almost exclusively measured by adiabatic clorimetry [7]. A precision of 0.1% or better could routinely be achieved, but measurement was involved and data generation was slow. When the first larger survey of such data for linear macromolecules was made [1] we found that due to sample difficulties, overall agreement between data of different laboratories was in many cases not better than ± 3%. Such accuracy could also be achieved with the newly developed scanning calorimeters [8,9]. Furthermore, computerization of data collection could improve this accuracy even further [10], so that now differential scanning calorimetry is the method of choice for large volume heat capacity measurement on linear macromolecules. Some examples and comparisons of differential scanning and adiabatic calorimetry will be given.

For the continuation of a treatise on macromolecular physics [11], the equilibrium melting transitions of about 40 linear macromolecules have been critically evaluated. Extrapolations and direct measurements on extended chain crystals were used to arrive at a new data base which often is largely different from prior uncritical collections. Volume changes and changes in packing fraction between crystal and melt at room tempearature, heats of fusion and entropies of fusion at the melting temperature, and equilibrium melting temperatures have been tabulated. It can on this basis be shown that simple models of chain flexibility are sufficient to explain melting temperature trends if cohesive energy density, volume changes, and intramolecular heats of fusion are also considered [12].

INSTRUMENTATION

Instrumentation for heat capacity measurement had its beginning in the isothermal ice calorimetry of the 18th century [13] and developed into highly sophisticated, costly and time consuming precision adiabatic calorimetry [7]. A parallel development was that of simple heating curves, which developed into differential thermal analysis with the application of thermocouples for temperature measurement and the invention of automatic recording [14]. With the increasing development of electronics for signal amplification, smaller samples could be analyzed and classical twin calorimetry [15] and differential thermal analysis approached each other in accuracy [16]. Microcalorimeter with 1 to 30 mg of sample at heating rates of 1 to 50 K/min emerged finally, known generally as differential scanning calorimeters [17]. The increase of computer technology allowed finally to maximize data analysis and increase accuracy to a level of presently perhaps $\pm$0.1% under ideal conditions. A typical computer flow diagram for measurement and data analysis from our laboratory is shown in Fig. 1 [10].
A comparison of data by classical adiabatic calorimetry with those by scanning calorimetry is shown in Table 1. [10]. A comparison of various data



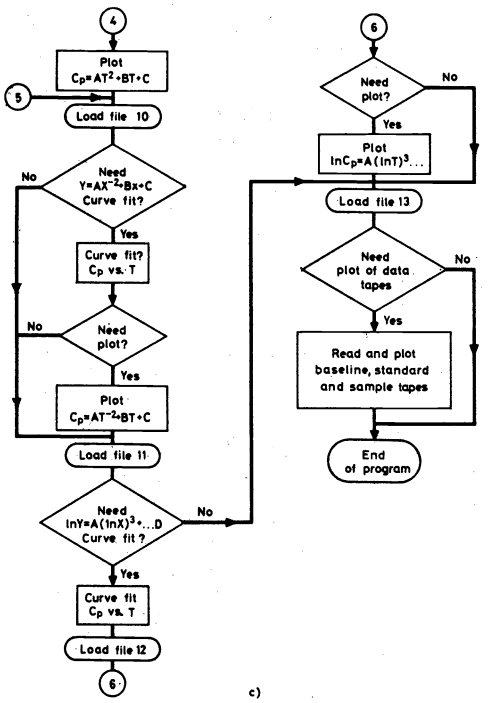


Fig. 1 . Flow diagram of a heat capacity program fitted to a Perkin Elmer DSC-2 differential scanning calorimeter. For details of instrumentation see [10,18].

liquid selenium are shown in Fig. 2. One must observe that in the case of uid selenium, measurement must be done on cooling because of fast crystal- :ation of supercooled selenium shortly above the glass transition tempera- -e. Both examples show good agreement between micro and macrocalorimetry.

TABLE 1. Comparison of heat capacities of zinc measured by adiabatic calorimetry [19] and scanning calorimetry [10].

Temperature (K)	Adiabatic calorimetry ($JK^{-1}mol^{-1}$)	Scanning calorimetry (JK^{-1} mol^{-1})
410	26.48	26.43
430	26.62	26.57
450	26.78	26.72
470	26.94	26.96
490	27.11	27.18
510	27.28	27.33
Standard deviation		$\pm$0.06 (0.2%)

the selenium heat capacity curves, an improvement from normal scanning lorimetry to computer assisted scanning calorimetry can be observed. :ure developments which are hoped for are: a three probe calorimeter lank, reference, and sample) which could on computer coupling yield -ectly a heat capacity-temperature output, omitting the present multiple ı calorimetry; and smaller mass calorimeters (µg instead of mg) which ıld permit the increase in heating rate by a factor 100 to measure even -e metastable samples and to simulate production processes of macro- lecular materials.

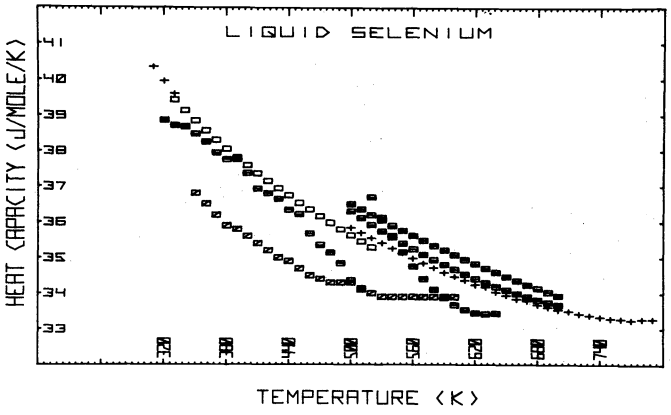


Fig. 2. Comparison of heat capacities of liquid selenium measured by adiabatic calorimetry [20] (+), scanning calorimetry [10, 21] (⊟, ⊡), and computer assisted scanning calorimetry [22] (□).

THE HEAT CAPACITY DATA BANK

Over many years we have monitored the literature of heat capacities of linear macromolecules [1]. Over the past five years a heat capacity data bank has been set up which contains in more than 500 tables information on all published measurements [23]. The data are collected on magnetic tape, accessible through a Hewlett-Packard 9821 A minicomputer. Present efforts involve critical discussion of one set of macromolecules after the other and publication in the J. Phys. Chem. Ref. Data. Presently completed discussions are those of selenium, which is an example of a macromolecule with a monatomic repeating unit und undergoes various polymerization-depolymerization reactions; polyethylene, which is the most studied macromolecule with presently more than 100 samples analyzed; polypropylene, the key example of a linear macromolecule with stereospecificity; and a series of 12 polyoxides, which enable an analysis of the influence of a heteroatom on the heat capacity [24]. Table 2 gives a listing of groups of macromolecules analyzed.

TABLE 2. Best data for heat capacity of polymers.

Macromolecules	Temp. Range (K)
Selenium	0 - 1000
Polyethylene	0 - 600
Polypropylene	0 - 600
Polystyrenes (4)	
Polyoxides (12)	
Vinyl Polymers (23)	
Polyesters (5)	
Nylons (5) and Polypeptides (3)	
Polyacrylates and Polymethacrylates (10)	
Inorganic (15) and Aromatic (12) polymers	

These "best heat capacities" are, when possible, extrapolated to the amorphous and crystalline states for evaluation of the thermodynamic functions S, H and G. Selection criteria involve a judgement of the purity and characterization of the sample. Uncharacterized commercial plastics are considered

unreliable. Besides molecular weight and thermal history, crystallinity is the key characterization parameter. A second group of judgements concern the experimental aspects. Below 200K adiabatic calorimetry are considered more reliable than scanning calorimetry data. Special techniques are needed for data below 10K. Between 200 and 350K both techniques may be equally good, depending on sophistication of instrument and data handling procedures. Above 350K scanning calorimetry is often preferred because of more adequate handling of metastable samples. A third set of criteria involves the data presentation in the literature. Often data become useless because of representation in minute graphs. Finally, thermal measurements are often plagued by systematic errors for no apparent reason. These can only be eliminated if sufficient duplicate measurements are reported.
All data, critically selected, are plotted and tables of the various "best heat capacities" derived. If available, tables for completely crystalline, glassy, and molten states are produced. Figures 3 and 4 show some examples for best heat capacities of polyoxides, poly(vinyl fluorocarbon)s. Figures 5 and 6 show all input data for glassy and trigonal selenium. For the selenium case the molten state is shown as Fig. 2. The metastable monoclinic selenium was measured to complete the selenium discussion [25].

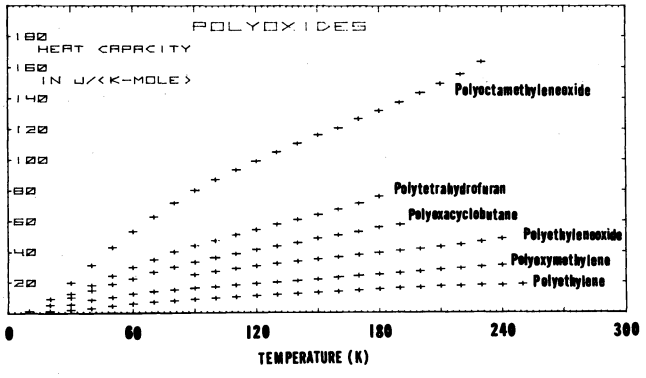


Fig. 3. Best heat capacities for a series of polyoxides [24].

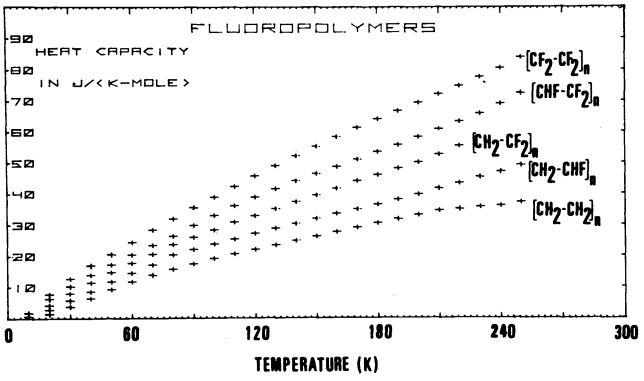


Fig. 4. Best heat capacities for a series of poly(vinyl fluorocarbon)s (unpublished).

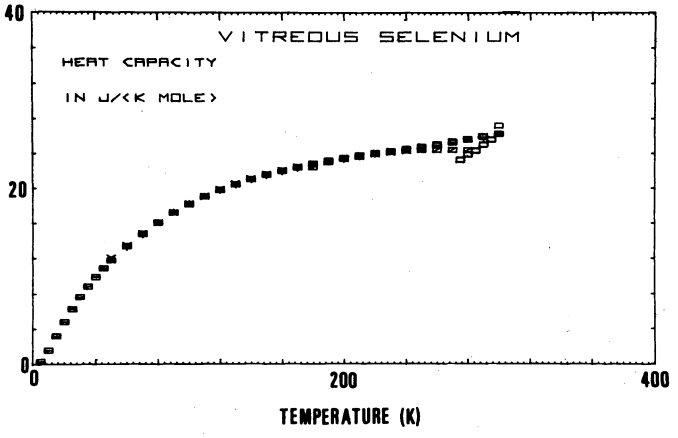


Fig. 5. Computer plot of heat capacity data of glassy selenium used for the best data derivation [24]. Measurements with systematic errors are easily recognized.

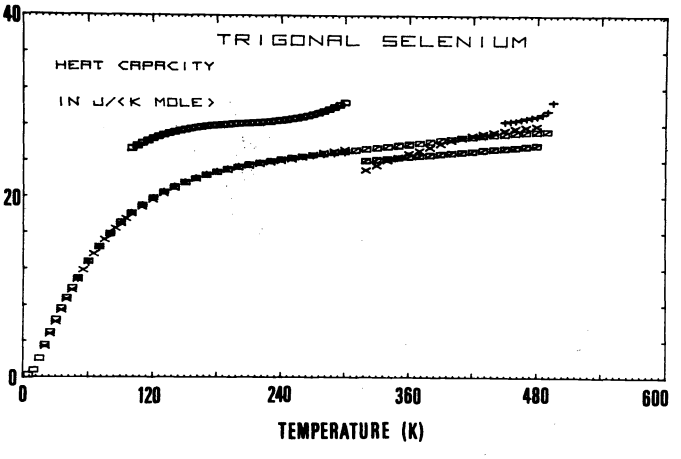


Fig. 6. Computer plot of heat capacity data of trigonal selenium [24]. Measurements with systematic erros are easily recognized.

The major goals of the heat capacity data bank is to develop a base to check various possible addition schemes of heat capacities, as is discussed below, and to derive reliable values for the thermodynamic functions H, S, and G.

ADDIVITY OF HEAT CAPACITIES OF LINEAR MACROMOLECULES

At temperatures above 50K, heat capacities of solid linear macromolecules are additive. Heat capacity contributions of various chemical groups which, when linked together, give the macromolecule can be added to give the heat capacity of the macromolecule [5]. Table 3 gives some typical examples. The heat capacity of polypropylene is simply obtained by adding columns 2, 6 and 7; of poly(vinyl chloride), by adding columns 2 and 4; etc. The data so obtained are usually good to about $\pm$ 5%. After completion of the critical evaluation of the data given in Table 2, an updated addition scheme will be developed (1980).
A question which is not fully resolved involves the additivity of heat capacities of liquid macromolecules. In the first set of data [24] sufficient information on aliphatic polyoxides were derived to study the heat capacity contribution of the O-group in the molten state. The results are illustrated in Table 4. The repeating units are given by listing oxygen and methylene units, i. e. OM_3=poly(trimethylene oxide). The heat

TABLE 3. Heat capacity contributions of some typical C-backbone repeating units in $JK^{-1}mol^{-1}$

T (K)	CH_2	CF_2	CHCl	CCl_2	$CHCH_3$	CH_2 (side chain)
50	4.6	10.5	10.5	12.6	9.6	5.0
60	5.9	12.1	12.1	15.9	11.3	6.3
70	7.1	14.2	13.8	18.8	13.0	7.5
80	7.9	15.9	15.1	22.2	15.1	8.4
90	8.8	18.0	15.9	24.7	16.7	9.6
100	9.6	19.7	17.2	27.2	19.2	10.5
110	10.5	21.3	18.0	28.9	19.7	11.3
120	10.9	23.0	18.8	30.1	20.9	12.1
130	11.7	24.7	19.7	31.4	22.6	13.0
140	12.6	25.9	20.5	32.6	24.3	13.8
150	13.0	27.6	21.3	34.3	25.1	14.6
160	13.8	29.3	21.8	35.6	26.8	15.5
170	14.6	30.5	22.6	37.2	28.0	16.3
180	15.5	32.2	23.4	38.1	29.3	17.2
190	15.9	33.5	24.3	39.7	30.5	18.0
200	16.7	34.7	24.7	41.0	32.2	18.8
210	17.2	36.0	25.9	42.7	33.5	20.1
220	17.6	37.7	26.8	44.4	34.3	20.9
230	18.0	38.9	27.6	46.0	36.0	21.8
240	18.4	40.2	28.5	47.7	37.7	23.0

capacity contributions of poly(ethylene oxide) and poly(trimethylene oxide) are somewhat higher than those of the other polyoxides. The reason for this deviation can be traced to a larger heat capacity increase of the short CH_2-sequence polyoxides at the glass transition temperature. An observation

TABLE 4. Heat capacity contributions of O- in $JK^{-1}mol^{-1}$ in the molten state

T (K)	OM_2	OM_3	OM_4	$OMOM_2$	$OMOM_4$
250	32.4	28.1	19.6	22.2	21.0
280	31.1	27.2	19.6	21.9	20.5
310	29.9	26.4	19.6	21.6	19.9

of interest is the decreasing heat capacity with temperature of O-, an observation also made for the Se- heat capacity (see Fig. 2). One concludes that probably all liquid macromolecules of monatomic repeating units have decreasing heat capacities. The normal heat capacity increase for linear macromolecules must be attributed to the group vibrations.

GLASS TRANSITIONS

For many glassy macromolecules (and other materials) the heat capacity increases by about 11 $JK^{-1}mol^{-1}$ when calculated per "bead". The bead is the backbone unit which can be considered rigid. Polyethylene, polypropylene, polyisobutylene, and polyisoprene have thus 1, 2, 2, and 3 beads per repeating units, respectively. Their increases in heat capacity at the glass transition are, in sequence, 10.4, 11.8, 11.3, and 10.4 $JK^{-1}mol^{-1}$. This regularity was found first in 1960 [6]. Additional macromolecular results are listed in Ref. [5]. Presently, particularly in connection with the discussion of additivity of heat capacities of liquid macromolecules, new tables are derived on a larger data base. In Table 5 heat capacity increases for polyoxide glasses are listed. For many glasses the rule of constant heat

TABLE 5. Heat capacity increase of polyoxide glasses at the glass transition temperature in $JK^{-1}mol^{-1}$ [24].

Macromolecule	Beads	T_g	ΔC_p/bead
Polyoxyethylene	3	232	(14.3)
Polyoxytrimethylene	4	195	12.7
Polyoxytetramethylene	5	189	9.3
Polyoxymethyleneoxyethylene	5	209	10.7
Poly(oxymethylene-oxytetramethylene)	7	189	10.6
Polyoxypropylene	3	198	10.7
Poly(oxy-1,4-phenylene)	2	358	10.7
Poly(oxy-2,6-dimethyl-1,4-phenylene)	2	482	(16.0)
Poly(oxy-2,6-diphenyl-1,4-phenylene	4	493	(19.2)

capacity increase is obeyed. Two exceptions seem to appear. One for poly(ethylene oxide), the other for polyoxides with many benzene rings. The first remains unexplained. The latter can be removed assuming phenyl groups have a larger heat capacity increase at the glass transition temperature (21.6 $JK^{-1}mol^{-1}$) [26]. A size dependence can also be applied to the larger macromolecules containing naphthalene- and anthracene-size rings (32.4 and 43.2 $JK^{-1}mol^{-1}$, respectively). The measurements of a large group of such aromatic macromolecules were made by Wrasidlo [27].

MELTING TRANSITIONS

Melting data on a series of flexible linear macromolecules for which equilibrium crystals were available or could be extrapolated to, are listed in Table 6. Column 3 gives the melting temperature in K, followed in column 4 by the entropy of fusion per rigid backbone chain group (CR_1R_2-, O-, CR=CH-, COO-, C_6H_4-, and CONH-). The number of rigid chain groups per repeating units is given in parentheses. Column 5 gives the heat of fusion per mole of interacting groups, which is the total number of interacting

TABLE 6. Equilibrium melting data of flexible linear macromolecules

#	Macromolecule	T_m° K	Δs_f[a] $JK^{-1}mol^{-1}$	Δh_f[a] $kJmol^{-1}$	Packing Fraction[b] Δ%	k_ℓ	Cohesive Energy Density $kJmol^{-1}$
1	Polyethylene	414.6	9.91(1)	4.11(1)	14	0.60	4.18
2	Polytetrafluoroethylene	600	5.69(1)	3.42(1)	15	0.68	3.35
3	Selenium	494.2	12.55(1)	6.20(1)	11	0.76	9.71
4	Polypropylene	460.7	7.55(2)	2.31(3)	9	0.60	4.74
5	Poly-1-butene	411	8.50(2)	1.75(4)	9	0.60	4.60
6	Poly-1-pentene	403	7.80(2)	1.26(5)	9	0.59	4.52
7	Poly(4-methyl-1-pentene)	523	9.50(2)	1.66(6)	-2	0.59	4.74
8	Poly(4-phenyl-1-butene)	439	5.00(2)	0.44(10)	3	0.64	4.14
9	Polystyrene	516	9.70(2)	1.25(8)	6	0.63	4.13
10	1,4-Polybutadiene, cis	284.7	10.67(3)	2.30(4)	10	0.61	4.18
11	1,4-Polybutadiene, trans	415	2.90(3)	0.90(4)	13	0.60	4.18
12	1,4-Poly(2-methyl-butadiene),cis	310	4.80(3)	0.87(5)	9	0.62	3.93
13	1,4-Poly(2-methyl-butadiene),trans, α	352.7	12.13(3)	2.57(5)	14	0.61	3.93
14	1,4-Poly(2-methyl-butadiene), trans,β	356	9.90(3)	2.11(5)	12	0.61	3.93
15	Polyoxymethylene	457	10.70(2)	4.89(2)	10	0.70	5.23
16	Poly(ethylene oxide)	342.1	8.43(3)	2.88(3)	10	0.65	4.88
17	Poly(tetramethylene oxide)	330	8.74(5)	2.88(5)	11	0.62	4.80
18	Polyglycolide	506	11.0(2)	3.70(3)	11	0.72	5.86
19	Poly-β-propiolactone	357	8.5(3)	2.27(4)	(6)	0.71	5.44
20	Poly(α,α'-dimethyl propiolactone)	518	9.6(3)	2.47(6)	11	0.63	5.02
21	Poly-ϵ-caprolactone	337	8.0(6)	2.31(7)	9	0.64	4.90
22	Poly(ethylene adipate)	338	7.8(8)	2.10(10)	11	0.67	5.19
23	Poly(ethylene suberate)	348	7.7(10)	2.22(12)	11	0.66	5.02
24	Poly(ethylene sebacate)	356	7.5(12)	2.28(14)	12	0.64	4.90
25	Poly(ethylene terephthalate)	553	9.7(5)	2.24(12)	9	0.68	5.02
26	Poly(4,4'-isopropylidene-carbonate)	568	11.8(5)	1.86(18)	10	0.65	4.58
27	Nylon 6, α	533	8.0(6)	3.72(7)	12	0.66	11.7

TABLE 6, continuation

Macromolecule	T_m° K	Δs_f[a] $JK^{-1}mol^{-1}$	Δh_f[a] $kJmol^{-1}$	Packing[b] Fraction %	k_ℓ	Cohesive Energy Density $kJmol^{-1}$
28 Nylon 8, γ	491	4.5(8)	1.98(9)	8	0.65	10.0
29 Nylon 6.6, α	553	10.2(12)	4.85(14)	12	0.66	11.7

[a] the number of units in the repeating unit is given in parenthesis. Flexible chain units for Δs_f, and total interacting groups for Δh_f.

[b] calculated using typical v.d. Waals and covalent radii; Δ, difference between melt and crystal, k_ℓ liquid packing fraction.

[c] calculated using Table 6.1 van Krevelen and Hoftyzer [28], calculated in moles of total interacting groups as given in the Δh_f column.

groups per repeating unit, given in parentheses. It involves counting all large atoms, disregarding only H and counting CO-as one unit. Column 6 shows the percentage change in packing fraction and the packing fraction of the amorphous macromolecule, both at room temperature. The last column contains a calculation of the cohesive energy density, calculated per mole of amorphous, interacting groups (as in column 5).

The entropy of fusion of the majority of macromolecules is 9.5 $JK^{-1}mol^{-1}$ of rigid backbone chain groups. This unique value supports the empirical subdivision of the molecule in "rigid" backbone groups. There are six exceptional macromolecules (2, 8, 11, 12, 14, 28) with frequently much smaller entropies of fusion. A check of the crystal structures or melting behavior of these macromolecules suggests that these crystals have high temperature crystal forms which contain already increased disorder.

Turning to the macromolecules for which the chains are practically in a fixed, ordered conformation before melting, one expects a large portion of the entropy of fusion to be due to purely conformational origin. Comparing the experimental data with calculated conformational entropies of fusion one finds typically 65 to 85% for the contribution of conformational entropy to the total entropy of fusion.

Among the macromolecules with a high entropy of fusion, further trends can be seen. Macromolecules with phenylene groups within the backbone (25, 26) seem to have a somewhat increased entropy of fusion over similar molecules which contain CH_2-groups instead. The same seems to hold true for polystyrene (9). Macromolecules which alternate CH_2- and other functional groups such as O-, COO-, and selenium (15, 18, 4) also have higher entropies of fusion.

The difference in volume between crystal and melt (at room temperature) shows also a correlation with structure. Columns 6 and 7 in Table 6 contain the pertinent data. Among the all-carbon backbone macromolecules those with close to all-trans-conformations in the crystal show the largest percentage difference in packing fraction (1, 2, 11, 13, 14). The more helical, all-carbon backbone macromolecules show a distinctly lower percentage difference (4-9). For poly(4-methyl-1-pentene) (7) this difference is even negative at room temperature, although at the temperatures above 50°C it changes to positive. The polyoxides (15-17), polyesters(18-26) and polyamides (27-29) distinguish themselves by a high packing fraction in the liquid and in the melt, approaching the hydrocarbon level only for long CH_2- sequences. Their percentage change, however, does not differ much from the pure hydrocarbons. All pure hydrocarbon macromolecules (1, 4-14) have a quite similar packing fractions in the liquid state of 0.61 ± 0.02 regardless of the molecular structure. The liquid packing fraction increases almost linearly with the cohesive energy (1, 4-25), but amide groups add an etraordinary amount to the cohesive energy density which is not matched by an increase in packing fraction (27-29). As the sequences of CH_2- increase in length in the polyethers, polyesters and polyamides (17, 24 and 27-29), the liquid packing fraction of polyethylene is approached, but at different rates for different types of macromolecules.

The heats of fusion in Table 6 have been calculated per mole of interacting groups, and not per mole of rigid chain units. This is done to account for

the major contribution to the heat of fusion which should be connected with the loss of interaction on expansion to the liquid. A quite uniform heat of fusion of about 2.4 $kJmol^{-1}$ results for many entries in Table 6 (4, 10, 13, 16, 17, 19-25), with others showing remarkable deviations. All macromolecules with exceptionally small entropies of fusion show also a 1-2 kJ mol^{-1} lower heat of fusion than expected, much in line with a high temperature crystal form of higher enthalpy (2, 8, 11, 12, 14, 28). The polyamides (27-29) have a 1-2 $kJmol^{-1}$ higher heat of fusion than the average, which goes parallel with their much higher cohesive energy density. The macromolecules with larger side chains (5-9) have also a lower heat of fusion than the average when calculated per total of interacting groups, as is done for Table 6. This loss in heat of fusion is also indicated to some degree in the small packing fraction difference. Finally, polyethylene, polytetrafluoroethylene, selenium, and the first polyoxide and polyester (1-3, 5, 18) have a 1-2 $kJmol^{-1}$ higher heat of fusion.

Although the cohesive energy densities and changes in packing fraction can explain some of the changes in heat of fusion with chemical structure, they are not sufficient. One must add the intramolecular contributions to the heat of fusion which results from the change to some high energy conformations on fusion. A particularly clear example is polyethylene, where in the crystal only the low energy trans-conformation is found. In the melt, however, each carbon-carbon bond may also be in one of the two gauche conformations which are higher in energy by about 2 $kJmol^{-1}$. At the melting temperature, the high temperature limit of equal distribution among the three rotational isomers is not reached, but even on equal distribution among trans and gauche conformations, the intramolecular heat of fusion would be 1.0 $kJmol^{-1}$, or about 25% of the total heat of fusion.

Combining all the conclusions on entropy of fusion, packing fraction differences, cohesive energy density, and heat of fusion, one can make some general statements about the melting temperatures of flexible, linear macromolecules: The high melting temperature of polyethylene (1) relative to cis-polybutadiene (10) does not rest with a higher conformational entropy of fusion, but rather with the higher heat of fusion of polyethylene, a good part of which must result from intramolecular contributions and the larger volume change on fusion. The trans-polydienes, particularly in their high temperature form (11) with an on all-trans crystal structure come, as one would expect, close to the polyethylene melting temperature.

The particularly high melting vinyl polymers are polytetrafluoroethylene (2), poly(4-methyl-1-pentene) (7) and polystyrene (8). The polytetrafluoroethylene melting temperature is elevated due to the high mobility in the crystal and, perhaps to a lesser degree, to a lower entropy in the melt. The other two macromolecules have, in contrast, a high melting temperature because of a high molar heat of fusion. Despite less dense packing in the crystal than other vinyl polymers, there is a large enough side group to more than compensate the packing defect. For these two macromolecules it becomes also clear that the present discussion is still too simplified since sidegroup entropy gain on fusion is completely neglected, but should be included in a next step of refinement.

Selenium (3) is a macromolecule which needs for full discussion more information. Its melting temperature represents a balance of high heat of fusion and high enthalpy of fusion. The complicating factor is in this case the partial depolymerization to Se_8-rings on melting, a process which is endothermic and naturally goes also with an increase in entropy.

Polyoxymethylene (15) does not have, as was frequently suggested, a low entropy of fusion, rather its relatively high equilibrium melting temperature must be connected, as in polyethylene, with an exceptionally high heat of fusion. Only a part of the increased heat of fusion can be accounted for by the higher cohesive energy contribution of the oxide group. Some of the increase must also come from intramolecular sources. The crystal consists practically of all-gauche conformations. The trans-conformations, which must also be present in the melt, are of higher energy. The high packing fraction may indicate an additional heat of fusion contribution from the dipole interaction which is still not too well understood. The higher analogues (16, 17) drop to levels much more in line with "normal" macromolecules.

The series of polyesters (18-26) is normal in its melting behavior for the aliphatic members; just that the ester group has an even higher cohesive energy contribution than the oxide. Furthermore, in addition, to dipole-interaction, hydrogen bonds have to be considered. Again, the first member (18) is exceptional, most likely because of the largely different crystal structure. The other high melting polyesters (20, 25, 26) are clearly resulting from the large differences between numbers of rigid backbone

chain groups and total numbers of interacting groups.
The polyamides (27-29) owe their high melting temperatures to their high heats of fusion. The amid group has a cohesive energy density per backbone chain atom 7.3 times that of CH_2-. This contrasts the ester and oxide groups which are only 1.6 and 1.5 times higher in cohesive energy density per chain atom than CH_2-.

CONCLUSIONS

Advanced instrumentation has led to an extended data base which in turn has made heat capacities one of the most important parameters for thermal characterization of linear macromolecules. Of particular interest is the ability of a direct link of the macroscopic measurement and the microscopic origin.

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