Heat capacities of 1,4-polybutadienes

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Heat capacities of solid cis- and trans-1,4-polybutadienes are calculated over the full temperature range from approximated normal mode frequency spectra and low temperature measurements in the ATHAS data bank. θ_3 and θ_1 are 87 K, 589 K and 95 K, 599 K, for the cis and trans isomers, respectively. The heat capacities of both isomeric liquids have been measured by differential scanning calorimetry to be $52.63 + 0.178T$ J K^{-1} mol^{-1}. Semicrystalline heat capacities between glass and first order disordering transitions are linear with crystallinity. The trans-isomer possesses a conformationally disordered crystal phase, which may be the only ordered phase in copolymers with more than 10% cis-content. At low temperature the trans-isomer may consist of three different phases: melt, fully ordered, and conformationally disordered (condis) crystals. At lower temperature, the condis crystals and the melt change to glasses. Thermodynamic functions H, S and G, transition temperatures, crystallinity and annealing are discussed.

INTRODUCTION

The heat capacities at constant pressure C_p of linear macromolecules have recently been critically reviewed[1], and a major effort is presently underway in our ATHAS Laboratory to discuss C_p of various, well-documented polymers and to measure C_p of those, where there are gaps in our knowledge. At present, well understood macromolecules are selenium[2], polyethylene[3], linear polyoxides[3], fluorinated[4,5] and chlorinated polyethylene[6], polystyrene and poly-p-xylylene[7], and polypropylene[8]. Work is in progress on polyesters, branched hydrocarbon vinyl polymers and substituted crosslinked polystyrene[9]. In the present publication we would like to present new C_p measurements on 1,4-polybutadienes of different trans- and cis-content and present a link between C_p values for the crystalline and glassy solids and their vibrational spectra. The heat capacities are then used to derive a table of the thermodynamic functions H, S and G for crystals, glasses and liquids.

Polybutadiene is a specially interesting material since in its trans-isomer it can exist in a conformationally disordered state, a condis state (crystal form II)[10]. High conformational mobility was proposed for this polymer already by Natta and Corradini in 1959 based on the double endotherm on heating and double exotherm on cooling[11]. Both crystalline phases (crystal form I, monoclinic; and form II, pseudo-hexagonal) show reasonable supercooling (>15 K) before phase transitions. An effort will be made in this paper to elucidate the correlation between the various phases. Since polymers are known to undergo only partial phase transitions to metastable states, there is a possibility that trans-1,4-polybutadiene may form at low temperature a three-phase homopolymer consisting of areas of condis crystal or glass, fully ordered crystal, and melt or glass.

The second isomer, cis-1,4-polybutadiene, in contrast, shows no condis phase, but goes on fusion directly from the fully ordered crystal to the melt. The transitions of the two isomers will be compared based on differential scanning calorimetry experiments. In a second paper the transition kinetics will be described.

EXPERIMENTAL

The characterization of the various polybutadienes used in this study is given in Table 1.

Heat capacity measurements were performed using a computer-interfaced Perkin–Elmer DSC-2 (differential scanning calorimeter). Details for the measuring technique and computer programs have been discussed earlier[4,14]. Measurements were carried out on heating at 10 K min^{-1} on samples of about 15 mg weight in N$_2$ atmosphere. The samples and reference materials were enclosed in non-hermetically sealed, matched aluminium cups. The temperature range of measurement was 220 to 450 K. The lower temperature limit was set by our present instrument cooling capability; the high temperature was

Table 1 Sample characterization

		Source
A	100%-trans	Hüls[a]
B	89%-trans, 9%-cis, 2%-vinyl, $\bar{M}_w = 3.67 \times 10^5$	General Tire[b]
C	83%-1,4-trans, 12.4%-cis, 4.6%-1,2 trans	Firestone[c]
D	100%-cis $M_w = 2$–3×10^5	Polysciences

Literature data for transitions:
100%-trans
$T_d^\circ = 356$ K $\Delta H_d^\circ = 7.79$ kJ mol^{-1} (ref. 12)
$T_i^\circ = 437$ K $\Delta H_i^\circ = 3.73$ kJ mol^{-1} (ref. 12)
100%-cis
$T_m^\circ = 284.7$ K $\Delta H_f^\circ = 9.20$ kJ mol^{-1} (ref. 13)
[a] Dr U. Hochmuth, Chemische Werke Hüls
[b] Dr I. G. Hargis, The General Tire and Rubber Co., Research Division, Akron, OH, USA
[c] Dr T. A. Authowiak, Firestone, Central Research Laboratories, Akron, OH, USA
The authors thank the contributors of samples.

determined by the need to avoid decomposition of the samples, which begins above ~470 K.

Some measurements, mainly to identify glass transition temperatures, were made with a duPont 990 thermal analyser and a standard 910 DSC unit. All temperatures were calibrated using NBS and other sharp melting standards (acetone, methylene chloride, n-octane, n-decane, n-dodecane, naphthalene, p-nitrotoluene and benzoic acid).

RESULTS

Heat capacity of liquid 1,4-polybutadiene

Typical heat capacity and heat of transition results for the four samples are shown in *Figure 1*. Above the highest transition, the melt of all samples is isotropic and shows minimal differences in heat capacity from sample to sample. One linear function

$$C_p = 52.63 + 0.178T \quad (\text{J K}^{-1}\text{mol}^{-1}) \quad (1)$$

represents the liquid heat capacities of both *cis*- and *trans*-1-4-polybutadienes with a standard deviation of ±0.2%. It is noteworthy to observe that the condis crystals of the pure *trans*-isomer have also the heat capacity of the liquid polymers (at 348 K). Since data on liquid polybutadienes were not available in the data bank[1], we offer equation (1) as Recommended Data (1985) (see also *Tables 5* and *6*).

Crystallinity-dependence of heat capacity

The heat capacity of semicrystalline polybutadiene with *trans*-polybutadiene crystallinity is shown in *Figure 2*. The 0% crystallinity points are computed from equation (1); the 100% crystallinity points are calculated from the vibrational spectrum as described below. The lower crystallinity (~40%) data of the 89%-*trans* polybutadiene and the even lower crystallinity (~33%) of 83%-*trans* polybutadiene clearly do not fit the data derived by different crystallization of the 100%-*trans* polybutadiene (points in brackets). The 100%-*trans* heat capacities are practically linear with crystallinity at 250 and 260 K and join the data of equation (1), so that one can extend the range of equation (1) down to the glass transition temperature. A lesser slope is found at 240, 230
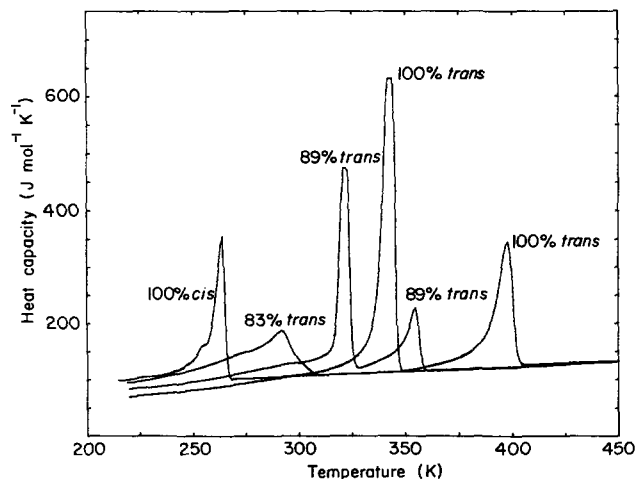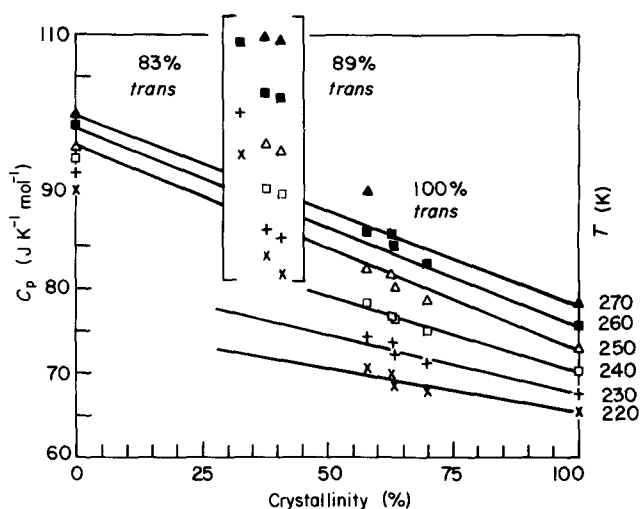

Figure 2 Heat capacity of *trans*-1,4-polybutadienes of different crystallinity at 220 to 270 K. The 38 and 41% crystallinity data refer to the 89%-*trans* isomer and show positive heat capacity deviations due to beginning phase transition

and 220 K, an indication that one has reached the upper end of the glass transition. This behaviour is quite similar to polyethylene[15] where 250 K represents the upper temperature limit of the glass transition, i.e. from 250 K to the transition peak the semicrystalline sample can be treated for thermodynamic discussions as a two-phase melt–crystal structure, just as below the glass transition most polymers can be treated as a two-phase glass–crystal structure. The higher heat capacities of the partially-*cis* polymers are most likely caused by the early beginning of the phase transitions.

The melting transition of the *cis*-polybutadiene is too low for our instruments to derive a similar plot for the crystallinity dependence of the heat capacity.

First-order transitions

The heats of transition and peak temperatures of the transitions of the samples as received (first run), cooled quickly (nominally 320 K min⁻¹), and slowly (10 K min⁻¹) are shown in *Table 2*, together with crystallinities computed using the equilibrium heat of transition listed in *Table 1*. Subscript 'd' indicates 'disordering' transition, i.e. the transition from the fully ordered, rigid crystal to the condis state. Subscript 'i' stands for 'isotropization', i.e. the transition condis-crystal to isotropic-melt. For the *cis*-isomer only the direct transition from the fully ordered crystal to the isotropic melt is found, making it a normal melting transition.

Additional peak temperatures in parentheses indicate shoulders or small peaks on the low temperature side of the transition (see also *Figure 1*). The most prominent double-peak is that of the first-run 100%-*trans* polymer at 325 K. Since it is lost on subsequent heatings, we propose that it results from extended-time, room-temperature annealing (annealing peak, see also *Figures 5* and *6*, below). Similarly, we suggest that the (much smaller) shoulders and secondary peaks of the other samples result from variation in crystal size due to thermal history and/or chemical composition.

It should be noted that only slowly cooled *trans*-polybutadienes (samples A and B) show close to identical condis and fully ordered crystallinity. All fast cooled and first run samples have higher condis crystallinity.

Figure 1 D.s.c. traces of four 1,4-polybutadienes after crystallization from the melt on quick cooling. For sample characterization see *Table 1*. For transition data, *Table 2*. (Perkin–Elmer DSC 10 K min⁻¹ heating rate)

Table 2 First order transitions of poly-1,4-butadienes

Samples	First run						Cooled at 320 K min⁻¹						Cooled at 10 K min⁻¹					
	T_d (K)	ΔH_d (kJ mol⁻¹)	w^c (%)	T_i (K)	ΔH_i (kJ mol⁻¹)	w^c (%)	T_d (K)	ΔH_d (kJ mol⁻¹)	w^c (%)	T_i (K)	ΔH_i (kJ mol⁻¹)	w^c (%)	T_d (K)	ΔH_d (kJ mol⁻¹)	w^c (%)	T_i (K)	ΔH_i (kJ mol⁻¹)	w^c (%)
A (100%-trans)	(325) 341.3	5.57	71	407	3.24	87	349	4.59	59	402	2.54	68	349	5.33	68	403	2.58	69
B (89%-trans)	308	2.87	37	362	1.94	52	(295) 321.3	2.96	38	355.3	1.63	44	(295) 321.3	3.19	41	355.3	1.61	43
C (83%-trans)				(284.7) 310.0	2.57	69				(272.6) 289.2	2.58	69				(277) 291.2	2.61	70
D (100%-cis)				(254.3) 263.6	2.18	24				(256.7) 263.6	2.10	23				(246.8) 261.8	2.48	27

The single, broad transition in the 83%-*cis* polymer (sample C) is assigned largely to the isotropization transition of the condis crystals rather than to two overlapping transitions or a single, fully ordered crystal to melt transition. The major reason for this assignment is the better agreement of heat capacity with a 30% amorphous sample (ΔC_p at T_g, see *Table 3*). If the sample would have been of the fully ordered type crystallinity, its crystallinity could have been only 22% (78% amorphous).

Glass transitions

Sample d.s.c. traces of polybutadienes B–D, indicative of the glass transitions, are shown in *Figure 3*. Data are listed in *Table 3*. The 100% *trans*-1,4-polybutadiene glass transition is very broad and the du Pont d.s.c. traces could not be evaluated quantitatively. *Figure 2* reveals the upper end of the glass transition to be 240 K. Data of Dainton *et al.*[16] by adiabatic calorimetry from 22 K lets one find the temperature of half-devitrification (T_g) to be about 190 K. The 89%-*trans* polymer is similarly difficult to analyse, particularly for quenched samples which show crystallization and melting effects immediately above T_g. *Figure 3* shows the trace with the clearest glass transition of a sample of 44% fully ordered crystallinity (compare also with *Table 2*). The observed increase in heat capacity at T_g of 17 J K mol⁻¹ would then correspond to a 25.8 J K mol⁻¹ increase for the amorphous fraction. The 83%-*trans* polymer shows a clearer glass transition, but of rather small magnitude. *Figure 1* indicates that its heat capacity at 220 K is that of the melt, i.e. the total ΔC_p must be close to that of a completely amorphous sample of 28.2 J K⁻¹ mol⁻¹ (see *Figure 9* below). The observed ΔC_p of 10–12 J K⁻¹ mol⁻¹ at temperatures of 187–188 K is where one might expect the fully amorphous glass transition. The remaining 2/3 of the transition is thus the 'glass transition of the condis crystal' and occurs largely below 180 K. The semicrystalline *cis*-1,4-polybutadiene, finally, shows a clear glass transition at 171–172 K. The baseline construction is shown to be somewhat arbitrary, but it is clear that the crystallization and melting peaks are matched in area, indicating a close to completely amorphous sample. Correcting all measurements for crystallinity gives the four values for 100% amorphous polymer, or an average of 27.1 ± 5.6 J K⁻¹ mol⁻¹.
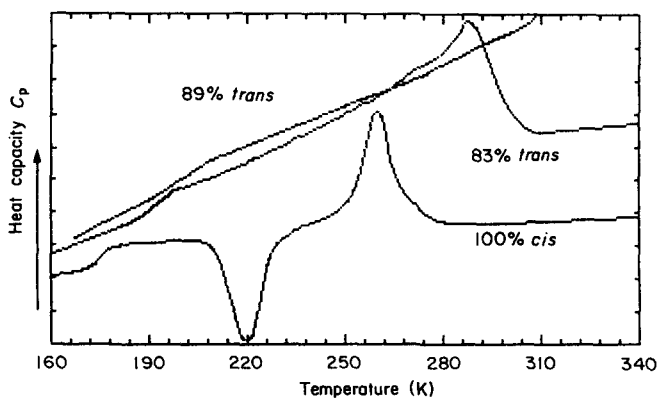

Figure 3 D.s.c. traces of three 1,4-polybutadienes of different thermal history to show the glass transition. D: *cis*-polymer, quenched in liquid nitrogen, approximately fully amorphous. C: 89%-*trans* polymer, cooled at 10 K min⁻¹. B: 83%-*trans* polymer, cooled uncontrolled at about 10–20 K min⁻¹. (du Pont DSC, samples C and D were run at approximately 2.5 times higher sensitivity, heating rates 10 K min⁻¹)

Table 3 Glass transition data of poly-1,4-butadienes

Samples	T_g^a (K)	ΔC_p^a (J K^{-1} mol^{-1})	ΔC_p^b (calc.) (J K^{-1} mol^{-1})	w^c $(\Delta H_f)^d$ (%)	Thermal^e history
A (100%-*trans*)	no apparent glass transition separable from d.s.c. traces (but see *Figure 2*)				a–d
B	188	difficult to observe		31	a
(98%-*trans*)	192	17.0	25.8	44	c
C	187	10.8	28.2^f	67.5	a
(83%-*trans*)	187	11.7	28.2^f	70.7	b
	188	10.4	28.2^f	66.1	e
D	171	34.9	35.3	1.2	a
(100%-*cis*)	172	21.7	26.4	18.3	e
	171	17.5	22.9	23.6	c
	172	18.2	23.9	23.8	d

^{a} Taken at the half-devitrification temperature T_g
^{b} Calculated increase in heat capacity at T_g for 100% amorphous assuming that crystals do not participate in the glass transition
^{c} This is part of the symbol w^c
^{d} Crystallinity computed from the heats of transition
^{e} Sample treatment: (a) quenched in liquid N$_2$, (b) cooled at 20 K min^{-1}, (c) cooled at 10 K min^{-1}, (d) cooled at 5 K min^{-1}, (e) uncontrolled cooling, varies between 10 and 20 K min^{-1}
^{f} Assuming that all crystallinity is condis crystallinity

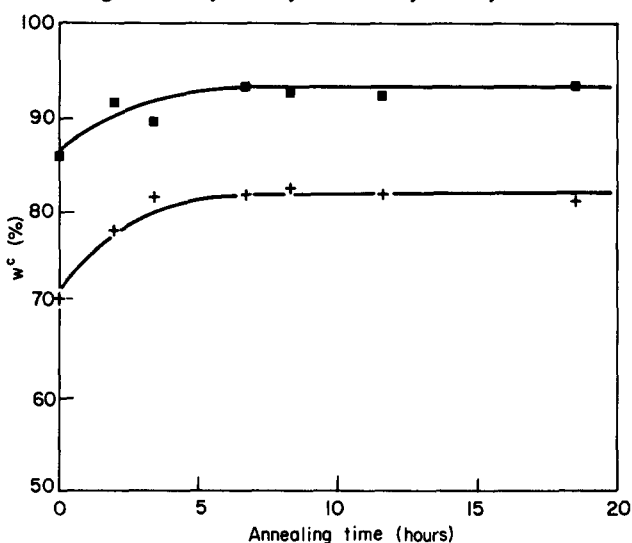**Figure 4** Change of condis (■) and fully-ordered (+) crystallinity of 100% *trans*-1,4-polybutadiene on annealing at 337 K as a function of time

Figure 5 D.s.c. traces of 100% *trans*-1,4-polybutadiene after annealing for the indicated times at 393 K in the condis state (Perkin–Elmer DSC, analysis after quick cooling to 350 K)

Annealing experiments

To check on the discrepancy between condis and fully-ordered crystallinities of the first-run samples, a series of annealings of the as received 100%-*trans*-1,4-polybutadienes was attempted at 337 K, just below the T_d peak temperature. The results are shown in *Figure 4*. Both, the fully-ordered and the condis crystallinities increase, but the former increases almost double as much (from 70.8 to 81.5%) as the latter (from 86.1 to 93.3%). The annealing is thus likely to permit all transitions to greater stability: amorphous to condis crystal, amorphous to fully ordered crystal, as well as condis crystal to fully ordered crystal.

High temperature annealings in the condis crystal state were attempted on the 100%-*trans*-1,4-polybutadienes cooled at 320 K min^{-1} (see *Table 2*) for various times (1–10 min) and temperatures (381–339 K). The analyses were then carried out by heating with 10 K min^{-1} after quick cooling to 350 K. *Figures 5* and *6* show the results. The surprising observation is that all annealings led to no increase in condis crystallinity (66.5 ± 3.2%), 12 measurements). There is, however, a clear record of the annealing temperature in the minimum of the double
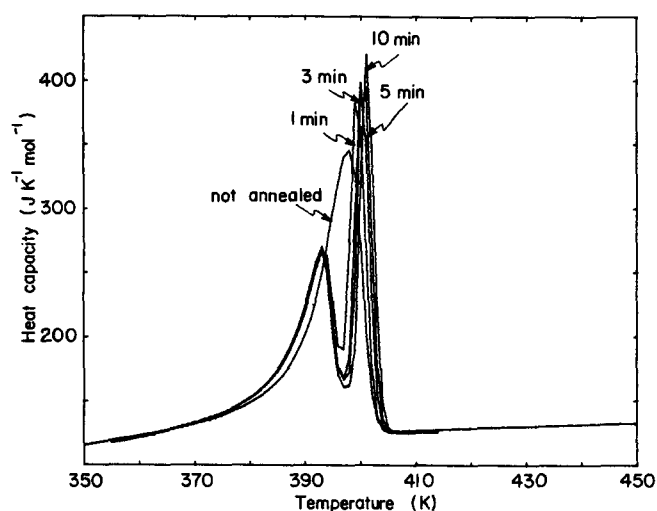

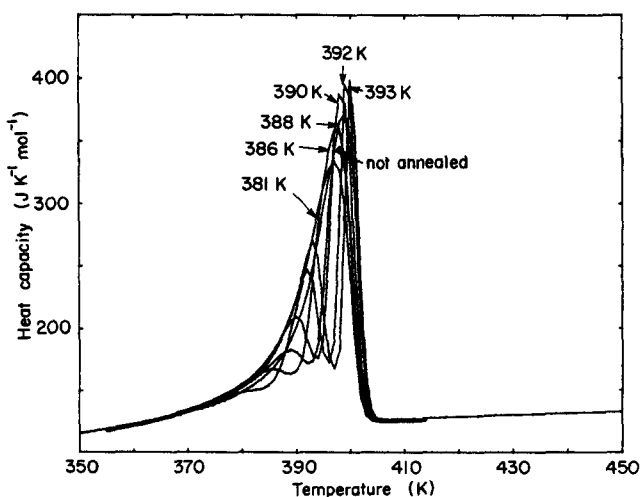**Figure 6** D.s.c. traces of 100% *trans*-1,4-polybutadiene after annealing for 3 min at the indicated temperatures in the condis state (Perkin–Elmer DSC, analysis after quick cooling to 350 K)

peaks of the annealed samples. The condis crystals molten at the annealing temperature become slightly less perfect on recrystallization during the cooling for analysis, and the perfection of remaining, unmolten condis crystals

increases slightly with increasing annealing time and temperature (maximum increase in T_i was 3 K).

COMPUTATION OF THE HEAT CAPACITIES OF SOLID 1,4-POLYBUTADIENE

The vibrational spectra of *cis-* and *trans-*1,4-polybutadiene can be approximated from two sources. Raman and i.r. spectra have been analysed and interpreted[17,18], and polyethylene, which has many of the same group vibrations, is well known[3]. *Table 4* shows the frequencies used in the subsequent calculations. Since it was found that the difference in frequencies for CH-, CH_2- and C=C- stretching and CH_2- scissoring are less than 50 K between *trans-* and *cis-*configurations, the average values of the i.r. and Raman frequencies were taken for both isomers. CH_2- scissoring is practically of the same frequency as found in polyethylene[3]. CH_2- wagging, twisting and bending have frequencies in the same range as polyethylene. Since for these lower frequencies more exact phase distributions may be advantageous for C_v calculations, polyethylene normal mode vibrations are listed in *Table 4* instead of the isolated Raman and i.r. frequencies. It was found that even the C–C stretching frequencies fall in the same range as for polyethylene, although two of them should be influenced by the change in hybridization due to the adjacent C=C double bonds. Again, polyethylene data are listed in *Table 4*. Four CH in-plane and out-of-plane bendings have upper frequency limit close to that for polypropylene[8], but their low frequency limit is at much lower frequency, so that a box distribution of lowest and highest frequencies given by i.r. and Raman frequencies were taken for calculation.

Knowing the frequencies for the 22 group vibrations, it is possible to fit the low temperature heat capacity discussed in the ATHAS data bank[1] to a Tarasov expression to derive θ_3 and θ_1, the parameters which characterize the eight skeletal vibrations. The detailed calculation programs are given in refs. 19 and 20; the general theory is discussed, for example, in ref. 21. First,

Table 4 Vibrational frequencies of 1,4-polybutadiene

Group vibrations:	N	θ-Temperature (K)[a]
CH stretching	2	4347
CH_2 asym. stretching	2	4204
CH_2 sym. stretching	2	4097
C=C stretching	1	2387
CH_2 scissoring	2	2078
CH_2 wagging	0.70	1977
	1.30	1698–1977
CH_2 twisting	0.96	1698–1874
	1.04	1874
CH bending	4	1016–1914
C–C stretching	0.93	1525
	1.02	1378–1638
	1.05	1378–1525
CH_2 rocking	0.08	1494
	1.18	1038–1494
	0.74	1079

Skeletal vibrations:	*trans*:	*cis*:
total of 8 vibrations	$\theta_3=95$	$\theta_3=87$
	$\theta_1=599$	$\theta_1=589$

[a] Frequencies in kelvin (θ = hv/k; 1 K = 2.08.10[10] Hz, 1 K = 0.695 cm⁻¹)
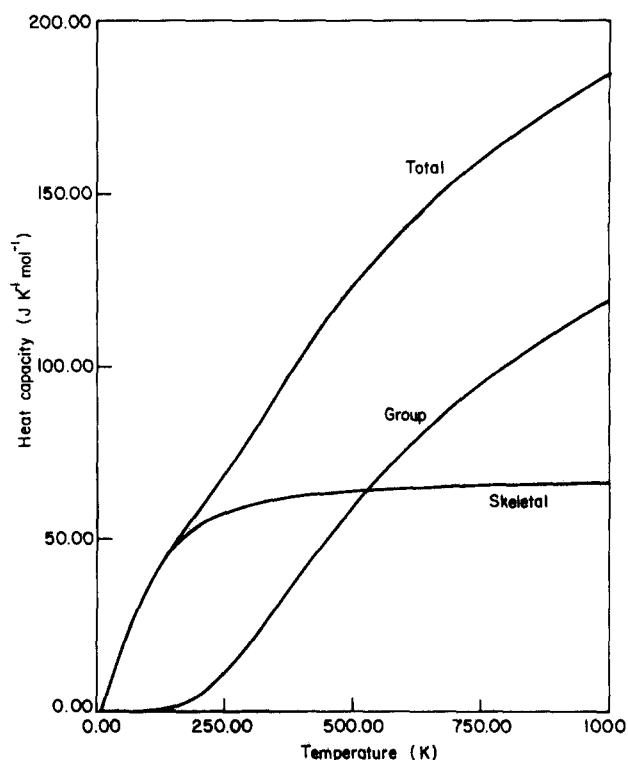

Figure 7 Heat capacity of solid 1,4-polybutadiene as calculated from the vibrational spectrum as given in *Table 4*

the group-vibration contributions are subtracted from the experimental C_v (heat capacity at constant volume, for C_p to C_v conversion see below). Then a preliminary three-dimensional Debye-temperature (175 K for *trans*, 164.5 K for *cis*) was obtained by extrapolation of the experimental heat capacities to temperatures below 10 K. With these Debye-temperatures the computation routine (inversion) for heat capacity to θ_3 and θ_1 was used[19]. For *trans-*1,4-polybutadiene, data bank[1] heat capacities from 20 to 170 K were used and yielded $\theta_1 = 598.7 \pm 18.9$ K and $\theta_3 = 94.7 \pm 1.5$ K. For *cis-*1,4-polybutadiene data bank[1] heat capacities from 30 to 150 K were used to give $\theta_1 = 589.4 \pm 48.8$ K and $\theta_3 = 87.1 \pm 3.9$ K.

With all vibrational information of *Table 4* it is then possible to calculate the heat capacity at any temperature[20]. *Figure 7* shows the results for the heat capacity at constant volume C_v. The differences between *cis-* and *trans-*polybutadiene are not large enough to show in the graph.

Furthermore, C_v was converted to heat capacity at constant pressure, C_p, using the Lindemann equation with its universal value $A_0 = (5.12/4) \times 10^{-3}$ = 1.28×10^{-3} K mol J⁻¹ (ref. 22). *Figure 8* shows the percentage difference between calculated and measured C_p. The deviations above 150 K are clearly due to the glass transitions. From 20 to 280 K the calculated and measured *trans-*1,4-polybutadiene heat capacities agree within $+1.2 \pm 2.8\%$. From 60 to 160 K the calculated and measured *cis-*1,4-polybutadiene heat capacities agree within $-1.6 \pm 3.5\%$. At lower temperatures errors are larger, but in this range absolute heat capacities are small so that integral errors remain small. This is also the temperature range where differences in crystallinity would affect the heat capacity more significantly.

THERMODYNAMIC FUNCTIONS
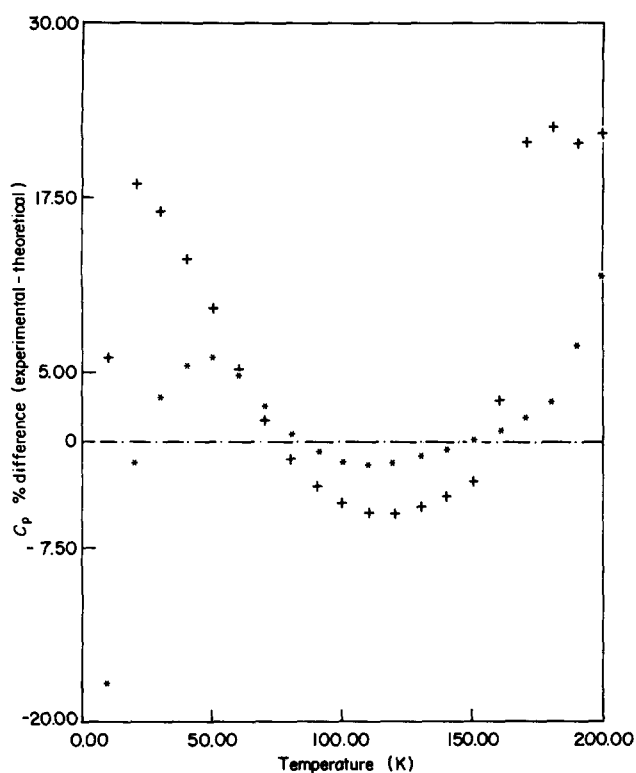
Tables 5 and *6* contain the thermodynamic data of the

Figure 8 Differences between experimental and measured heat capacities at constant pressure (+) cis-1,4-polybutadiene, (*) trans-1,4-polybutadiene

crystal, glass, condis and liquid phases of *trans-* and *cis-*1,4-polybutadienes based on the computed heat capacities at constant pressure, equation (1), and the transition data listed in *Table 1*. Extrapolations beyond the transition temperatures are easily possible using the established heat capacities.

DISCUSSION

Heat capacities

While the original ATHAS data bank[1] contained only the measurements by Dainton *et al.*[16], the new measurements (equation (1)) and calculations (*Tables 5* and *6*) provide full data for all states of 1,4-polybutadiene (recommended data, 1985). Both solids, glass and fully ordered crystal, as well as *cis-* and *trans-*isomers, have practically the same heat capacities. *Figure 9* shows a summary of the heat capacity data. At low temperatures (below about 50 K) the data presented here refer to semicrystalline samples and changes are expected for different crystallinities. The order of magnitude can be estimated by comparison with the full-range data available for polyethylene[1,3].

A comparison of θ_1 of polybutadienes (*Table 4*) with polyethylene ($\theta_1 = 519$ K) shows an increase of 70 to 80 K, as expected from the larger force constant of the C=C bond. The masses of the backbone chains are otherwise identical. It was found before that θ_1 is largely independent of crystallinity[19]; one can see on the polybutadienes that going to the *cis* isomer has also only little influence on θ_1.

The θ_3-values of *Table 4* fall into the range of amorphous (80 K) and crystalline (158 K) polyethylene. *Trans*-polybutadiene has, however, rather high crystallinity so that overall, the θ_3-values are probably somewhat lower than those of polyethylene. The sequence of θ_3's goes parallel with the packing fractions of the three

Table 5a Thermodynamic functions of crystalline *trans*-1,4-polybutadiene

T (K)	C_p (J K^{-1} mol^{-1})	$H_T^c - H_0^c$ (J K^{-1} mol^{-1})	S_T^c (kJ mol^{-1})	$G_T - H_0^c$ (J K^{-1} mol^{-1})
0.0	0.0000	0.0000	0.0000	0.000
10.0	0.94	0.005	0.47	−0.000
20.0	4.89	0.034	2.16	−0.009
30.0	9.39	0.105	4.95	−0.043
40.0	13.60	0.220	8.21	−0.108
50.0	17.60	0.376	11.67	−0.207
60.0	21.47	0.571	15.22	−0.342
70.0	25.21	0.805	18.81	−0.512
80.0	28.81	1.075	22.41	−0.718
90.0	32.23	1.380	26.00	−0.960
100.0	35.45	1.719	29.57	−1.238
110.0	38.47	2.088	33.09	−1.551
120.0	41.29	2.487	36.56	−1.900
130.0	43.95	2.913	39.97	−2.283
140.0	46.47	3.365	43.32	−2.699
150.0	48.89	3.842	46.61	−3.149
160.0	51.24	4.343	49.84	−3.631
170.0	53.56	4.867	53.01	−4.146
180.0	55.87	5.414	56.14	−4.692
190.0	58.19	5.984	59.23	−5.269
200.0	60.55	6.578	62.27	−5.876
210.0	62.96	7.196	65.28	−6.514
220.0	65.44	7.838	68.27	−7.182
230.0	67.98	8.505	71.23	−7.879
240.0	70.61	9.198	74.18	−8.606
250.0	73.32	9.917	77.12	−9.363
260.0	76.11	10.664	80.05	−10.143
270.0	79.00	11.440	82.98	−10.964
273.2	79.93	11.690	83.90	−11.227
280.0	81.97	12.245	85.90	−11.808
290.0	85.03	13.080	88.83	−12.682
298.2	87.59	13.784	91.23	−13.417
320.0	94.74	15.775	97.67	−15.479
330.0	98.15	16.739	100.6	−16.471
340.0	101.7	17.739	103.6	−17.492
350.0	105.3	18.773	106.6	−18.543
356.0	107.5	19.412	108.4	−19.188

Table 5b Thermodynamic functions of condis crystals of *trans*-1,4-polybutadiene

T (K)	C_p (J K^{-1} mol^{-1})	$H_T^c - H_0^c$ (J K^{-1} mol^{-1})	S_T^d (kJ mol^{-1})	$G_T - H_0^c$ (J K^{-1} mol^{-1})
356.0	115.9	27.201	130.3	−19.189
360.0	116.6	27.666	131.6	−19.712
370.0	118.4	28.841	134.8	−21.045
380.0	120.2	30.034	138.0	−22.409
390.0	122.0	31.245	141.2	−23.805
400.0	123.7	32.473	144.3	−25.232
410.0	125.5	33.719	147.3	−26.690
420.0	127.3	34.983	150.4	−28.179
430.0	129.1	36.265	153.4	−29.698
437.0	130.4	37.173	155.5	−30.779

Table 5c Thermodynamic functions of the melt of *trans*-1,4-polybutadiene

T (K)	C_p (J K^{-1} mol^{-1})	$H_T^a - H_0^c$ (J K^{-1} mol^{-1})	S_T^a (kJ mol^{-1})	$G_T - H_0^c$ (J K^{-1} mol^{-1})
437.0	130.36	41.061	164.0	−30.623
440.0	130.90	41.453	164.9	−31.117
450.0	132.60	42.770	167.9	−32.781
460.0	134.40	44.105	170.8	−34.475
470.0	136.20	45.458	173.7	−36.197
480.0	138.00	46.829	176.6	−37.949
490.0	139.70	48.218	179.5	−39.730
500.0	141.50	49.624	182.3	−41.539

Table 6a Thermodynamic functions of crystalline *cis*-1,4-polybutadiene

T (K)	C_p (J K^{-1} mol^{-1})	$H^c_T - H^c_0$ (J K^{-1} mol^{-1})	S^c_T (kJ mol^{-1})	$G_T - H^c_0$ (J K^{-1} mol^{-1})
0.0	0.0000	0.0000	0.0000	0.0000
10.0	1.11	0.006	0.55	−0.000
20.0	5.31	0.038	2.44	−0.011
30.0	9.83	0.113	5.40	−0.049
40.0	14.03	0.233	8.79	−0.119
50.0	18.05	0.393	12.35	−0.225
60.0	21.95	0.593	15.99	−0.366
70.0	25.74	0.832	19.66	−0.544
80.0	29.39	1.107	23.33	−0.759
90.0	32.86	1.419	26.99	−1.011
100.0	36.13	1.764	30.63	−1.299
110.0	39.20	2.140	34.22	−1.624
120.0	42.08	2.547	37.75	−1.983
130.0	44.79	2.981	41.23	−2.379
140.0	47.37	3.442	44.64	−2.808
150.0	49.85	3.928	48.00	−3.271
160.0	52.28	4.439	51.29	−3.768
170.0	54.68	4.973	54.53	−4.297
180.0	57.08	5.532	57.73	−4.859
190.0	59.51	6.115	60.88	−5.452
200.0	62.00	6.723	63.99	−6.076
210.0	64.55	7.355	67.08	−6.732
220.0	67.19	8.014	70.14	−7.418
230.0	69.93	8.700	73.19	−8.134
240.0	72.78	9.413	76.23	−8.882
250.0	75.74	10.156	79.26	−9.659
260.0	78.82	10.929	82.29	−10.467
270.0	82.03	11.733	85.33	−11.305
273.2	83.09	11.993	86.28	−11.575
280.0	85.38	12.570	88.37	−12.173
284.0	86.78	12.914	89.59	−12.529

Table 6b Thermodynamic functions of liquid *cis*-1,4-polybutadiene

T (K)	C_p (J K^{-1} mol^{-1})	$H^a_T - H^c_0$ (J K^{-1} mol^{-1})	S^a_T (kJ mol^{-1})	$G_T - H^c_0$ (J K^{-1} mol^{-1})
284.0	103.1	22.114	121.60	−12.420
290.0	104.2	22.736	123.77	−13.156
298.2	105.7	23.593	126.68	−14.178
300.0	106.0	23.787	127.33	−14.412
310.0	107.7	24.856	130.83	−15.703
320.0	109.5	25.942	134.28	−17.028
330.0	111.3	27.046	137.68	−18.388
340.0	113.1	28.168	141.03	−19.782
350.0	114.9	29.308	144.33	−21.209

crystalline polymers: *cis*-1,4-polybutadiene 0.68, *trans*-1,4-polybutadiene 0.69, and polyethylene 0.70[23].

Improvements between calculation and measurements (see *Figure 8*) must await more detailed frequency information and lower temperature and broader crystallinity range measurements of heat capacity.

The condis state of trans-1,4-polybutadiene

The condis state of *trans*-1,4-polybutadiene was recognized as a special state before[11]. The high mobility of conformations was proven by n.m.r.[24]. The volume of the crystal increases by about 9% on going to the condis crystal, and the chain-length in the crystal decreases by 4%[25,26]. The here used entropies of transition from the fully ordered crystal to the condis state of 21.9 J K^{-1} mol^{-1} agrees well with the estimate of Corradini[26] that 9 of the 27 conformations of the repeating unit become accessible (18.3 J K^{-1} mol^{-1}). Volume expansion effects have been estimated to account for an additional 3.2 J K^{-1} mol^{-1}.[27] The here observed high heat capacity (liquid-like) is in accord with the high mobility (see *Figure 9*).
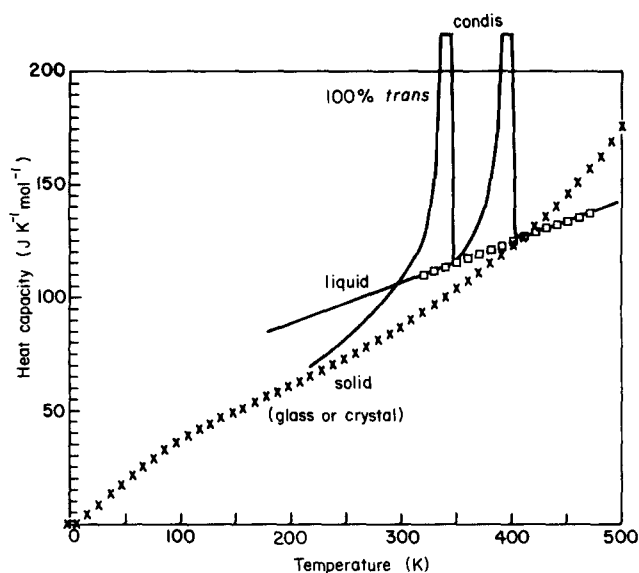

Figure 9 Experimental liquid and calculated heat capacity at constant pressure of *cis*- and *trans*-1,4-polybutadiene. Also shown is the measured heat capacity of a well crystallized sample of *trans*-1,4-polybutadiene

Of interest are the crystallinity determinations (*Table 2*) and the annealing experiments (*Figures 4–6*). They reveal that below T_d there can be three phases in a semicrystalline *trans*-1,4-polybutadiene. Only well annealed, isomerically pure samples approach the two-phase structure. The observation that larger number of defects in a condis crystal prohibits the conversion to the fully ordered crystal was also made for the case of polytetrafluoroethylene[4]. The attempts to anneal in the condis state seem to indicate that once created, perfection of the condis state or its increase is difficult above T_d, quite in contrast to the condis state of polyethylene, which quickly anneals to 100% crystallinity and full chain extension[10,28]. More about the especially broad transition peak to the isotropic state will be discussed in connection with further work on the kinetics.

Glass transitions

The glass transition of the *trans*-1,4-polybutadiene seemed somewhat difficult to establish because of the high crystallinity of most samples. The extrapolation of the heat capacities (*Figure 2*) makes it certain that the upper end of T_g is 250 K and the full transition is rather broad. The temperature of half-devitrification is 190 K, in good agreement with prior calorimetric work[16], but somewhat lower than listed in the data bank[1]. The change in heat capacity at T_g can best be evaluated from the data in *Table 5*. It is 28.2 J K^{-1} mol^{-1}, close to the value expected for three mobile groups (beads) per repeating unit. A large number of linear macromolecules have a ΔC_p of about 11 J K^{-1} mol^{-1} of bead[1,29]. The question of the glass transition of the condis state remains to be discussed. From the data of *Table 3* and *Figure 3* it seems that the observed sharper glass transition at 190 K can only be attributed to the normal melt. The condis state would then have to freeze over a wider temperature range below the normal glass transition to account for the observed high heat capacity (*Figure 1*, 83%-*trans*).

The *cis*-isomer glass transition is, based on our data, best taken at 171 K, close to the prior data bank value[1]. This is within the range of data from ref. 30 and prior calorimetry[16] (160 to 171 K). The relatively large spread may be due to different heating rates, as well as different

choices of definition of glass transitions and different chemical and configurational purity of the samples. Again, ΔC_p is taken from the heat capacity table (*Table 6*) to be $29.1 \, J \, K^{-1} \, mol^{-1}$, quite similar to the *trans*-isomer. Again, 3 'beads' fit the repeating unit as mobile unit. This value is also in agreement with the average of the crystallinity corrected ΔC_p of *Table 3* $(27.1 \pm 5.6 \, J \, K^{-1} \, mol^{-1})$.

The thermodynamic functions

A comparison of the absolute entropies of the molten *cis*- and *trans*-isomers at 350 K shows a 5% higher entropy for the *cis*-isomer $(7.4 \, J \, K^{-1} \, mol^{-1})$, which should be just outside the error limit. The intermediate mobile condis state of *trans*-1,4-polybutadiene is thus strictly a crystal property. Its combined two transition entropies $(21.9 + 8.5 \, J \, K^{-1} \, mol^{-1})$ are even slightly less than the *cis*-isomer single transition entropy $(32.3 \, J \, K^{-1} \, mol^{-1})$.

Although there are some uncertainties on the exact glass transition shape and the true low-temperature heat capacity, one can make an attempt to estimate the entropy of the glassy polymers at 0 K. For the *trans*- and *cis*-isomers the back-integration from the melt yield 17 and $22 \, J \, K^{-1} \, mol^{-1}$, respectively. This means that the *cis*-isomer, despite a lower glass transition temperature, may still have a higher entropy in the glassy state (although the difference is close to the error limit). Compared with polyethylene, which has a glassy zero kelvin entropy per CH_2- of $2.59 \, J \, K^{-1} \, mol^{-1}$, the entropies of 1,4-polybutadienes are much higher. For all three polymers the liquid packing fractions are similar (0.60–0.61) and the cohesive energy densities are identical ($4.18 \, kJ \, mol^{-1}$ of carbon atoms)[13]. The differences are thus most likely linked to the higher order found in amorphous polyethylene enhanced by the large decrease in intramolecular energy on *gauche–trans* conversion which leads to a more extended macroconformation. For *trans*-1,4-polybutadiene a similar conformation is possible, but it is not favoured by as much intramolecular energy gain. For the *cis*-isomer no such extended macroconformation is possible.

The stability sequence of the condis and fully ordered crystal was already established by the size of the endotherms. *Table 5* gives quantitative information. Even assuming a very low T_g of the condis state can not lead to a reverse of the low temperature sequence: crystal (most stable), condis glass (less stable), amorphous glass (least stable), but all three states are metastable and can coexist in a microphase separated structure. For full description at least two crystallinity parameters must be given (see *Table 2*).

An earlier attempt to calculate thermodynamic properties of *trans*-1,4-polybutadiene by Evans and Woodward[31] with a much simplified frequency spectrum led in the limited temperature region 320 to 380 K to 8–16% lower heat capacities than given in *Table 5* and did not lead to absolute entropies.

CONCLUSIONS

Polybutadienes were included in the series of thermodynamically well characterized linear macromolecules. Of special interest is the three-phase

semicrystalline state of *trans*-1,4-polybutadiene. In the molten and glassy states *cis*-1,4-polybutadiene has the higher entropy. A possible condis glass transition is suggested below T_g of the melt of *trans*-1,4-polybutadiene. The heat capacity parameters θ_1 and θ_3 reflect our knowledge of vibrational spectra of polybutadienes relative to polyethylene, i.e. a stronger coupling along the chain due to the double bond, but a weaker coupling between the chains because of a lower crystal packing fraction of the polybutadienes.

REFERENCES

1 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
2 Shu, P., H.-C., Wunderlich, B. in 'Thermal Analysis in Polymer Characterization', (Ed. E. Turi), Wiley and Sons, New York, 1981, p. 124
3 Grebowicz, J., Suzuki, H. and Wunderlich, B. *Polymer* 1985, **16**, 561
4 Lau, S.-F., 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* 1985, **27**, 563
7 Kirkpatrick, D. E., Judovits, L. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1985, to be published
8 Grebowicz, J., Lau, S.-F. and Wunderlich, B. *J. Polym. Sci., Polym. Symp. Edn.* 1984, **71**, 19
9 Lim, S., Aycock, W., Judovits, L. and Wunderlich, B. *Polymer* to be published
10 Wunderlich, B. and Grebowicz, J. *Adv. Polym. Sci.* 1984, **60/61**, 1
11 Natta, G. and Corradini, P. *J. Polym. Sci.* 1959, **39**, 29
12 Fintner, J. and Wegner, G. *Makromol. Chem.* 1981, **182**, 1859
13 See Wunderlich, B. 'Macromolecular Physics', Vol. 3, 'Crystal Melting', Academic Press, New York, NY, 1980
14 Suzuki, H. and Wunderlich, B. *J. Thermal Anal.* 1984, **29**, 1369
15 Wunderlich, B. *J. Chem. Phys.* 1962, **37**, 1203
16 Dainton, F. S., Evans, D. M., Hoare, F. E. and Melia, T. P. *Polymer* 1962, **3**, 297
17 Hsu, S. L., Moore, W. H. and Krimm, S. *J. Appl. Phys.* 1975, **46**, 4082
18 Coleman, M. M., Tabb, D. L., Farmer, B. L. and Koenig, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 445
19 Cheban, Yu. V., Lau, S.-F. and Wunderlich, B. *Colloid Polymer Sci.* 1982, **260**, 9
20 Lau, S.-F. and Wunderlich, B. *J. Thermal Anal.* 1983, **28**, 59
21 Wunderlich, B. and Baur, H. *Adv. Polym. Sci.* 1970, **7**, 151
22 Grebowicz, J. and Wunderlich, B. *J. Thermal Anal.* 1985, **30**, 227
23 Wunderlich, B. 'Macromolecular Physics', Vol. 1, 'Crystal Structure, Morphology, Defects', Academic Press, New York, NY, 1973
24 Iwayanagi, S. and Miura, J. *Rept. Progr. Polym. Phys. Jpn.* 1965, **8**, 303
25 Suehiro, K., Takayanagi, N. *J. Macromol. Sci., Phys.* 1970, **B4**, 39
26 Corradini, P. *J. Polym. Sci., Symp.* 1975, **50**, 327
27 Bautz, G., Leute, U., Dollhopf, W., Haegele, P. C. *Colloid Polym. Sci.* 1981, **259**, 714
28 Wunderlich, B., Davidson, T., Prime, R. B., Melillo, L., Gruner, C. L. and Bopp, R. C. *J. Polym. Sci. A-2*, 1969, **7**, 2043, 2051, 2061, 2073, 2091, 2099
29 Wunderlich, B. *J. Phys. Chem.* 1960, **64**, 1052
30 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', J. Wiley and Sons, New York, NY, 1975 (second edition)
31 Evans, H. and Woodward, A. E. *Macromolecules* 1978, **11**, 685