Thermal expansion and Grüneisen parameter of polyethylene between 5 and 320 K

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The linear thermal expansion coefficient, α, of polyethylene with crystallinity $X=0.44$, 0.62, 0.77 and 0.98 has been measured between 5 and 320 K with an experimental accuracy of about 5% above 15 K and 10% below 15 K using an interferometric dilatometer system. In the temperature range 40 to 100 K the thermal expansion is found to be independent of crystallinity, whereas at lower as well as higher temperatures, α increases with increasing noncrystallinity. By linear extrapolation the thermal expansion coefficient of the noncrystalline phase can be estimated. The influence of the phonon spectrum on the thermal expansion is discussed in terms of the Grüneisen parameter. For completely crystalline polyethylene, a bulk-Grüneisen parameter of $\gamma_b \simeq 2$ is found below 20 K. This value is smaller than expected from theories for polymer crystals. For noncrystalline polyethylene, γ_b is constant ($\gamma_b \simeq 1.6$) between 30 and 100 K, showing a rapid increase at lower temperatures with $\gamma_b \simeq 12.5$ at 5 K. This high value for γ_b can be related to excess modes in the vibration spectrum of the noncrystalline phase, which have previously been found to contribute also to the heat capacity at these temperatures.

(Keywords: crystalline polyethylene; noncrystalline polyethylene; low temperature; thermal expansion; Grüneisen parameter)

INTRODUCTION

Thermal expansion measurements on solids at low temperatures can be useful in obtaining information about the anharmonicity of intermolecular interaction potentials. Usually, the discussion is based on the Grüneisen parameter, which has been extensively investigated for inorganic solids over wide temperature ranges[1]. In the past there has been growing interest in the lattice dynamics and associated physical properties of polymers representing an extreme form of anisotropy in the crystalline state. Various measurements[2-6] of the thermal expansion for polycrystalline samples of polyethylene (PE) have been reported. However, most of the experimental data concerning the specific heat data and the elastic constants of PE-samples having different crystallinities were not complete. Thus, the observed temperature dependence of the Grüneisen parameter was influenced by contributions from the noncrystalline state and the crystalline state, respectively. In order to compare the experimental results with model calculations[2,7-9] (for the lattice dynamics of polymers) it would be more helpful to be able to distinguish between the thermoelastic behaviour of noncrystalline and crystalline PE.

In this paper, we will present thermal expansion measurements on polyethylene (PE) with crystallinity varying from $X=0.44$ to 0.98. Thermal expansion coefficients of completely noncrystalline and crystalline PE were obtained by extrapolation of the experimental data in the temperature range 5 to 320 K. From these values and specific heat data on the same samples published earlier[10] Grüneisen parameters for both phases were calculated and will be discussed in terms of appropriate models for amorphous materials and polymer crystals, respectively.

THEORY

Due to the nature of the samples we investigated, we will obtain the macroscopic bulk-Grüneisen parameter γ_b, which can be calculated from experimental values of linear thermal expansion coefficient α, the specific heat at constant volume C_v, the density ρ and isothermal volume compressibility K_T

$$\gamma_b = \frac{3\alpha}{\rho K_T C_v} \tag{1}$$

In theoretical treatments the microscopic or normal mode Grüneisen parameter γ_i is introduced

$$\gamma_i = -\left(\frac{\partial \ln \omega_i}{\partial \ln V}\right) \tag{2}$$

In (2) the anharmonicity of forces between two atoms in a crystal is described by the change of atomic vibration frequency ω with the change of crystal volume V. Assuming interaction to be represented by a Mie-potential

$$\Phi = -\frac{A}{r^m} + \frac{B}{r^n} \tag{3}$$

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where r is the distance between two atoms (A and B are constants), it can be shown from (2) and (3) for $T \rightarrow 0$ K that[1]

$$\gamma = \frac{n+m+3}{k} \qquad (4)$$

If the volume change is due to changes in three orthogonal directions in the crystal, i.e. the interatomic distance varies as $V^{1/3}$, $k=6$ is obtained. For a Lennard–Jones potential ($m=6$ and $n=12$) from (4) it follows $\gamma=3.5$. If volume changes are due to changes in two dimensions only, $k=4$ and $\gamma=5.25$, and for one dimension, $k=2$ and $\gamma=10.5$ is obtained. Neglecting thermal length changes along the chain, $\gamma=5.25$ should be the proper value for polymer crystals. Similar high values for Grüneisen parameters at low temperatures have been calculated from several theories[2,7,9] for polymer crystals.

It should be noted that the above calculation is based on some simplified approximations—e.g. the neglect of 'tension' effects which decrease γ[9]. Furthermore, the only temperature dependence in equation (4) is through the change in volume, whereas γ varies directly with temperature due to the changing thermal population of the normal modes. Thus, a macroscopic Grüneisen parameter is given by the weighted average of the microscopic $\gamma(\omega)$

$$\gamma = \frac{\int \gamma(\omega) C(\omega) \mathrm{d}\omega}{\int C(\omega) \mathrm{d}\omega} \qquad (5)$$

where $C(\omega)$ is the specific heat contribution of a phonon with frequency ω. For a polymer crystal the value $\gamma=5.25$ should be valid for the low frequency range of the phonon spectrum only, whereas higher frequency acoustic and optical phonons have small Grüneisen parameters[5] ($\gamma(\omega) \leqslant 0.5$), leading to a drop in the overall Grüneisen parameter (equation (5)) with increasing temperature[9].

For amorphous solids, the situation is somewhat more complicated. Additional anomalous contributions to the vibration spectrum are found to influence the thermal properties at low temperatures as can be seen from the temperature dependence of the specific heat below ~20 K

$$C_{\mathrm{p}} = c_{\mathrm{D}} \cdot T^3 + c_1 \cdot T + C_{\mathrm{Exc}} \qquad (6)$$

From equation (1) and the form of equation (6) the low temperature thermal expansivity would be expected to be given by

$$\alpha = \frac{\rho K_T}{3} (\gamma_{\mathrm{D}} \cdot c_{\mathrm{D}} \cdot T^3 + \gamma_1 \cdot c_1 \cdot T + \gamma_{\mathrm{Exc}} \cdot C_{\mathrm{Exc}}) \qquad (7)$$

The first term in equation (6) represents the Debye specific heat as can be calculated from the elastic constants. From thermal expansion data and the elastic constants of amorphous poly(methyl methacrylate) (PMMA) a value $\gamma_{\mathrm{D}} \simeq 3 \ldots 4$ has been estimated[11]. This is in good agreement with calculations on amorphous polymers made by Curro[8], yielding $\gamma=3.16$ with volume changes allowed along three directions. The second term in equation (6), giving a linear specific heat, is associated with low energy excitations and dominates the other contributions below 1 K[12]. Large negative Grüneisen parameters have been observed in vitreous SiO_2 and PMMA[11] demonstrating the strong anharmonic coupling between the low energy excitations and phonons. The last term in equation (6) describes an excess specific heat which is dominant around 5 K and can be described by Einstein-terms in addition to the Debye phonon density of states[13,14]. The physical origin of these modes (i.e. localized modes or low frequency phonon dispersion) is still not understood. In case of PMMA a value $\gamma_{\mathrm{Exc}} = 0.2 \pm 0.6$ was obtained[11], which favours the Debye contribution γ_{D} to be dominant in the temperature range ~2 K to ~10 K.

RESULTS

PE samples with different crystallinity, X, were supplied by BASF AG, Ludwigshafen, Germany. These were: Lupolen 1840 D, $X=0.44$ (PE 44); Lupolen 4261 A, $X=0.62$ (PE 62); Lupolen 6011 DX, $X=0.77$ (PE 77) and Lupolen 6011 L, $X=0.98$ (PE 98). The latter is brought to a high crystallinity by melting and recrystallization under pressure[15] and from electron scanning microscopy we estimate its lamellae thickness to be about 440 nm which makes an extended chain structure reasonable. It should be noted, that the sample PE 98 investigated in this paper was not taken from the same charge as PE 98 discussed previously in ref. 10. Reproducible differences in thermal expansion coefficients of about 15% were found in the temperature range 100 to 250 K. For all samples, X-ray studies indicated a statistically disordered lamellae distribution.

For thermal expansion measurements, cylinders of about 10 mm length and 5 mm diameter were machined. The accuracy of the interferometric dilatometer cell used from 5 to 300 K was tested with high purity copper and vitreous silica samples[16]. In addition, a commercial Perkin Elmer TMS-1 thermomechanical scanner was used between 100 K and 350 K for thermal expansion measurements. Agreement between both methods was better than 5% in the overlapping temperature range. Measurement error is about 5% above 15 K and less than 10% below.

Results for the linear thermal expansion coefficients, α, for some of the PE samples have been published already[10]. In *Figure 1* we present a complete set of data for α as a function of crystallinity in the temperature range 5 to 300 K (data above 300 K are omitted for clarity). Within the experimental error, the dependence on the crystallinity can be represented by a linear relationship. However, this does not hold at temperatures above 250 K, where PE 44 shows higher α-values. A similar behaviour is observed in the specific heat data[13], and one could argue that in low density PE the branched chain structure gives rise for deviations in the linear relationship between thermal quantities and crystallinity. Furthermore it can be seen from *Figure 1*, that the thermal expansion coefficient is independent of crystallinity between 40 and 100 K, whereas at higher and lower temperatures α increases with increasing noncrystalline content. As no samples with $X<0.44$ have been investigated, one cannot be sure whether the extrapolation $X \rightarrow 0$ leads to amorphous PE or to the expansion behaviour of the interlamellar phase of linear PE. Thus, we have limited our discussion to noncrystalline PE.

Figure 2 shows the experimentally obtained linear thermal expansion coefficient for PE 98 and the extrapolated values for noncrystalline PE. Satisfactory agreement with available literature data for both phases is found. Above about 80 K, α for PE 98 varies only slightly with temperature, whereas noncrystalline PE shows steps at

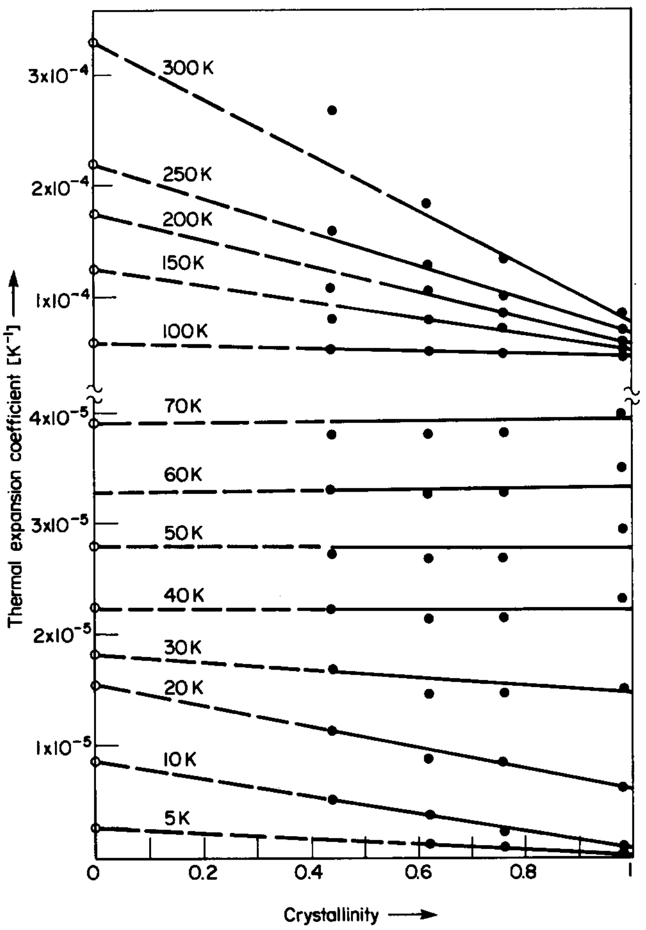

Figure 1 Linear thermal expansion coefficients of polyethylene as a function of crystallinity in the temperature range 5 to 300 K

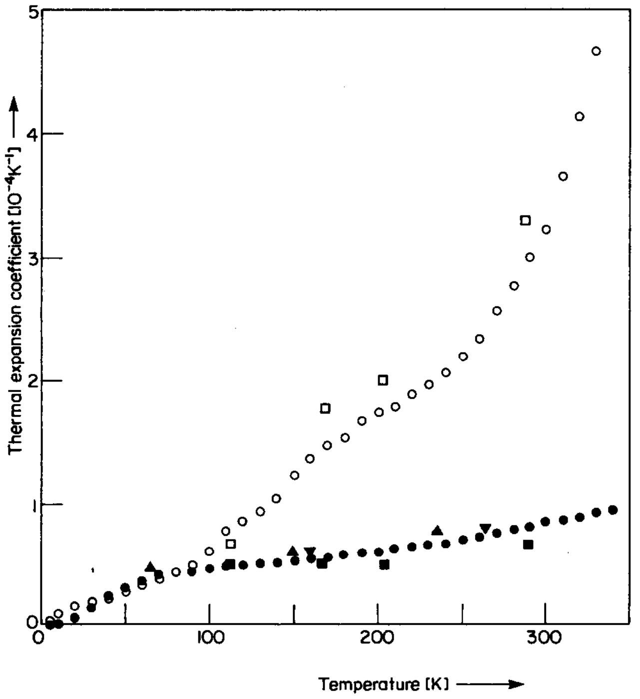

Figure 2 Linear thermal expansion coefficients for noncrystalline PE: (○) (extrapolated data); and nearly completely crystalline PE 98: (●) (experimental data). In addition, literature values are shown, for noncrystalline PE ((○), (□)) and for completely crystalline PE (▼), (▲), (■), (●): ▼ *ref. 3*, ■, □ ref. 4, ▲ ref. 6

about 110 and 140 K, and a strong increase above 250 K. A more extensive plot for the lower temperature region is given in *Figure 3* for noncrystalline PE, where both the thermal expansion coefficient and the specific heat data are shown. In the temperature region above 100 K both curves exhibit steps according to well known transition temperatures. In the lower temperature range, similar temperature dependences for C_p and α can be observed down to about 40 K. Below 20 K none of the curves show a T^3-dependence as is usually obtained for crystalline insulators. Bars plotted in *Figure 3* indicate errors due to the extrapolation procedure in *Figure 1* without taking into consideration absolute errors due to the thermal expansion measurement.

In *Figure 4* thermal expansion coefficients and specific heat data for crystalline PE 98 are shown, the latter being in excellent agreement with values given in ref. 13. Both curves clearly show a T^3-dependence below 12 K for C_p and below 17 K for α. In *Table 1* smoothed values of the linear thermal expansion coefficients at selected temperatures for non-crystalline polyethylene and for PE 98 are compiled.

DISCUSSION

In this section we discuss the low temperature thermal expansion behaviour of polyethylene in terms of the bulk-Grüneisen parameter, γ_b, as calculated from equation (1). Crude approximations to the phonon spectra have been extracted from fits of the specific heat data to obtain the relations to microscopic molecular dynamics. This allows

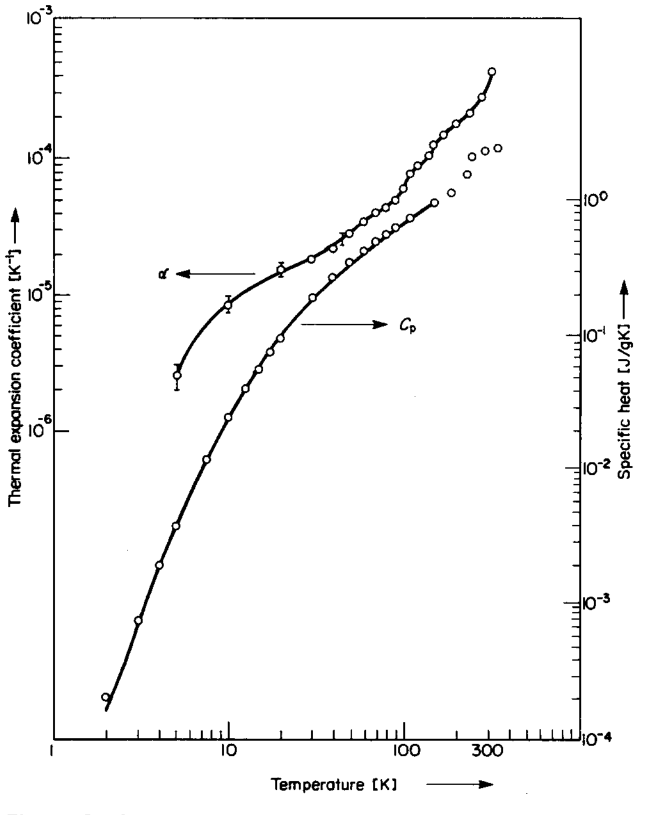

Figure 3 Completely noncrystalline polyethylene. Left-hand scale: linear thermal expansion coefficient α (obtained by extrapolation). The bars indicate errors due to linear extrapolation procedure in *Figure 1*. Right-hand scale: specific heat C_p taken from ref. 13. The solid curve has been calculated using the Tarasov model and an Einstein-term in addition (see text and *Table 2*)

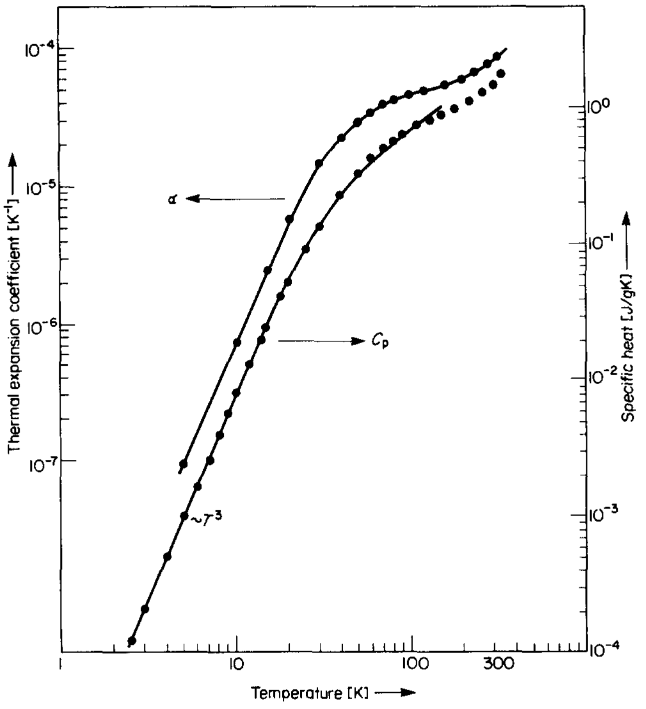

Figure 4 Crystalline polyethylene PE 98. Left-hand scale: linear thermal expansion coefficient α. Right-hand scale: specific heat C_p taken from ref. 10. The solid curve has been calculated using the Tarasov model (see text and *Table 2*)

Table 1 Smoothed values for the coefficients of linear thermal expansion α of noncrystalline polyethylene (obtained from extrapolation) and of nearly completely crystalline polyethylene PE 98.

T (K)	α (1/K)	
	noncryst.	PE 98
5	2.50×10^{-6}	9.20×10^{-8}
10	8.50×10^{-6}	7.40×10^{-7}
20	1.55×10^{-5}	5.90×10^{-6}
30	1.80	1.50×10^{-5}
40	2.21	2.30
50	2.77	2.95
60	3.42	3.50
70	3.90	4.00
80	4.30	4.30
90	4.90	4.50
100	6.03	4.67
110	7.70	4.85
120	8.60	4.97
130	9.35×10^{-5}	5.10
140	1.04×10^{-4}	5.22
150	1.24	5.32
160	1.37	5.50
170	1.48	5.60
180	1.54	5.75
190	1.68	5.90
200	1.74	6.05
210	1.79	6.20
220	1.89	6.40
230	1.97	6.57
240	2.07	6.75
250	2.19	7.00
260	2.33	7.25
270	2.56	7.55
280	2.76	7.85
290	3.00	8.15
300	3.23	8.45
310	3.66	8.67
320	4.15×10^{-4}	8.90×10^{-5}

us to separate the frequency ranges in the phonon density of states for individual values for the microscopic Grüneisen parameters.

To calculate γ_b it is necessary to know the isothermal compressibility K_T. As low temperature K_T-data of PE are very rare, extrapolations to low temperatures were carried out with the help of literature values at 300 K and 77 K[17-19]. Assuming pressure induced volume changes to be equivalent to thermal volume changes of the sample, compression data from ref. 17 were extrapolated to $T \rightarrow 0$ K and $X \rightarrow 0$, yielding $K_T = 1.8 \times 10^{-10}\ \mathrm{m^2\ N^{-1}}$ for noncrystalline PE. For completely crystalline PE, compressibilities calculated from elastic constants given at 77 K and 300 K in ref. 18 were extrapolated to $T \rightarrow 0$ K, resulting in $K_T = 1.7 \times 10^{-10}\ \mathrm{m^2\ N^{-1}}$. These values are in reasonable agreement with $K_T = 1.4 \times 10^{-10}\ \mathrm{m^2\ N^{-1}}$ given for semi-crystalline polyethylene at 4.2 K[19].

In equation (1) the specific heat C_v at constant volume has to be known which differs from the experimentally observed specific heat C_p at constant pressure. At low temperatures $T \lesssim 100$ K the difference $C_p - C_v$ becomes smaller than 1%, and the experimentally obtained C_p-values can be used in equation (1).

Noncrystalline polyethylene

Neglecting the temperature dependence of density, ρ, and compressibility, K_T, the bulk-Grüneisen parameter for noncrystalline PE was calculated in the temperature region 5 to 100 K as shown by (○) in *Figure 5*. From 100 to 40 K, γ_b is constant ($\gamma_b = 1.6$), then rapidly increases at lower temperatures to a maximum value $\gamma_b = 12.5$ at 5 K. The higher temperature value is in agreement with $\gamma = 1.85$ deduced from Brillouin scattering studies[20] for polyethylene PE 6600.

Extreme variations in $\gamma_b(T)$ at low temperatures are not unusual for organic and inorganic noncrystalline solids as has been discussed in the Theory section. In order to give a quantitative description for the increase of γ_b with decreasing temperature we now turn to the vibration spectrum of noncrystalline PE. In a previous paper[10], specific heat data for polyethylene have been analysed in the temperature range 2 to 150 K by approximating the phonon density of states using the Tarasov model and an additional Einstein term $E(\theta_E/T)$, which characterizes the excess specific heat contribution occurring around 5 K. The specific heat data were fitted to the phonon density of states as given in the lower part of *Figure 5* (parameters are listed in *Table 2*), and good agreement with the C_p-data in the temperature region 2 to 150 K was obtained as shown by the solid curve in *Figure 3*. Based on the extracted phonon density of states, a calculation on the temperature dependence of the Grüneisen parameter was carried out. Relating a microscopic Grüneisen parameter γ_E to the Einstein oscillators and an overall Grüneisen parameter $\gamma_3 = \gamma_1$ to the remaining Tarasov spectrum, $\gamma_b(T)$ was calculated from equation (5) with γ_E and γ_3 as fit parameters (see *Table 2*). With $\gamma_E = 32$ and $\gamma_3 = 1.3$ good agreement to the experimentally observed $\gamma_b(T)$ could be achieved (see solid curve in upper part of *Figure 5*). Despite the crude approximations involved in the calculation, the high γ_b-value at 5 K is explained to be due to an anomalous high positive value of γ_E related to the excess modes. From this simple model, $\gamma_b(T \rightarrow 0\ \mathrm{K}) = 1.3$ follows (dashed line in upper part of *Figure 5*) which of course only holds if no additional anomalous contributions to the vibration spectrum at the lowest frequencies are taken into consideration. The value of $\gamma_3 = \gamma_1 = 1.3$ according to the Tarasov spectrum is found to be smaller than expected from equation (4). We will discuss this point later.

For comparison, the bulk-Grüneisen parameter of amorphous polystyrene (PS), calculated from literature data[13,21] is shown in the upper part of *Figure 5*, exhibiting similar temperature dependence as PE. To point out that the situation is not that simple for amorphous organic polymers as could be concluded from the low temperature γ_b-data for PS and PE, the Grüneisen parameter for amorphous PMMA is shown, calculated from specific heat[13,14] and thermal expansion data[11]. For PMMA a high positive γ_b-value is not obtained. With decreasing temperatures, γ_b increases reaching a maximum value of ~ 2.8 at about 6 K and then dropping to $\gamma_b \approx 1.6$ at 1.5 K. It seems that in PMMA the anharmonic coupling of the excess modes to the lattice modes is much weaker than in PE and PS, respectively.

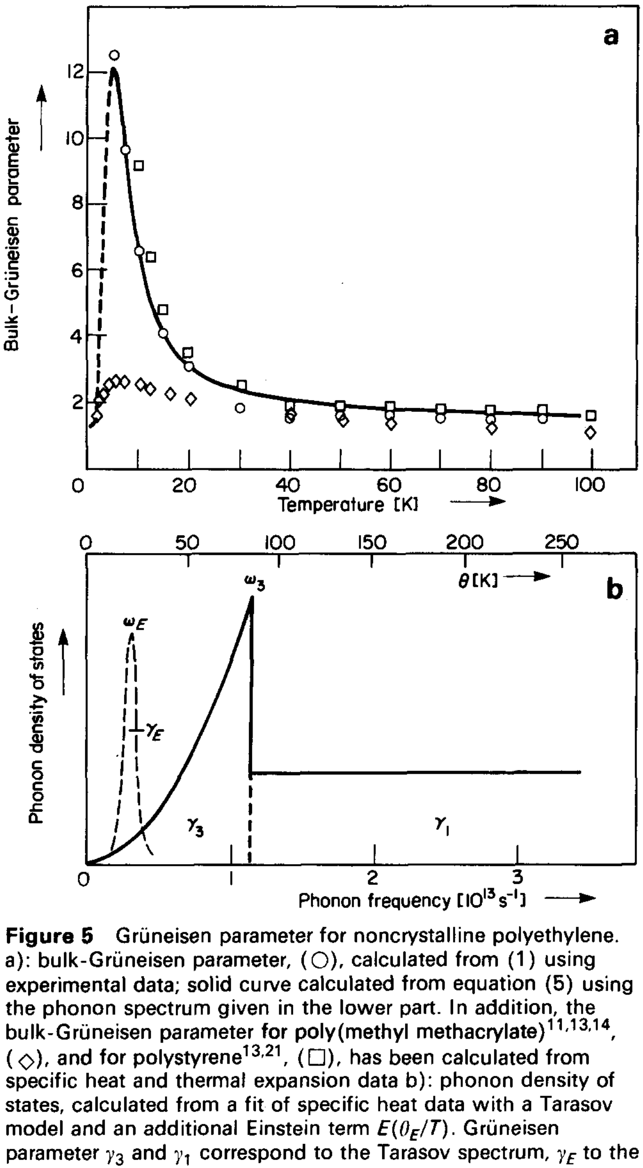

Figure 5 Grüneisen parameter for noncrystalline polyethylene. a): bulk-Grüneisen parameter, (○), calculated from (1) using experimental data; solid curve calculated from equation (5) using the phonon spectrum given in the lower part. In addition, the bulk-Grüneisen parameter for poly(methyl methacrylate)[11,13,14], (◇), and for polystyrene[13,21], (□), has been calculated from specific heat and thermal expansion data b): phonon density of states, calculated from a fit of specific heat data with a Tarasov model and an additional Einstein term $E(\theta_E/T)$. Grüneisen parameter γ_3 and γ_1 correspond to the Tarasov spectrum, γ_E to the excess modes described by $E(\theta/T)$

Crystalline polyethylene

The bulk Grüneisen parameter for crystalline PE 98, calculated from experimental data using equation (1) is shown in *Figure 6* (●). Below 12 K, both the specific heat and the thermal expansion coefficient follow a T^3-law (see *Figure 4*), and thus a low temperature limit $\gamma_b = 1.7$ is obtained. At higher temperatures, a maximum occurs at 25 K followed by a continuous decrease down to $\gamma_b = 0.6$ at 300 K. In order to extract Grüneisen parameters for selected frequency ranges from these results, the phonon density of states was approximated by the Tarasov model with appropriate cut-off frequencies and by fitting the specific heat data (parameters are given in *Table 2*). The fit is shown by the solid curve in *Figure 4*. Although no satisfactory agreement could be achieved above 50 K, the spectrum should be sufficient for our simple considerations. Better fits taking into account bending and stretching phonons of the chain in a continuum approximation for polymer crystals can be applied[22,23].

Although it seems to be a little speculative, the Tarasov spectrum as plotted in the lower part of *Figure 6* was divided into three frequency regions. The lower frequency range of the spectrum, $\gamma_3 = 1.7$... was assumed to describe the low temperature limit of γ_b. For an intermediate frequency range $\omega_3 < \omega < \omega'_3$, a Grüneisen parameter γ'_3 was introduced. The value of ω_3 is identical with the onset of the in-plane-bending branch of the dispersion relation calculated for the polyethylene crystal and leading to a singularity in the density of states in the frequency range $1.4 \times 10^{13} \lesssim \omega \lesssim 1.8 \times 10^{13}$ s^{-1}.[24,25] From pressure dependent infra-red studies of the 73 cm^{-1} band[26], which corresponds to the in-plane-bending branch for wave number $k \to 0$, a value of $\gamma'_3 = 3.5$ has been taken from ref. 26, assuming pressure induced volume change to be equivalent to thermal volume change of the sample. For the remaining high frequency part $\omega > \omega'_3$ of the Tarasov spectrum, small Grüneisen parameters $\gamma_1 = 0.3$ were assumed[5]. Calculating γ_b with Equation (5), the solid curve in the upper part of *Figure 6* is obtained. Thus, the maximum in $\gamma_b(T)$ has been assigned to in-plane-bending vibrations, and the decrease at higher

Table 2 Parameters used to fit the specific heat data[10] and to calculate the Grüneisen parameter according to equation (5) of completely noncrystalline and crystalline polyethylene, using the Tarasov model and an additional Einstein term $E(\theta_E/T)$. Cut-off frequencies ω_i (in 10^{13}s^{-1}) are also given as characteristic temperatures $\theta_i = \hbar\omega_i/k_B$ (in K), where $\hbar = 2\pi h$ is the Planck constant and k_B is the Boltzmann constant. N_E/N is the proportion of the number of Einstein oscillators related to the total number of oscillators N. For definitions of ω_i and γ_i see *Figures 5* and *6*.

	N_E/N	ω_E θ_E	γ_E	ω_3 θ_3	γ_3	ω'_3 θ'_3	γ'_3	ω_1 θ_1	γ_1
Noncrystalline PE	0.0037	0.306 23.4	32	1.15 88	1.3	–	–	11.4 871	1.3
Crystalline PE 98	–	–	–	1.43 109	1.7	1.86 142	3.5	11.4 871	0.3

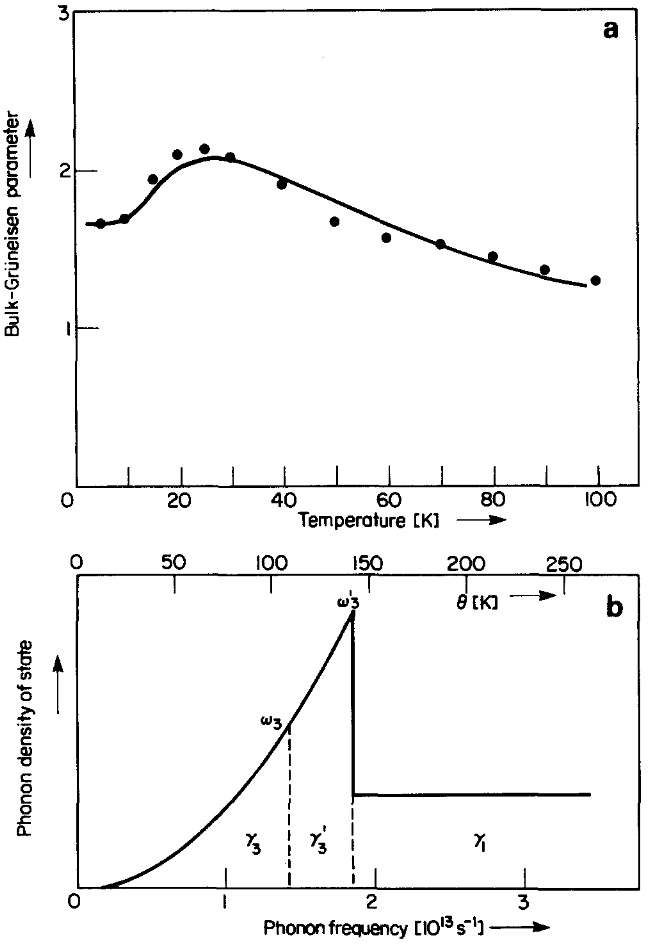

Figure 6 Grüneisen parameter for crystalline polyethylene. a) bulk-Grüneisen parameter, (●); calculated from equation (1) using experimental data; (——) calculated from equation (4) using the phonon spectrum given in the lower part. b) phonon density of states, calculated from a fit of specific heat data with a Tarasov model. Grüneisen parameter γ_3 corresponds to low frequency phonons with frequencies governed by chain interaction forces, γ_1 corresponds to high frequency phonons with small Grüneisen parameters. In the intermediate frequency region $\omega_3 < \omega \leqslant \omega_3'$ a Grüneisen parameter γ_3' is related to in-plane-bending modes

temperatures to the influence of high frequency phonons with small Grüneisen parameters.

The Grüneisen parameter for low frequency phonons and $T \to 0$ K is $\gamma_b = 1.7$. Due to the experimental errors, which mainly arise from uncertainties of compressibility data, the low temperature limit can only be given to be $\gamma_b = 2.0 \pm 0.5$. Nevertheless, this value is smaller than expected from equation (4) for polymer crystals. Thermal expansion studies for other chain-like crystals gave bulk-Grüneisen parameters $\gamma_b = 1.3 \ldots 1.5$ for trigonal tellurium[27] and selenium[28] as well as for a polyoxymethylene crystal[29] below 10 K, whereas for a polydiacetylene single crystal $\gamma_b = 3.4$ at 100 K was found[30]. All these values are well below the theoretical estimate from equation (4) with $\gamma = 5.25$, and we outline some possible reasons here. The first could be the choice of the Lennard–Jones potential with $m = 6$ and $n = 12$. Although established for particle–particle interaction and extended to the 'bundle of tubes' model[2], deviations might occur for the real chain in a real polymer crystal. A second reason could be the assumption that volume changes of the sample are due to two orthogonal directions only. However, for the polyoxymethylene crystal, the absolute value of the thermal expansion coefficient $\alpha_\parallel$ parallel to the chain is at least a factor of five smaller than perpendicular to the chains[29]. Furthermore, polyoxymethylene, selenium and tellurium have Grüneisen parameters $\gamma_\perp$ perpendicular to the chain with bulk-values $\gamma_b \approx \gamma_\perp$[27–29] indicating that thermal expansion along the chain is not responsible for the small Grüneisen parameters at low temperatures. The third reason refers to the stiffness of the polymer chain, which is a property of intrachain forces only. As phonon frequencies will also be influenced by the bending force constant, a smaller microscopic Grüneisen parameter can be expected. This also would explain the relative small γ-values for noncrystalline PE between 40 and 100 K. It should be noted, however, that for the organic polymer crystals mentioned above, a T^3-law can be found at lowest temperatures for the specific heat, which indicates that stiffness of the chain loses influence for $T \to 0$ K.

CONCLUSION

The bulk-Grüneisen parameter of noncrystalline PE is constant between 40 and 100 K ($\gamma_b = 1.6$), whereas at lower temperatures a rapid increase can be observed, reaching $\gamma_b = 12.5$ at 5 K. This high value is assumed to be due to excess modes with extremely high positive Grüneisen parameters ($\gamma_E = 32$). While PS and other organic amorphous polymers[19] show similar behaviour, detailed investigation down to 1.5 K made on PMMA[11] point out that these results should not be generalized and more detailed measurements in the lower temperature region on other amorphous polymers are desirable. For nearly completely crystalline PE 98, the temperature dependence of the bulk-Grüneisen parameter can principally be understood. Below 10 K, a low temperature limit of $\gamma_b = 2.0 \pm 0.5$ is reached. At about 25 K, a maximum in $\gamma_b(T)$ occurs, which has been related to in-plane-bending vibrations of the polyethylene chain. The maximum is followed by a continuous decrease to $\gamma_b = 0.6$ at 300 K, due to an increasing influence of high frequency phonons with small Grüneisen parameters. However, the low temperature limit $\gamma_b(T \to 0\ \text{K}) \approx 2$ is smaller than expected from theory ($\gamma = 5.25$). The discrepancy can only be cleared up, if macroscopic polymer single crystals with a simple linear chain structure were available for thermal expansion studies at low temperatures.

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