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EFFECT OF PRESSURE ON THE THERMAL CONDUCTIVITY OF POLYMERS

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The thermal conductivity of polyolefins and halogen-substituted polymers was studied in a broad temperature interval spanning both solid and melt states, in the range of pressures from 0.1 up to 100 MPa with the aid of a high-pressure λ–calorimeter in the continuous heating regime. Treatment of data on the pressure dependence of the thermal conductivity of melts in terms of Barker's equation yielded the values of 'quasilattice' Grueneisen parameter γ_B which exhibited the same dependence on molecular structure of a polymer as the parameter $3C/p$ from the Simha-Somcynsky equation of state (number of external degress of freedom per chain repeat unit). Analysis of the dependence of the thermal conductivity of polyethylene on the degree of crystallinity revealed the inadequacy of the current two-phase model which does not account for the microheterogeneity of the 'amorphous phase'. It was concluded that interchain heat transfer makes the dominant contribution to the thermal conductivity of polymers both in amorphous and in crystalline states.

Keywords: polymers, thermal conductivity

Introduction

Measurements of the thermal conductivity of polymers under elevated pressures are necessary to deal with both practical as well as fundamental problems. In respect of practical aspects, accurate values of the thermal conductivity are needed to optimize the regimes of melt processing and subsequent solidification of thermoplastic polymers, and to predict the thermomechanical behaviour of the latter in actual service conditions. On the other hand, from the pressure dependence of the thermal conductivity one may expect to obtain unique information on the polymer defect state since it is the structural defects that are believed to contribute most to the thermal transport resistance of a polymer both in solid and molten states.

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Experimental

Both the theory of the measurement principle as well as the design of the high-pressure λ–calorimeter similar to that used in the present study were described earlier by Platunov *et al.* [1, 2], so that only essentials will be mentioned here. The pressure cell is formed by two pistons, one fixed and the other movable, tightly fitting to the polished inner surface of the outer, thick-walled cylinder made of stainless steel. A copper rod (7 mm in diameter and about 60 mm long) bearing a thin-walled (of the order of 1 mm), cylindrical polymer sample on its outer surface, is fixed concentrically within the pressure cell with the aid of three tiny, equally-spaced needles on its periphery, and the pressure cell is filled with the pressure-transmitting liquid (in our case, thermally stable silicone oil PPhMS–400). To eliminate the leakage of the latter, the movable piston was provided with an uncompensated area-type seal. The copper rod is heated exclusively by a radial heat flow from external heaters on the cylinder through the pressure transmitting liquid and the layer of the studied polymer. The temperature difference, Δt, between the inner and outer surfaces of the cylindrical polymer sample is measured with the aid of two thermocouples placed within the central boring in the copper rod and the transversal boring in the cylinder, respectively, approximately at the half-height of the sample.

In the experiments the sample of a studied polymer in the shape of a hollow cylinder was molded on the copper rod and capped on both ends of the latter with two discs of the same polymer having the same thickness as the cylinder wall. The experiments were carried out in isobaric regime with continuous heating at constant rate, q =0.05 deg/sec. Simultaneous recording of the heating rate q and the temperature difference Δt permitted to distinguish the real instability of q from periodic random variations due to instantaneous (quasiadiabatic) pressure jumps needed to maintain isobaric conditions. This latter effect was minimized with the aid of a special electronic regulation of the electric power supplied to the external heater [3].

A typical example of the experimental temperature dependence of the temperature difference Δt at various pressures for a sample of low density polyethylene is shown in Fig. 1. The peaks on the curves correspond to endothermic heat effects of the melting of polymer crystalline phase at the melting point, $T_m(P)$.

The thermal conductivity of the studied polymer was calculated from the following equation [1, 2]:

$$\lambda = (2R/S)\,[(C_o + 0.5C_p)q/\Delta t\,]\,(1 + \sum \sigma) \qquad (1)$$

where $2R$ is the sample thickness, S is the overall area of the heat transfer, C_o is the heat capacity of the copper rod, C_p is the heat capacity of the polymer, and the term $\sum \sigma$ accounts for the cumulative corrections for non-linearities of the heating rate, of temperature fields, etc. [1, 2].

The thermal conductivity at normal pressure was calculated by substitution into Eq. (1) of calibration constants (S, C_o and $\sum \sigma$) together with the experimental values of C_p, which were measured in independent experiments with the aid of a differential calorimeter on diathermal cells (mean error of the order of 3%) [3, 4]. To calculate λ at higher pressures we used the same values of C_p but shifted to higher temperatures to match the experimental shifts of T_m (Fig. 1).

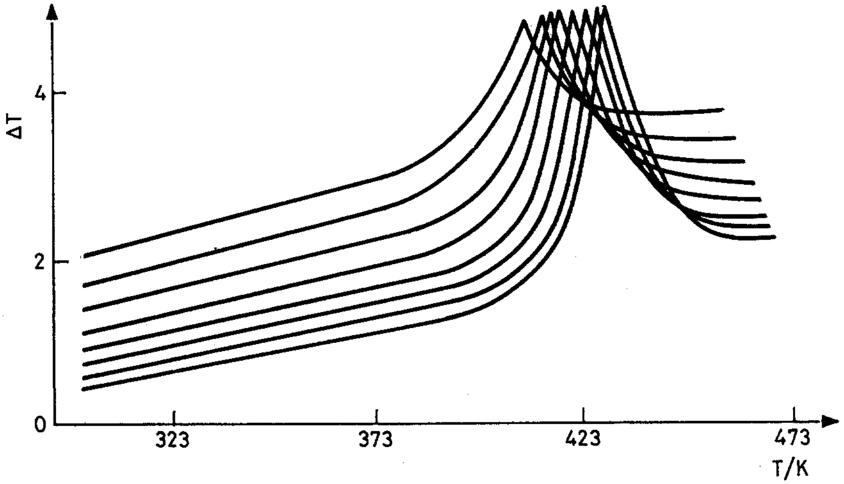

Fig. 1 Temperature difference ΔT for PELD at pressures, resp. (from top to bottom) :0.1; 10; 20; 30; 40; 60; 80; 100 MPa

According to our estimates, the mean square error of a single heat conductivity determination by Eq. (1) is within 5%, while the reproducibility tests revealed that the maximum deviation did not exceed 2–3% [3].

The thermal conductivity was measured in the temperature interval from 303 K up to T_m +30 K and in the pressure range 0.1–100 MPa. To minimize the uncertainties due to the possible thermal degradation of the polymer heated to high temperatures (this problem was encountered occasionally in dealing with fluorine-containing polymers), in each isobaric run we used a fresh polymer sample prepared in identical conditions.

Polymers

The objects of the present study were the following polymers produced in the USSR: polyethylenes (PE) of low density (PELD), of high density (PEHD), and 'superhigh molecular weight' (HMWPE); isotactic polypropylene (PP), polybutene-1 (PB) and poly–4–methylpentene–1 (PMP); polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE) and polytetrafluoroethylene (PTFE). In Table 1 are collected the values of the weight-average molecular weight ($<M_w>$), melt flow index (MFI), density (ρ), glass transition temperature of the amorphous phase (Tg), melting point of the crystalline phase (T_m), its derivative (dT_m/dP), as well as the degree of crystallinity $X = \Delta H_m^* / \Delta H_m^0$, where ΔH_m^* and ΔH_m^0 are the melting heats of the crystalline phase of the studied sample and of the ideal polymer crystal, respectively.

Results

As an example, the temperature dependence of the thermal conductivity of PEHD and PCTFE at various hydrostatic pressures are shown in Fig. 2. Similar plots were constructed for all other polymers. The thermal conductivity in the melting interval of crystalline phases was not calculated because measurements with the aid of calorimeter on diathermal cells permitted to determine the so-called 'dynamic heat capacity' [3] rather than 'true heat capacity' which is necessary to calculate thermal conductivity by Eq. (1).

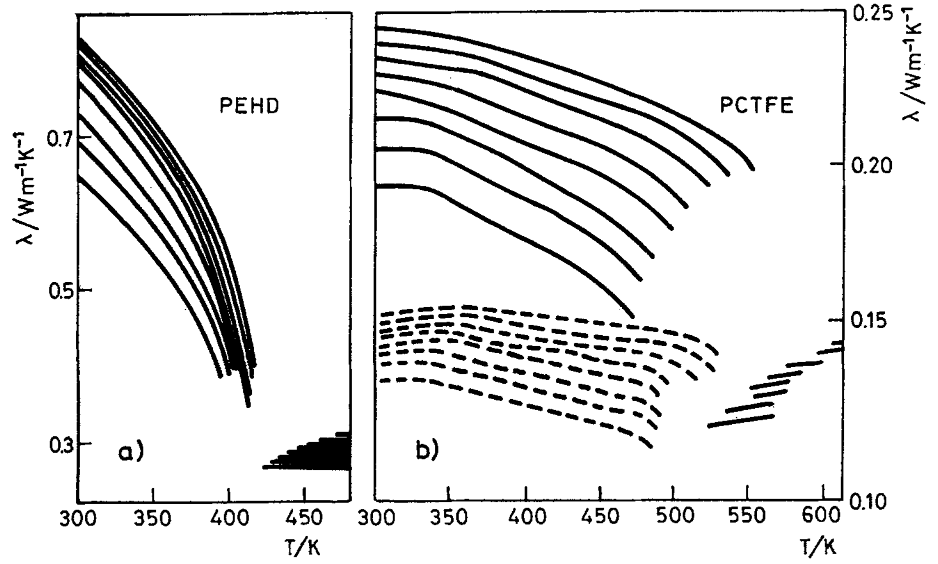

Fig. 2 Thermal conductivity of PEHD (a) and PCTFE (b) crystallized at $P = 10$ MPa (broken lines) and at $P = 100$ MPa (solid lines)

Our experimental data turned out to be in a reasonable agreement with those of Eiermann [5–7] for PELD, PEHD, PP, PCTFE and PTFE at normal pressure, as well as with the results of Dietz [8] for the thermal conductivity of PEHD and PP

Table 1 Material properties of the polymers studied

No	Polymer	$<M_w>10^{-5}$	MFI/g·10 m^{-1}	ρ/g·cc^{-1}	T_g/K	T_m/K	dT_m/dP/K·MPa^{-1}	X
1	PELD	–	2.00	0.924	181	386	0.35	0.49
2	PEHD	1.4	–	0.973	172	409	0.36	0.85
3	HMWPE	30.0	–	0.945	178	408	0.34	0.59
4	PP	–	–	0.911	253	435	0.45	0.50
5	PB	1.5	–	0.925	243	406	0.52	0.70
6	PMP	–	70.0	0.833	290	503	0.34	0.64
7	PVF	–	–	1.385	303	473	0.45	0.44
8	PVDF	–	27.8	1.785	228	449	0.48	0.49
9	PCTFE/10	–	0.48	2.080	328	487	0.80	0.42
10	PCTFE/100	–	0.48	2.161	333	491	0.83	0.85
11	PTFE	–	–	2.200	160	601	1.00	0.57

in the melt phase at pressures up to 100 MPa. Preliminary analysis of the data obtained permitted to establish the following general trends:

a) The pressure rise is accompanied by a regular thermal conductivity increase in both the solid and liquid (i.e., melt) phase.

b) Transition through the T_g interval manifests itself as a break on the thermal conductivity curve which shifts to higher temperatures as the pressure increases (cf. Fig. 2b, broken lines).

c) An increase in the degree of crystallinity X brings about a concomitant increase of the thermal conductivity, breaks in the T_g intervals becoming less pronounced (cf. solid and broken lines in Fig. 2b).

d) The thermal conductivity of all polymers in the solid state exhibits a more or less pronounced decrease with temperature, while in a limited temperature interval above T_m (i.e. in the melt state) one observes much weaker temperature dependence of λ.

Discussion

Thermal conductivity of molten polymers

As already mentioned, in a limited temperature interval of our measurements the thermal conductivity of polymers in the melt state changes little with temperature (in fact, one may notice a slight trend to increase). However, both the absolute values of the thermal conductivity at normal pressure, $\lambda_m(0)$, as well as the corresponding pressure derivatives, $\chi = (\partial \ln \lambda_m / \partial P)_T$, exhibit rather significant dependence on the molecular structure of a polymer.

It is pertinent to remark here that our data qualitatively support the intuitive belief that the thermal conductivity of amorphous polymers gradually decreases as their molecular structure becomes more complicated [8–12]. In fact, in a series of polyolefins the maximum thermal conductivity was found for PE which has the simplest and the most symmetrical molecular structure; apparently for the same reason the highest $\lambda_m(0)$ in a series of halogen-substituted polymers is that for PTFE. Replacement of a proton in the PE chain by a methylene group (as in PP), or with a fluorine atom (as in PVF) brings about a decrease in $\lambda_m(0)$; however, as the molecular structure becomes more complex, one observes changes in the thermal conductivity of the melt which cannot be readily explained within the framework of the above qualitative reasoning.

According to the theory of Fecsiyan *et al.* [13], the transport of thermal energy in the polymer melt proceeds *via* a mechanism of intersegmental collisions between neighbouring chains which are favoured by stronger intermolecular interactions as expressed by energy parameter δ, and disfavoured by stronger intermolecular friction effects expressed by parameter ζ. Treatment of the thermal transport problem with the aid of time correlation functions technique yielded the following final results [13]:

$$\lambda_m \approx (\delta / V A)^2 (T \zeta)^{-1} \tag{2}$$

where V is the molar volume and A is the segment length. Unfortunately, quantitative analysis of our data within the framework of Eq. (2) turned out to be impossible due to the uncertainty in the numerical values of parameters δ and ζ, although one may notice that Eq. (2) correctly predicts the lowering of λ_m as the polymer molecular structure becomes more complex since the increasing bulkiness of the chain side substituents in most cases results in chain stiffening [14] (that is, in an increase of statistical segment length A).

For more quantitative analysis of our data we will start from the premise of a fundamental similarity of thermal transport phenomena in polymer melts, on the one hand, and in simple molecular liquids, on the other. According to the theory of MacLaughlin [15], transport of a portion of the thermal energy along the temperature gradient in the liquid is probable on the condition of collision between molecules oscillating around their equilibrium positions within the cells formed by their nearest neighbours, at maximum amplitude of oscillations. For this case the following relationship was derived:

$$\lambda = 2 \nu C^* / a, \tag{3}$$

where $C^*=3k/2$ is the portion of the molar heat capacity of a liquid which is involved in the thermal transport event; $\nu = (8kT/m)^{1/2}/4\,(a-\sigma)$ is the frequency of thermal oscillations; a is the nearest-neighbour distance between molecules in the cell; σ is the intrinsic (hard-core) molecular diameter, m is the molar mass and k is the Boltzmann's constant.

Now, to switch over to polymers one must recognize that in polymer melts the intrinsic kinetic entity endowed with its own thermal mobility is not a molecule as is the case with molecular liquids but a statistical chain segment. Therefore, in the subsequent discussion we shall make the following assumptions: $m=m^*$; $a^*=Vm^*$; $\sigma^*=V^*m^*$, where $m^*=m_o\,(3C/p)$ and V^* are, respectively the effective mass of the chain segment and characteristic volume of polymer melt from the Simha–Somcynsky equation of state [16], and $3C/p$ is the number of external degrees of freedom per repeat unit of the model chain with degree of polymerization p; m_o is the mass per repeat unit of the real macromolecule.

In Table 2 are listed the tabulated values of characteristic parameters V^* and $(3C/p)$ [17–19], as well as calculated values of C^* which were obtained by treatment of our experimental data for the thermal conductivity of polymer melts according to Eq. (3) with the substitutions mentioned. It turned out that the values of C^* obtained in this fashion for the majority of the polymers studied are about an order of magnitude smaller than the corresponding values of the isobaric molar heat capacity, C_p. Taking into consideration that the Simha-Somcynsky model is

Table 2 Properties of the melt phase

No	Polymer	$\lambda_m(0)$/W·m^{-1}·K^{-1}	$3C/p$	V^*/cc·g^{-1}	γ_T	C^*/J·g^{-1}·K^{-1}	γ^*	γ_B
1	PELD	0.26	0.88	1.129	0.16	0.20	0.8	1.9
2	PEHD	0.27	0.88	1.129	0.12	0.20	0.9	1.4
3	HMWPE	0.26	1.11	1.129	0.19	0.22	1.3	2.0
4	PP	0.18	1.84	1.195	0.17	0.40	1.1	0.6
5	PB	0.25	1.32	1.164	0.11	0.15	1.2	1.6
6	PMP	0.11	1.47	1.230	0.05	0.10	1.3	1.5
7	PVF	0.17	0.53	0.720	0.07	0.18	–	0.7
8	PVDF	0.13	0.37	0.622	0.04	0.11	1.4	0.5
9	PCTFE	0.12	0.38	0.510	0.02	0.09	1.9	0.3
10	PTFE	0.19	1.35	0.424	0.06	0.34	–	0.2

aimed at the description of 'excess' thermodynamic properties of polymer melts (that is, those which are sensitive to intermolecular interactions only), it is safe to conclude that the calculated values of C^* account for the contribution to the total heat capacity of weak interchain vibrations which are responsible for heat transport in polymer melts. The data obtained may be used to estimate the value of the so-called 'quasilattice' Grueneisen parameter, γ^*, from the thermodynamic relationship [19, 20]:

$$\gamma^*/\gamma_T = C_V/C^*, \tag{4}$$

where $\gamma_T = \alpha V/\beta_T C_V$ is the thermodynamic Grueneisen parameter, α and β_T are coefficients of volumetric thermal expansion and of isothermal compressibility, respectively. Values of γ^* calculated from Eq. (4), are also included in Table 2.

As can be seen from Fig. 3, densification of the melts with pressure leads invariably to the curvilinear thermal conductivity rise with the trend for a levelling-off at higher pressures. In terms of Eq. (3) this behaviour may be explained by a decrease in the interplanar distance, a, in the denominator, and/or an increase of the frequency of intermolecular vibrations, ν in the numerator, as a result of free volume decrease, $(a-\sigma)$. Differentiating Eq. (3) with respect to P, one obtains [15]:

$$\chi = \beta_T(1/3 + \gamma_B), \tag{5}$$

where $\gamma_B = -(\partial \ln\nu/\partial \ln V)_T$ is the effective Grueneisen parameter for a liquid. This latter equation is very similar to the one derived by Barker *et al.* [21], viz.:

$$\chi = \beta_T \gamma_B \tag{6}$$

for a different model. Assuming a dominating contribution of the free volume compressibility to β_T, one may get, approximately, [21]:

$$\beta_T = f_o(0, T)[1 - \exp(-PV_o/kT)] \tag{7}$$

where $f_o(0, T) = \exp(-1)\exp(-E_o/kT)$ is the melt free volume fraction at normal pressure, E_o and V_o are the hole formation energy and the hole volume, resp. (as originally proposed [21], a universal value, $f_o(0, T_g)=0.025$ was used in calculations for all the polymers studied at the corresponding glass transition temperatures T_g).

It can be seen from Table 2 that the values of γ_B calculated with the aid of Eqs (6) and (7) are similar in magnitude to the values of γ^* derived earlier from the normal pressure data. These results thus support the notion of the dominating contribution of interchain vibrations to the thermal transport phenomenon in polymer melts. In this context it is pertinent to note that not only do parameters γ_B and γ^*, on the one had, and parameter $3C/p$, on the other, exhibit similar dependence on the polymer nolecular structure, but their numerical values are also similar in magnitude (cf. Table 2). The correlation observed looks quite reasonable on account of the physical meaning of parameters $\gamma^{*} \approx \gamma_B$ as a measure of the anharmonicity of thermal vibrations in the melt with dominant contribution from weak (external) interactions between segments, and the meaning of parameter $3C/p$ as a measure of equilibrium thermal mobility of segments in polymer melts.

Thermal conductivity of solid polymers

As already demonstrated with PCTFE (Fig. 2) the increase of the degree of crystallinity X is accompanied by a concomitant increase of polymer thermal conductivity in the solid state (i.e., in the temperature interval below T_m). Qualitatively similar behaviour is predicted by various theoretical models for the dependence of the thermal conductivity of a two-phase system, λ, on the volume content, X, of a dispersed phase 1 with high intrinsic thermal conductivity λ_1 [22, 23]. For example, in the case of spherical inclusions of a dispersed phase 1 with conductivity λ_1 in a continuous phase 2 with conductivity λ_2 with perfect thermal contact at the interface (i.e., with vanishing resistance to heat flow) Maxwell's equation is believed to apply:

$$(\lambda - \lambda_2) / (\lambda + 2\lambda_2) = X(\lambda_1 - \lambda_2) / (\lambda_{1-2} \lambda_2), \tag{8}$$

Direct check of the validity of Eq. (8) in respect of the dependence of the thermal conductivity of a semi-crystalline polymer, λ, on crystallinity X, is somewhat uncertain because it contains two unknown quantities, that is the thermal conductivity of both the crystalline (λ_1) and amorphous (λ_2) phase which, in the majority of cases is not amenable to direct experimental determination. In usual practice, the parameters λ_1 and λ_2 are estimated by treatment of experimental λ values for several samples of the same polymer differing in the degree of crystallinity X with the aid of Eq. (8) [23]. Unfortunately, since for the majority of the polymers studied such information was not available, in the subsequent discussion we applied as λ_2 the values of the thermal conductivity of supercooled melts obtained by linear extrapolation to the temperature interval $T<T_m$. The validity of such extrapolation is supported also by Choy's data [23].

Treatment according to Eq. (8) of our experimental data at T =303 K and normal pressure for PELD, PEHD and HMWPE, on the one hand, and for two samples of PCTFE crystallized from the melt at pressures P =10 MPa (PCTFE–10) and P =100 MPa (PCTFE–100), on the other, led to a rather unexpected result, namely that the calculated values of λ_1 for different samples of the same polymer do not coincide but rather tend to increase with X. Special tests on the reproducibility have convincingly shown that this result is in no way connected with uncertainties in the determination of λ or X. The other possible cause of the observed discrepancy might be fundamental inapplicability of a simple Eq. (8) to analyze the experimental data for thermal conductivity of polymers since it does not take into account explicitly the anisotropy of the force constants of intra- and interchain interactions which is responsible for a giant difference of longitudinal (i.e., measured along the chain axis, λ_{1l} and transversal, λ_{1t} thermal conductivities of a polymer crystal [23, 24]. Taking this into consideration Choy [23] derived the following equation:

$$(\lambda-\lambda_2 / (\lambda+2\lambda_2)=X\,[2(\Lambda_t-1)/3\,(\Lambda_t+2)+(\Lambda_t-1)/3(\Lambda_l+2)], \tag{9}$$

where $\Lambda_l=\lambda_{1l}/\lambda_2$; $\Lambda_t=\lambda_{1t}/\lambda_2$.

Assuming $\Lambda_l \gg 1$, Eq. (9) may be simplified, as [23]

$$(\lambda-\lambda_2)/(\lambda+2\lambda_2)=X\,[2(\Lambda_t-1)/3(\Lambda_t+2)+1/3] \tag{9a}$$

It follows from Eq. (9a) that it is the interchain thermal energy transport that makes the dominant contribution to the thermal conductivity of the crystalline phase of polymers. Since the cohesive energy density of the crystalline lattice, $\Delta H^0_m\,\rho_1$, may be used as a qualitative measure of interchain interactions within the crystalline phase of polymers [14], one should expect a correlation to exist between that quantity and λ_{1l}. As can be seen from Fig. 4, in spite of a relative large scatter of data points which owes much to the discrepancies between calculated values of λ_{1t} for various PEs (points 1, 2, 3) and PCTFE (points 9, 10), the expected correlation seems to exist.

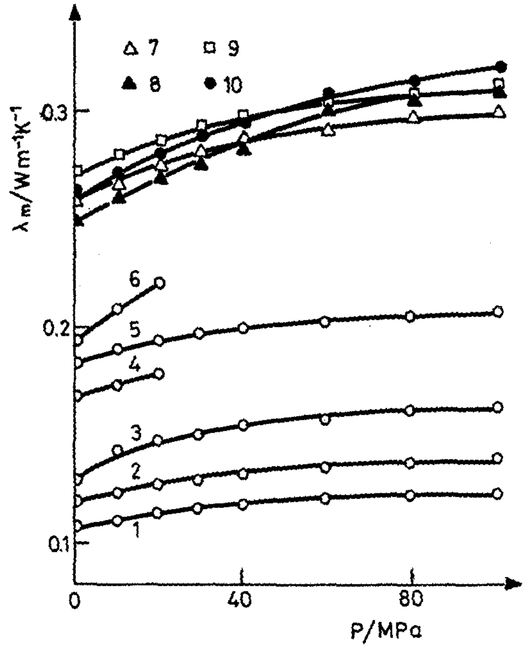

Fig. 3 Pressure dependence of the thermal conductivity in the melt. Numbers at the curves refer to the corresponding entries in Table 2

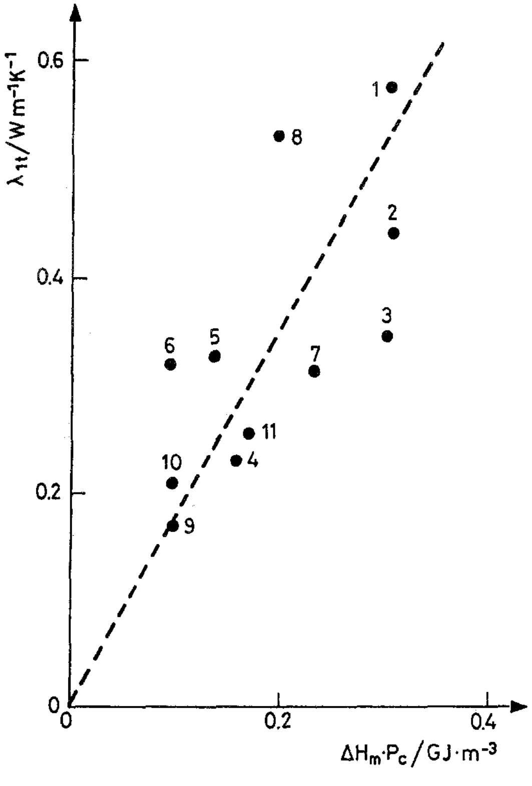

Fig. 4 Correlation between λ_{1t} and $\Delta H_m \rho_1$

It follows from the above analysis that the observed tendency of the calculated values of λ_1 and/or λ_{1t} to change with X is real. In our opinion, this result may be considered as a direct proof of the invalidity of an elementary, two-phase model of the type, 'continuous amorphous medium with isolated crystalline inclusions', which was implicitly assumed in the treatment of experimental thermal conductivity data for semi-crystalline polymers according to Eqs (8) and (9a). In other words, it becomes imperative to account for the structural microheterogeneity of the so-called 'amorphous phase' in semi-crystalline polymers, namely, to recognize the difference in resistance to heat flow transfer between 'tie chains' within the intercrystalline space, on the one hand, and the molecular loops ('folds') in a specific 'boundary layer' on the basal planes of lamellar microcrystals, on the other.

According to the general theory of heat transfer in microheterogeneous systems [25, 26], the effective thermal conductivity, λ, is the function not only of the thermal conductivities of continuous and dispersed phases (λ_2, λ_1, resp.) and the volume content of the latter (X), but also of the characteristic parameter $Z_2 = (\lambda_2 /$

λ_M) ($\Delta r/r$), where λ_M is the effective thermal conductivity of a continuous phase in the boundary layers, Δr is its thickness, and r is the average size of the inclusion.

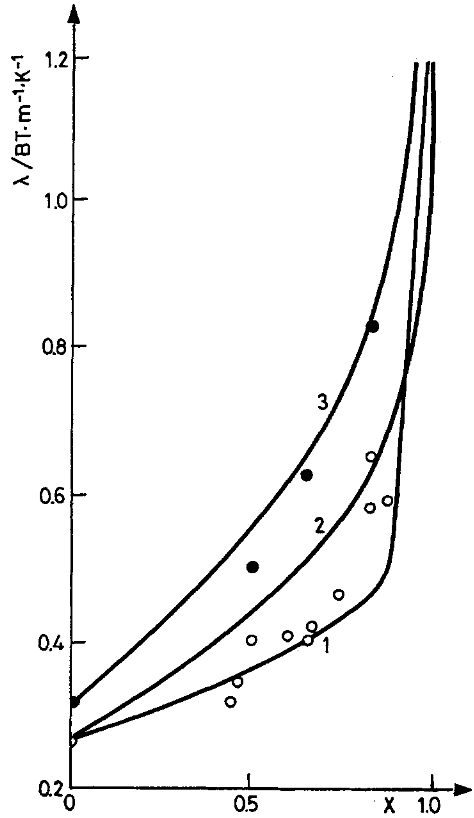

Fig. 5 Crystallinity dependence of the thermal conductivity of PEs at normal pressure (open points) and at P =100 MPa (filled points). For explanation see text

To check the validity of this model we made use of both our and literature data [19, 23] on the thermal conductivity of PEs at normal pressure, as well as our data obtained at P =100 MPa (Fig. 5). The experimental data were treated in the following manner. At first, the effective thermal conductivity of a crystalline 'core' (that is, defect-free crystal), λ_1, was computed with the aid of a computer program [26] in which Z_2 =0 was assumed for a sample with maximum X and λ. The values of λ_1 obtained in this fashion (1.28 W/m·k and 1.83 W/m·k at 0.1 MPa and 100 MPa, resp.) were assumed to be constant on the whole range of X, and the optimum value of Z_2 was chosen from the condition of a minimum discrepancy between theory and experiment. It turned out that at normal pressure the experimental values of λ adequately obey theoretical predictions at Z_2 =0.15 in the range $X < 0.80$ (curve 1 in Fig. 5) and at $Z_2 = 0$ in the range of extremely high values of X (curve 2 in Fig. 5). On the other hand, at $P = 100$ MPa one observes a rather encouraging agreement between experiment and theory (curve 3 in Fig. 5) in the whole range of X at $Z_2 = 0$. Assuming typical values for the thickness of the defect layer on basal (that is, fold-containing) faces of lamellar crystals of PE, $\Delta r = 2$ nm, and lamellar height, $r = 10$ nm [27], we estimate $\lambda_2/\lambda_M = 0.7$ from $Z_2 = 0.15$. Literally, this means that at normal pressure the thermal conductivity of basal, defect layers of lamellar crystals of PE is about 30% higher compared to that for a supercooled, continuous amorphous phase. These differences are minimized, however (i.e., $Z_2 \to 0$, presumably, as a result of $\Delta r \to 0$), at normal pressure in the range $X > 0.80$ where the 'phase inversion' phenomenon (that is, transition to morphology of the type, 'continuous crystalline phase with isolated amorphous inclusions') seems to take place, and due to different rates of densification under elevated pressures of different 'amorphous' microphases. Unfortunately, we were not able to carry out a similar, more refined treatment for other polymers in view of the unavailability of thermal conductivity data for samples with different crystallinities; therefore, in subsequent discussion we shall switch once again to values of λ_1 calculated with the aid of a simple Maxwell's equation (8).

Our preliminary analysis has shown that in a limited temperature interval the values of λ_1 calculated by Eq. (8) from experimental data at normal pressure, tend to decrease with temperature, in approximate agreement with Eucken's rule, $\lambda_1 \sim 1/T$ [23]. If such dependence were entirely due to three phonon-type interactions, the temperature dependence of thermal resistance, $W_1 = 1/\lambda_1$ would be described by a straight line running through the origin, that is,

$$W_1 = W_o T \tag{10}$$

where W_o is the intrinsic material constant. It turned out, however, that such dependence was observed only for PEHD (Fig. 6), while for other polymers the experimental data appear to be better described by a straight line intersecting the ordinate at point W_B, i.e.[28]:

$$W_1 = W_s + W_o T \tag{11}$$

where W_B is the temperature-invariant contribution from structural defects. Taking into consideration that among the studied polymers it is only PE which has the most extended (planar) chain conformation in the crystalline state [27], it is safe to conclude that transition from extended chain conformation into more twisted (e.g., helical) one as a result of substitution of protons in a hydrocarbon chain with bulkier side groups (in the polyolefin series) or by heavier halogen atoms (in a series of halogen-substituted polymers), leads to a loosening of interchain packing and thus lowers the efficiency of interchain heat transfer in polymer crystals, which manifests itself by the appearance of an additional W_s term in Eq. (11).

Let us turn now to a more detailed discussion of the data obtained under elevated pressures. We will start from the assumption that the calculated values of λ_1 refer to a hypothethical, isotropic crystalline phase which is, however, not continuous but rather looks like a 'mosaic' of randomly distributed microcrystallites. Since the microstructure of such a hypothethical system will be roughly similar to that of a compressed melt, we make use once again of Barker's equation (6) to analyze the pressure dependence of λ_1 at room temperature.

In Table 3 are collected the calculated values of parameter V_o and the product, $f_o(0, T)\gamma_B$. The value of the quasilattice Grueneisen parameter, γ_{1B}, must be obtained from an independent source, and for this purpose we employed the results of Bohlin *et al.* [29] who treated the problem of crystal melting under elevated pressure in terms of Lindemann's approximation and derived the following equation for the derivative of the melting temperature, with respect to pressure dT_m/dP:

$$dT_m / dP = (\gamma_{1B} - 1) T_m \beta_1, \tag{12}$$

where β_1 is the compressibility of a crystal. The values of γ_{1B} were calculated by substitution into Eq. (12) of our experimental values of dT_m/dP (cf. Fig. 1 and Table 1) and tabulated values of β_1 [19, 30] (in case where the experimental values of β_1 were not available we used the empirical correlation [14], $\ln \beta_1$ (MPa^{-1}) $=-1.63 - 3.0 K_1$, where K_1 is the polymer packing coefficient in the crystal). It can be seen from Table 3 that the values of γ_{1B} for PEs are in a reasonable agreement with both $\gamma_{1B}=5$ determined experimentally from the pressure dependence of sound velocity in single crtstals [31], as well as with a theoretical value $\gamma_{1B}=4$, derived from a simple model accounting only for the interchain contribution to the thermal conductivity [14]. These data are thus consistent with a notion of a dominant contribution of weak, interchain thermal vibrations to the thermal conductivity of crystalline phase of polymers.

In an analysis of calculated values of $f_o(0, T)$ we shall start from the assumption that this parameter has the meaning of an equilibrium concentration of structural defects in the crystalline phase of polymers which are usually identified either as paracrystalline lattice distortions and/or molecular folds on the end faces of lamellar crystals [27, 32]. For polymers like PE having extended planar chain conformation (ttttttt) in the crystalline state, by far the most probable type of a paracrystalline distorsion is the so called 'kink-defect' of the type, 2*g*l, which may be visualized as randomly distributed gauche-bonds in a continuous trans-sequence (e.g., ttttgtgttttt) which shift the chain fragment into the neighbouring lattice plane. For the majority of the remaining polymers which crystallize in the helical conformation of the type 3/1 with regular alternation of gauche- and trans-bonds (conformation gtgtgtgtgt), the most probable are kink-defects of the type (gtgtttgtgt). Unfortunately, the detailed structure of chain folds remains somewhat obscure, although it is usually assumed that in the case of, say, PE each fold

Table 3 Properties of the crystalline phase

No	Polymer	$\lambda_1(0)$/ W·m^{-1}·K^{-1}	$\lambda_1(100)$/ W·m–1·K^{-1}	V_o/ nm_3	β_1/ 10^4 MPa^{-1}	$f_o(0, T)$./γ_B	γ_B	$f_o(0, T)$ 10_2
1	PELD	0.56	0.78	0.77	1.56	0.261	6.81	3.8
2	PEHD	0.78	1.09	1.30	1.56	0.233	6.64	3.5
3	HMWPE	0.49	0.87	0.83	1.56	0.431	6.34	6.8
4	PP	0.29	0.55	0.99	2.07	0.485	6.00	8.1
5	PB	0.45	0.59	1.12	2.02	0.215	7.34	2.9
6	PMP	0.20	0.23	1.12	3.67	0.116	2.80	4.1
7	PVF	0.31	0.33$^{a)}$	1.60	1.00	0.219	10.5	2.1
8	PVDF	0.33	0.45	1.38	1.18	0.263	9.5	2.8
9	PCTFE/10	0.21	0.25	1.43	1.53	0.212	12.2	1.7
10	PCTFE/100	0.24	0.29	1.18	1.53	0.229	12.5	1.9
11	PTFE	0.32	0.39$^{a)}$	1.04	1.89	0.354	9.80	3.6

$^{a)}$ – at P =20 MPa

consists of 12 to 20 main chain bonds, of which at least 4 are in the gauche-state [27, 32].

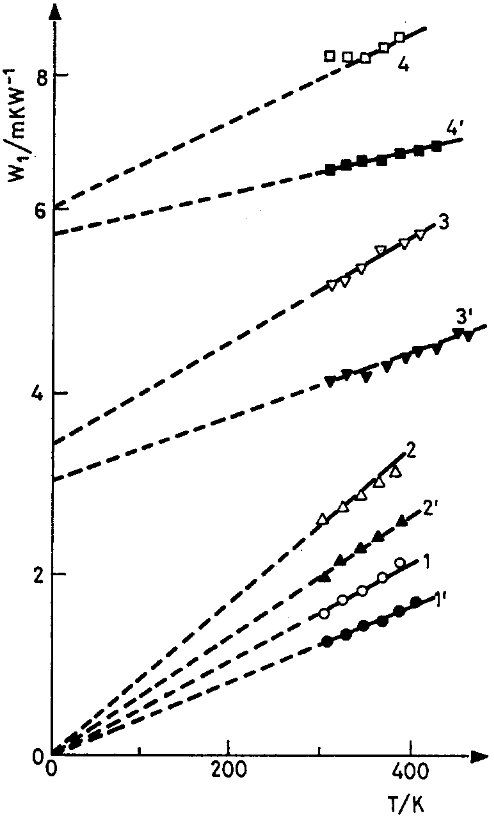

Fig. 6 Temperature dependence of the thermal resistance for PEHD (1, 1'), PELD (2, 2'), PCTFE–100 (3, 3') and PCTFE–100 (4, 4') at normal pressure (open symbols) and at P =100 MPa (filled symbols)

We were not able to estimate the concentration of defects referred to above in the polymers studied, although the calculated values of the parameter $f_0(0, T)$ for PE (0.03–0.07) are, at least, by an order of magnitude higher than the theoretically predicted overall concentration of both kink-defects and chain folds (about 0.005 [27, 32]). In our opinion, the observed discrepancy may be a consequence of one of the following reasons:

a) Equation (12) underestimates the values of γ_{lB} and thus obviously leds to overestimated values of $f_o(0, T)$.

b) Theory [32] takes into consideration only a rather modest amount of thermodynamically equilibrium defects of a crystalline lattice, while in real polymer crystals it is the non-equilibrium defects that are much more numerous.

c) In crystallizable polymers the amorphous phase below T_m is structurally different from the equilibrium melt which was not taken into account explicitly in the calculation of the effective thermal conductivity of the polymer crystalline phase λ_1 from Maxwell's Eq. (8) with extrapolated values of thermal conductivity of a supercooled melt, λ_m, used as λ_2.

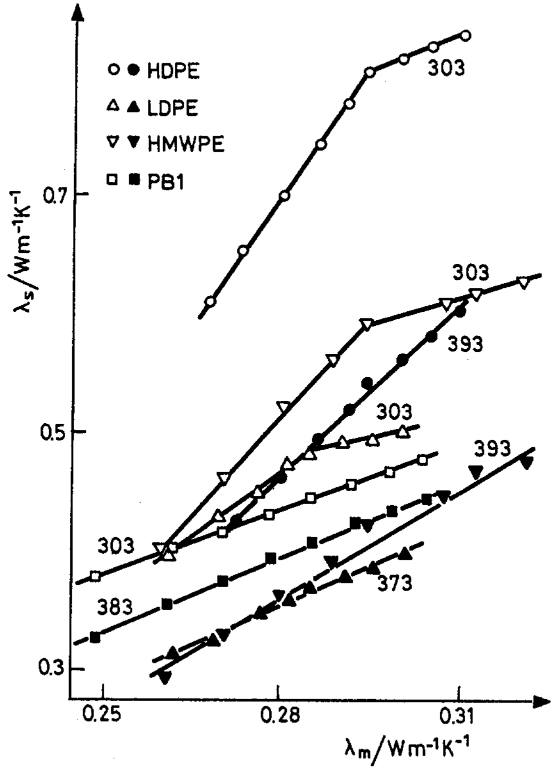

Fig. 7 Correlation between λ_1 and λ_m for selected polymers

The validity of this latter suggestion is indirectly supported by the following reasoning. If the pressure dependences of the thermal conductivity of the amorphous phase in a semi-crystalline polymer, on the one hand, and of a supercooled equilibrium melt, on the other, were identical, one should observe a linear correlation between values of λ and λ_m measured at the same temperature but at different pressures. In fact, such correlation was established for all the polymers studied except PEs for which breaks were observed on λ *vs.* λ_m plots at low temperature (T =303 K), while at higher temperatures approaching the premelting interval (T =383 K for PELD and T =393 K for PEHD and HMWPE) such breaks disappear and the plots become linear (Fig. 7). This means that from the viewpoint of thermal transport properties the amorphous phase of semi-crystalline PEs below T_m becomes identical to a supercooled equilibrium melt only in the premelting interval.

We believe that the observed phenomenon may be interpreted in the following way. PEs possess the highest crystallization rate among the studied polymers which may be attributed to the simplest molecular structure of the former and to the largest crystallization driving force $\Delta g = \Delta S_m \Delta T$ [14] (here ΔS_m is the melting entropy and $\Delta T = T_m - T$ is the supercooling of the melt). In the range of very deep supercoolings ($T \ll T_m$) the amorphous phase of semi-crystalline PE is subject to the action of a significant crystallization driving force Δg which tends to increase the degree of crystallinity X, but this is opposed by steric hindrances and thermodynamically unfavourable decrease of the conformational entropy of tie-molecules within the interlamellar space [14]. As a result, the structure (and, consequently, resistance to thermal transport) of the amorphous phase of a semi-crystalline PE will differ from those for an equilibrium melt, the more so, the larger is the supercooling below T_m. On the contrary, this effect will be weaker, the higher is the temperature since this diminishes Δg. At the same time, the described phenomena should manifest themselves much less for the other polymers which have by far lower (as compared to PE) values of ΔS_m and Δg.

These admittedly qualitative arguments permit to understand the reasons for the expected linear correlation between λ and λ_m for the majority of the polymers studied in the whole temperature interval of measurements, on the one hand, and the disappearance of breaks on such plots for PEs due to approach to a premelting range, on the other.

Conclusions

Evidence presented in this paper supports the concept of a dominant contribution of interchain thermal vibrations to the thermal transport properties of polymers both in the solid and in the melt state. It is emphasized that measurements of thermal conductivity under elevated pressures may well become a source of important additional information on the defect state of polymers.

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Zusammenfassung — Mit Hilfe eines Hochdruck-λ-Kalorimeters mit kontinuierlicher Aufheizung wurde im Druckintervall 0,1 bis 100 MPa und in einem breiten Temperaturbereich, in den sowohl feste als auch flüssige Zustände gehören, die Wärmeleitfähigkeit von Polyolefinen und halogenierten Polymeren untersucht. Drückt man die Druckabhängigkeit der Wärmeleitfähigkeit der Schmelzen mit Hilfe der Barkerschen Gleichung aus, erhält man die Werte für den "Quasigitter" Grueneisen-Parameter B, der die gleiche Abhängigkeit von der Molekular-struktur eines Polymers zeigt, wie der Parameter $3C/p$ aus der Gleichung von Simha-Somcynsky (Zahl der externen Freiheitsgrade geteilt durch Kettenstruktureinheit). Eine Untersuchung der Abhängigkeit der Wärmeleitfähigkeit von Polyethylen von Kristallinitäts-grad zeigt die Mängel dieses Zwei-Phasen-Modelles, was die Mikroheterogenität der "amorph-en Phase" nicht erklärt. Man zog die Schlußfolgerung, daß ein Wärmetransport zwischen den Ketten sowohl im amorphen als auch im kristallinen Zustand den entscheidenden Beitrag zur Wärmeleitfähigkeit von Polymeren liefert.