Microhardness model studies on branched polyethylene

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Abstract

Model samples of polyethylene (PE) with different degrees of branching (up to seven side groups, mostly of butyl type, at 100 C) are melt-crystallized at two undercoolings, 10 and 68°C, in order to obtain samples with various crystalline structures. The last is verified by the observation that the commonly reported equilibrium melting point T_m^∞ of PE is again obtained via extrapolation to infinitely large crystals from both small-angle X-ray scattering and wide-angle X-ray scattering measurements. The samples are also characterized with respect to their density and microhardness (H). The very strong effect of crystallinity and crystal sizes on H is clearly demonstrated. It is emphasized that the crystal size effect reflects rather the effect of crystal perfection, i.e. packing density. Via extrapolation of H the equilibrium microhardness of PE crystals $H_c^\infty = 160$ MPa is determined. It is also shown that H vanishes when the crystal size approaches 27 Å. Using the recently derived analytical expression for T_g and H, the T_g of completely amorphous samples of PE is calculated and a value of -25°C is obtained which agrees with the reported highest values for T_g of PE. In addition, a simple equation for the calculation of H from the paracrystalline lattice distortions $g_{(hk0)}$ is proposed ($H = H_c^{id} - kg_{(hk0)}$), provided the structure of the crystallites can be described by the one-phase paracrystalline concept. Finally, in addition to previous results on other systems, it is demonstrated that the application of the additivity law to multicomponent and/or multiphase systems is justified only in the case when all components (phases) have a melting or glass transition temperature (T_m, T_g) above the temperature at which the H-measurements are carried out. In the case where the system contains a liquid-like component (phase), its contribution to the overall H is by changing the deformation mechanism and in order to apply the additivity law, H must be expressed as $H = 1.97T_g - 571$. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polyethylene (PE) is the most common polymer nowadays. Nevertheless, it is distinguished by some peculiarities making it an unique polymer. It has an extremely high crystallization rate, arising from its high chain flexibility, mostly from its perfect chain structure, particularly, in the case of polymethylene. For this reason PE is not commonly available in amorphous state, and therefore many characteristics of amorphous PE are derived via extrapolation of semicrystalline samples.

Even the preparation of a good set of samples differing in their degree of crystallinity is not a routine task as is the case with many other polymers. For this reason the numerical values for many characteristics of the amorphous PE are quite different from each other and still far from being in complete consensus. A good example in this respect is the

glass transition temperature T_g. Values as different as -30 ± 15; -80 ± 10 and -128 ± 5 are derived [1] using various techniques for evaluation. That is why any contribution to the characterization of amorphous PE is of interest.

Since, for the above-mentioned reasons, the crystallization kinetics cannot be affected by cooling rates aimed at preparing samples with various crystallinity, another approach is frequently used, namely by affecting the crystallization ability of the main chain through chemical modification. The latter consists usually in introducing "defects" in the chains representing side groups with various size. Such irregularly distributed substituents considerably hamper the crystallization, and samples with decreasing crystallinity can be obtained with an increase of the amount and/or size of the side groups. An interesting characteristic of this approach is the fact that at low concentration of, let's say $-CH_3$ groups, the polymer can still be considered as substituted or branched PE, while at much higher CH_3 concentration the polymer is quite close to polypropylene (PP) in its behaviour.

Baltá Calleja and co-workers [2–6] used this approach very effectively. They selected commercial samples of PE

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Table 1
Some characteristics of branched PE crystallized from melt at small ($\Delta T = 10°$C—series A) and large ($\Delta T = 68°$C—series B) undercoolings. From left to right: molecular weight M_w, chain defects ϵ per 100 C-atoms; melting temperature T_m; macroscopic density ρ; crystal size D_{hk0}, long spacing L; crystal lamellae thickness l_c; crystallinity w_c (from WAXS and from density); microhardness H and paracrystalline distortions parameter g_{hk0}

Sample	$M_w \times 10^{-3}$	ϵ per 100°C	T_m (°C)	ρ (g/cm³)	D_{200} (Å)	D_{110} (Å)	L (Å)	l_c (Å)	w_c (%)	w_c (ρ)(%)	H (MPa)	$g_{(110)}$ (%)
1A	150.0	0.19	137.5	0.9680	264	379	322 ± 10	258 ± 8	70.1	80.5	84.7	1.16
2A	120.0	0.70	134.0	0.9602	229	280	386 ± 10	234 ± 6	62.1	75.6	72.8	1.54
3A	51.0	1.76	119.5	0.9311	141	215	228 ± 16	110 ± 7	50.5	56.4	37.2	1.86
4A	11.6	2.63	—	0.9402	—	242	253 ± 8	106 ± 4	43.5	62.5	45.2	2.32
5A	54.0	3.04	113.5	0.9165	100	186	250 ± 20	99 ± 8	42.1	46.3	20.0	—
6A	284.5	3.61	108.0	0.9123	87	198	259 ± 10	93 ± 4	36.8	43.3	16.6	3.22
7A	21.0	4.77	106.5	0.9038	79	199	270 ± 10	71 ± 3	31.0	37.2	12.5	3.36
8A	18.3	5.34	105.5	0.9102	91	188	202 ± 10	69 ± 4	36.8	41.9	15.8	2.90
9A	11.0	6.90	91.5	0.8900	56	125	251 ± 14	55 ± 3	23.4	27.1	6.9	3.00
1B	150.0	0.19	132.5	0.9531	203	277	264 ± 10	209 ± 6	62.0	70.9	70.5	1.40
2B	120.0	0.70	129.0	0.9462	169	239	250 ± 10	194 ± 5	55.5	66.5	53.6	1.64
3B	51.0	1.76	118.8	0.9250	125	232	204 ± 6	91 ± 3	47.1	52.2	26.2	2.70
4B	11.6	2.63	110.0	0.9368	117	254	195 ± 7	106 ± 4	56.4	60.2	39.5	2.00
5B	54.0	3.04	107.5	0.9110	97	171	164 ± 4	60 ± 2	38.7	42.4	18.1	2.30
6B	284.5	3.61	105.0	0.9078	87	193	178 ± 7	68 ± 3	40.6	40.1	11.9	3.06
7B	21.0	4.77	99.5	0.8990	62	196	171 ± 9	54 ± 3	34.2	33.7	9.5	3.54
8B	18.3	5.34	100.5	0.9081	117	251	176 ± 5	47 ± 2	26.6	40.3	12.5	3.30
9B	11.0	6.90	86.0	0.8868	50	158	178 ± 5	36 ± 1	21.3	24.7	4.4	3.80

differing in the degree of branching, and by applying two quite different crystallization temperatures they succeeded in preparing samples with systematic variation of the structural parameters. In this way they were able to study, in depth, the influence on the microhardness of such microstructural parameters as the dimensions of the crystalline unit cell, the thickness of the lamellae and the lateral dimensions of the coherently diffracting domains [2]. It was found that the unit cell expansion and lattice distortions increase in parallel as a consequence of increasing incorporation of chain defects within the lattice. This provokes a conspicuous decrease in the microhardness of the crystals. The increase in lattice distortions is consistent with the concurrent decrease of lamellae thickness and, hence, decrease of the coherently diffracting lattice volume. In addition, H is shown to depend on the packing density of the macromolecules in both, crystalline and amorphous phases and, as a result, it can be clearly correlated with the macroscopic density of the material [2].

The same set of samples has been used for verification of a novel concept in describing elastic and plastic properties of semi-crystalline polymers [3,4]. In this way a basic model of deformation under local compression is proposed in terms of the heat dissipated by the plastically deformed crystals and the volume of crystals destroyed under the indenter. The results indicate that the mechanism of deformation is dictated by the initial mosaic-block structure controlling the generation of a final system of shear planes [3,4]. In this case it should be mentioned that the model proposed and the derived equations account for the microhardness of low molecular weight paraffins ranging from C_{20} to C_{40} [5].

Finally, the same set of samples has been used for finding a correlation between the elastic modulus E and H [6]. The data suggest that E is very sensitive to the fraction of tight crystalline bridges between lamellae. The correlation found between E and H emphasizes, in addition, the different and complementary role played by the amorphous layer in each mechanical test. In the former case one measures the elastic deformation of the layer reinforced by tie molecules. In the latter test (H) the plastic deformation under compression of the lamellae sandwiched between noncrystalline layers is contemplated. In both cases the influence of the number of defects drastically affects the nature of the crystalline lamellae and the surface layer and consequently substantially modifies both types of property [6].

The cited studies [2–6] have a couple of common characteristic features, as for example: (i) the models and equations derived [3,4] concern only the crystalline phase of PE; (ii) the hardness of the amorphous PE H_a is approximated as zero when the additivity law has been used; and (iii) the graphical presentation of various data shows rather gradual (mostly exponential or rarely "S"-shaped) change of microhardness as dependent on various structural parameters, i.e. no attempt has been undertaken for the extrapolation of the linear sections of the plots [2–6].

Before formulating the task of this study let us note that very recently [7] by summarizing the known values of H for many completely amorphous polymers, including polyolefins, polyesters and polyamides, a linear relationship between their microhardness and T_g was found:

$$H = 1.97T_g - 571 \text{ (MPa)} \tag{1}$$

where T_g is in Kelvin. All the amorphous polymers used for deriving this relationship have T_g values above room temperature. Further on, it was demonstrated [7] that this relationship helps one to understand better the microhardness of complex systems comprising very soft, liquid-like
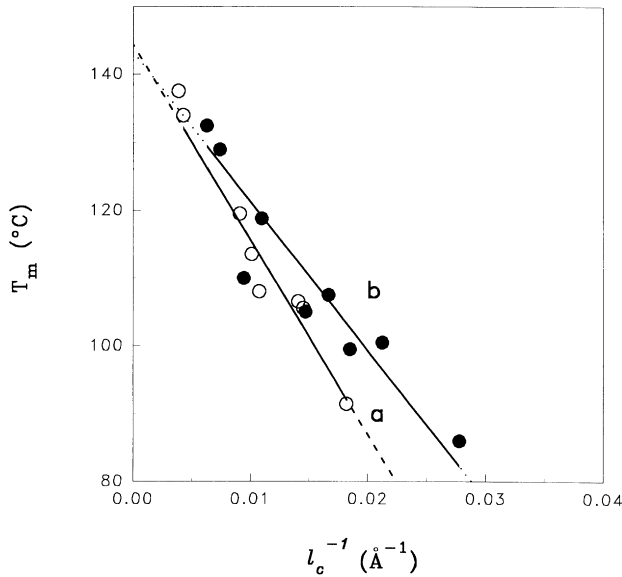
Fig. 1. Dependence of the melting temperature T_m on the reciprocal values of the crystal size evaluated by SAXS for branched PE crystallized from the melt at $\Delta T = 10°C$ ($\bigcirc$) and $\Delta T = 68°C$ ($\bullet$) (Table 1).
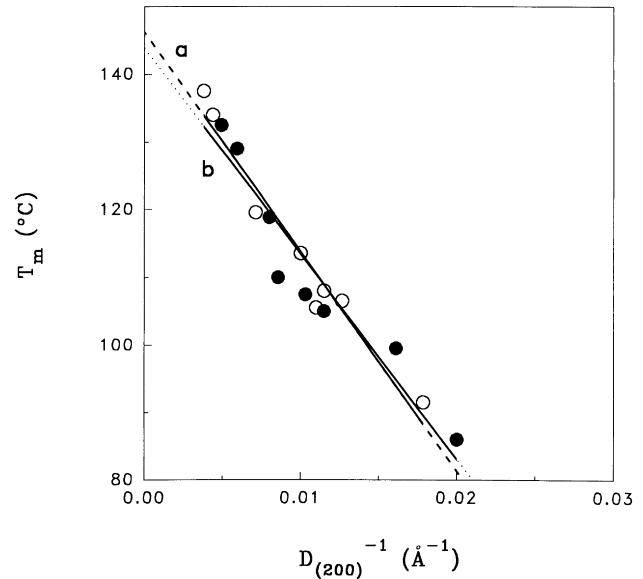

Fig. 2. Dependence of the melting temperature T_m on the reciprocal values of the crystal size evaluated by WAXS for branched PE crystallized from the melt at $\Delta T = 10°C$ ($\bigcirc$) and $\Delta T = 68°C$ ($\bullet$) (Table 1).

components and/or a phase with T_g for example as low as $-50°C$. This demonstrated that the linear relationship between H and T_g is also valid for substances having T_g below room temperature, i.e. being liquids at normal conditions. It also seems important to mention here that such systems, comprising a very soft component, deviate strongly from the additivity law and the assumption $H^{soft} = 0$ does not solve the problem since in these systems the deformation mechanism during indentation is completely different in contrast to the case when all the components have glass transition temperatures above room temperature.

The goal of this study is to analyse again the cited data [2–6] on PE samples differing in crystal sizes, perfection, degree of crystallinity, overall density and microhardness using the recent knowledge about the deformation mechanism of complex systems [7] as well as about the relationship between H and T_g, and in this way one obtains via extrapolation the numerical characteristics of inaccessible components or phases such as the completely amorphous and fully crystalline PE.

2. Experimental

The series of commercial samples of PE with a wide range of chain defect concentrations ϵ (from 0.17–6.9%) is listed in Table 1. According to i.r. analysis the branches are butyl or longer methylene sequences [8]. These materials have been pressed and cast from the melt in the form of plates of $20 \times 18 \times 1.5$ mm in size, and crystallized from melt at supercooling of either $\Delta T = 10$ or $68°C$, as described in more detail elsewhere [9].

Morphological properties have been investigated by

small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements. The details of the experimental procedure have been described in Ref. [10]. The volume fraction of crystallized material w_c (WAXS) has been determined using the X-ray method described by Vonk [11].

The H measurements have been carried out at room temperature with a Leitz tester using a Vickers square pyramidal diamond. The dimension of the diagonals, d, of the observed diamond shaped indentation was measured immediately after load removal with a micrometre eyepiece of the microscope. The accuracy of the measurements is ± 0.5 μm. The immediate elastic recovery has been found to be undetectable within the experimental error. For further details see Ref. [12]. The hardness value has been therefore calculated from the projected area of indentation according to

$$H = k\frac{P}{d^2} \text{ (MPa)} \tag{2}$$

In Table 1 are summarized all the characteristics gained by different techniques. These data are further used for plotting various relationships and making the necessary extrapolations.

3. Results

First of all an attempt was undertaken to "verify" the applicability of the samples for the intended purposes, i.e. it was checked to what extent the samples differ really systematically in their structural characteristics. This was done by plotting the experimentally measured melting temperature T_m as a function of the reciprocal value of the
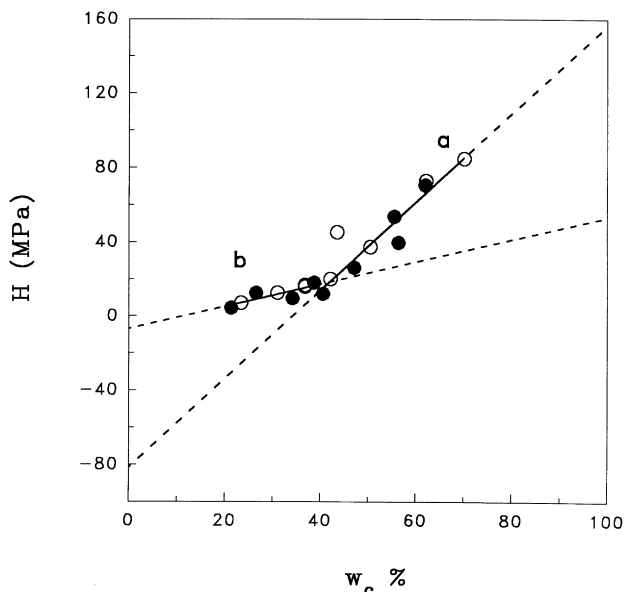
Fig. 3. Dependence of microhardness H on the degree of crystallinity w_c (WAXS) for branched PE crystallized from the melt at $\Delta T = 10°C$ (○) and $\Delta T = 68°C$ (●).

lamellae thickness l_c. The results are shown in Fig. 1. One can see two straight lines for the two series of samples: with $\Delta T = 10°C$—open circles, line a; with $\Delta T = 68°C$—filled circles, line b. Both lines yield very close values of the equilibrium melting point of PE $T_m^\infty = 144.4°C$ (line a) and $143.3°C$ (line b). These values are in excellent agreement with the reported ones [13] of $T_m^\infty = 141.1 - 145.5 \pm 1^C$ evaluated from the extrapolation of n-paraffins.

The same procedure is performed using the crystal size determined by WAXS (D_{200}, Table 1) and almost the same values for the two series of samples (145.6 and 143.8°C, respectively) are obtained[2] for T_m^∞ (Fig. 2).

The fact that the extrapolations in Figs. 1 and 2 yield the well known values for T_m^∞ shows that the prepared samples really differ from each other in a very systematic way with respect of characteristics of the crystalline phase—its

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[2] It seems interesting to note at this point that the observed straight lines in Figs. 1 and 2 are nothing else but graphical presentation of the Gibbs–Thomson equation relating the melting point T_m of crystals with their dimensions. They offer the opportunity for evaluation of the T_m of infinite large crystals (the equilibrium melting point T_m^∞) [15]. The same equation was rederived much later by Hoffman [16] and applied to polymer crystals, using crystal size as exclusively the lamellae thickness l_c determined by SAXS [17]. In fact, in the original version of the equation [15] there is no specification for a particular size direction. For a series of polyamides it was demonstrated [18–21] that the Gibbs–Thomson equation can be successfully used for evaluation of T_m^∞ using crystal sizes in any direction as determined by WAXS.The misleading point in the Hoffman's version [17] that only crystal sizes in the chain-axis direction can be used was so strong that it affected even similar developments in the microhardness treatment [2–6,14,22], where also crystal sizes exclusively in the chain-axis direction l_c have been used. Such a limitation with respect to the crystal size direction is not justified, as demonstrated for T_m earlier [18–21] and as it will be shown further in this study on the evaluation of H values.

amount, as well as size and perfection of crystallites. This conclusion is of particular importance because it is indicative for the reliability of the further extrapolations based on the same properties of the crystalline phase. Further, Figs. 1 and 2 clearly demonstrate that for the purpose of such an extrapolation one can use the crystal size in any direction.

Since synthetic polymers are semi-crystalline the microhardness depends strongly on the degree of crystallinity because the microhardness of the crystalline phase H_c usually differs significantly from that of the amorphous phase H_a [14].

This dependence can be seen in Fig. 3 where H is plotted vs degree of crystallinity w_c, evaluated from WAXS measurements for the two series of samples. The extrapolation of the straight lines a and b towards a fully crystalline material ($w_c = 100\%$) yields $H_c = 156$ MPa and $H_c = 53$ MPa, respectively. Unfortunately, it is difficult to say to what side-groups-content of the sample can be assigned these two H_c values, since basically a similar extrapolation can be performed for any sample with relatively low concentration of side-chain groups, provided samples varying in their crystallinity are prepared. Much more interesting is the extrapolation in the opposite direction ($w_c = 0$). For the completely amorphous material the extrapolation yields $H_a = -81.5$ MPa, (from the straight line a) and $H_a = -7$ MPa (from the straight line b). These values do not have any physical meaning but they can be used for further calculations as it will be shown later. From the same Fig. 3 one can see that $H = 0$ when crystallinity drops to less than 15%.

An interesting observation can be made from Fig. 3. The two straight lines comprise samples from the both series, A and B (Table 1) but differing in the w_c values: above 45% (samples of line a) and below 45% (samples of line b). From Table 1 one can conclude that the two groups of samples refer to two groups of degree of branching ϵ –below 3 side-groups per 100 C-atoms (line a) and between 3 and 7 side-groups per 100 C-atoms (line b). Taking into account these details it becomes understandable why the extrapolated H values differ so significantly and particularly the values of the fully amorphous samples H_a. While the samples with less perfect crystalline structure (because of the higher degree of branching) yield in a much lower H_c value, the corresponding H_a value is significantly higher than that for low branched samples. The reason for this last difference is in the different viscosities and consequently different T_g values for the less and more branched PE samples. The case is quite similar to the PE (unbranched) and PP (completely "branched" PE) distinguished by their rather different T_g values.

In Fig. 4 the dependence between H and the overall density of the branched PE samples is plotted. The experimental points define clearly two straight lines intercepting at around $\rho = 0.91$ g/cm^3. One of them covers the density interval between 0.91 and 0.97 g/cm^3 and the other one between 0.88 and 0.91 g/cm^3, both lines comprising data
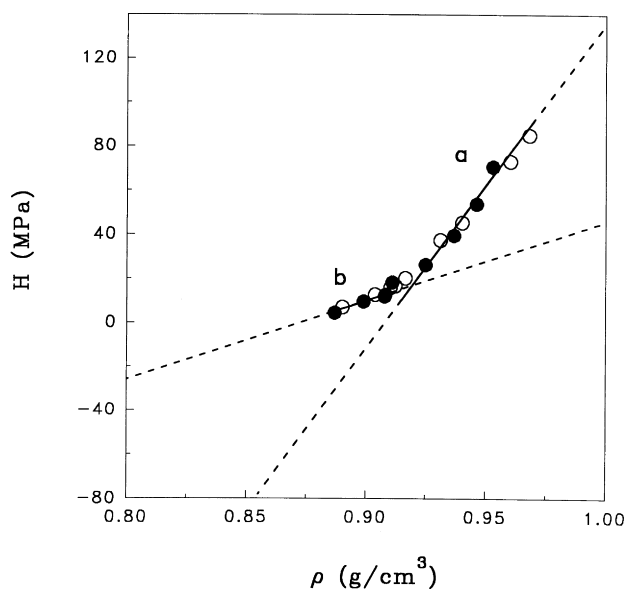
Fig. 4. Dependence of microhardness H on the macroscopic density $\bar{\rho}$ for branched PE crystallized from the melt at $\Delta T = 10°C$ ($\bigcirc$) and $\Delta T = 68°C$ ($\bullet$).

of the two series of samples (A and B, Table 1). If one takes into account that the higher density interval corresponds to PE samples containing up to three side-chain groups per 100 C-atoms, and the lower density interval to the higher content (Table 1) one can consider the first set of samples as lowly branched polyethylene and the second one as highly branched PE. In such a case the H value for $\rho = 1.0$ (ideal crystal density of PE [23]) yields $H_c^\infty = 136$ MPa. For the completely amorphous PE ($\rho = 0.855 g/cm^3$[23])
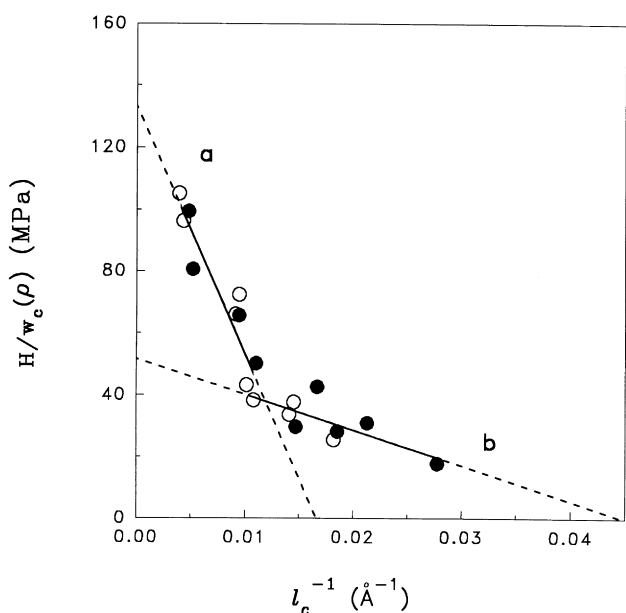

Fig. 5. Dependence of microhardness of fully crystalline branched PE $H/w_c(\rho)$ on the reciprocal value of the crystal lamellae thickness l_c for samples crystallized from the melt at $\Delta T = 10°C$ ($\bigcirc$) and $\Delta T = 68°C$ ($\bullet$).
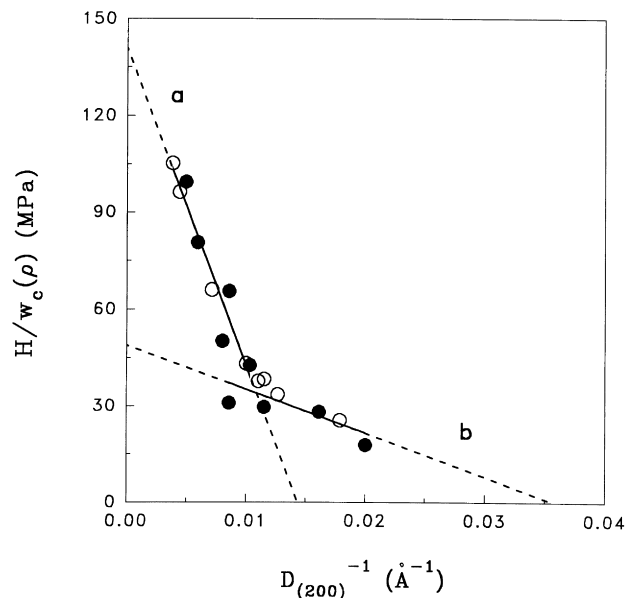

Fig. 6. Dependence of microhardness of fully crystalline branched PE $H/w_c(\rho)$ on the reciprocal value of the crystallites size D_{200} for samples crystallized from the melt at $\Delta T = 10°C$ ($\bigcirc$) and $\Delta T = 68°C$ ($\bullet$).

$H_a = -78$ MPa, which is very close to the value obtained from Fig. 3 for the same group of samples (straight line a). Another conclusion which follows from the same low branched PE straight line (line a, Fig. 4) is that PE (possibly unbranched) with density smaller than 0.90 g/cm^3 is supposed to be very soft in order it shows any microhardness by means of the used impression technique.

The second important factor determining H is the crystallite size, as documented manifolds [14,22]. The extremely strong influence of crystal dimension is shown in Figs. 5 and 6, where the normalized experimentally measured microhardness $H/w_c(\rho)$ is presented as dependent on the reciprocal values of the crystallite dimensions measured by SAXS as lamellae thickness (l_c) (Fig. 5) or by WAXS as a coherent length from the reflection (200) (Fig. 6). Such a normalization is undertaken in order to avoid to some extent the very strong effect of w_c on H as demonstrated above. It should be noted that the value $H/w_c(\rho)$ should not be considered as H_c because this would mean that $H_a = 0$, which hardly is the case. Recently it has been demonstrated for systems as thermoplastic elastomers, comprising very soft (liquid-like) components, that the deviation from the additivity law cannot be solved by assuming $H_a = 0$ [24].

The experimental data for $H/w_c(\rho)$ vs $1/l_c$ from SAXS again define two straight lines—for the low-branched PE (straight line a, Fig. 5) and for the highly branched one (straight line b, Fig. 5). The extrapolation of line a gives for a fully crystalline PE comprising infinite large crystals the value $H_c^\infty = 133$ MPa. In analogy with the ideal or equilibrium melting point, T_m^∞ reflecting the melting of the same system (Figs. 1 and 2) H_c^∞ can be considered as "ideal" or "equilibrium" microhardness of PE. Let us recall again that H_c^∞ refers to the case when the completely crystalline

sample consists of defect free, i.e. unlimited large crystals. This case contrasts to the previous one (Fig. 3) dealing again with full crystallinity but with unspecified crystal sizes.

The second straight line (b, Fig. 5) for the highly branched PE reflects the microhardness of the samples having much thinner lamellae. This line offers the opportunity to evaluate the lamellae thickness when $H = 0$. The extrapolation gives a value of l_c about 25 Å.

Quite similar to Fig. 5 is the graphical presentation of the dependence of H on the crystal sizes determined by WAXS as can be concluded from the plots in Fig. 6. Even more so, the two straight lines are better defined. The extrapolation in this case of line a leads to $H_c^\infty = 141$ MPa which is in a good agreement with the value obtained from Fig. 5. By extrapolation of line b for $H = 0$ one also derives $D_{200} = 27$ Å.

From Figs. 5 and 6 an important conclusion follows: for evaluating the effect of crystal size on H, crystal sizes measured from both SAXS and WAXS techniques can be successfully used.

4. Discussion

Before starting the discussion let us stress again the essential difference between the ways of analysing the experimental results in the earlier works [2–6] and in the present work.

In the previous reports [2–6] the same set of samples (Table 1) was analysed together with other PE samples and even together with low molecular weight paraffins strongly differing in their molecular weights and their structural parameters. In this way it was possible to demonstrate that the derived thermodynamically equations are rather universal although the parameter b, accounting for the surface/volume ratio of the original crystal blocks prior to deformation [5] changes in a quite large range (between 6 and 200) [2–6].

The analytical approach to the data of Table 1 in the present study is rather different. Attention is paid in forming as small a group of samples as possible characterized by as linear changes as possible of a given parameter; let us say degree of crystallinity, in one case, or crystal size, in another. Such an approach allows one to differentiate the effect of only one factor on the microhardness and, in addition, to get a better linearity, which makes the extrapolation to the extreme values of the studied factor more reliable.

Another comment related to the discussion refers to a very important peculiarity of the system under investigation. The samples subjected to crystallization from melt are not chemically uniform. Starting by polyethylene and introducing in the chain side groups one moves in the direction for example of PP (if the side groups are only of CH_3 type). Only samples with the lowest side groups-content can be considered as low or moderate branched PE while with increase of this content one approaches derivatives of PE

with completely different properties. Nevertheless, controlling the side groups content in PE, this approach is an useful tool for preparation of PE with differing crystalline characteristics.

4.1. Effect of crystallinity and crystal sizes on microhardness

Microhardness, like many physical properties of complex systems (with respect to composition), obeys the additivity law, known also as "mixture rule" [14,22]:

$$H = \sum_i \varphi_i H_i \tag{3}$$

where H is the microhardness of the system, H_i and φ_i; are the microhardness and the mass fraction of the individual components and/or phases. That is why H of semicrystalline polymers depends strongly on the degree of crystallinity as demonstrated also in Fig. 3. The extrapolation of this relationship allows one to evaluate H of a completely crystalline sample H_c containing crystallites of close perfection, but far from the "ideal" one.

Concerning the effect of crystal size it should be mentioned that there is no obvious reason for this dependence. Crystallites of different size but of the same perfection are supposed to have the same hardness. The tremendous effect of crystal sizes on H (Figs. 5 and 6) is related with the different perfection of the same set of samples expressed by their sizes. Let us remember that the crystal size determination by means of WAXS explores the widening of the crystal reflections. The latter is affected by three factors: the instrumental resolution, the crystal sizes and the crystal perfection. Unfortunately, there is no simple and accurate way of evaluation of the contribution of each factor [25]. Obviously, the measured by WAXS crystal sizes reflect and emphasize the contribution of crystal perfection at least for the formation of H.

The situation seems to be quite similar with SAXS technique where the lamellae thickness is evaluated. It is known from polymers with chemically uniform composition that different lamellae thickness can be produced by different undercooling ΔT during crystallization. Smaller the ΔT larger is the l_c and more perfect the crystallites. In the present case the same approach is used for preparation of samples with different l_c-two ΔT values have been selected. On the other hand, the crystal perfection is also affected by the chemical composition, by increasing the side group-content thinner lamellae are produced (Table 1) characterized by lower perfection.

The above considerations are supported by the following calculation aiming the evaluation of H_c from samples differing in their crystallinity and crystal sizes. For this purpose the additivity law (Eq. (3)) is used for expressing the overall experimentally measured microhardness H_{exp} as dependent on H_c and H_a and their mass fractions w_c and $(1 - w_c)$,

Table 2
Experimentally measured overall microhardness, H_{exp}, and calculated for completely crystalline sample H_c, using Eq. (3), for the two series (A and B) of branched PE

Sample	$w_c (\rho)$	H_{exp} (MPa)	H_c (MPa)	l_c (Å)
1A	0.805	84.7	127.1	250
2A	0.756	72.8	125.5	234
3A	0.564	37.2	135.8	110
4A	0.625	45.2	126.6	106
5A	0.463	20.0	57.4	99
6A	0.433	16.6	54.2	93
7A	0.372	12.5	54.3	71
8A	0.419	15.8	54.7	69
9A	0.271	6.9	58.4	55
1B	0.709	70.5	136.5	209
2B	0.665	53.6	126.1	194
3B	0.522	26.2	133.0	91
4B	0.602	39.5	125.4	106
5B	0.424	18.1	59.3	60
6B	0.401	11.9	48.0	68
7B	0.337	9.5	52.3	54
8B	0.403	12.5	43.2	47
9B	0.247	4.4	55.2	36

respectively,

$$H_{exp} = w_c H_c + (1 - w_c) H_a. \tag{4}$$

For H_a the values extrapolated from Fig. 3 are taken from the two straight lines (a and b) reflecting the two groups of samples differing in their branching degree (Table 1), namely the values -81.5 and -7 MPa.

The obtained values for the completely crystalline PE H_c are presented in Table 2 together with $w_c(\rho)$, H_{exp} and l_c
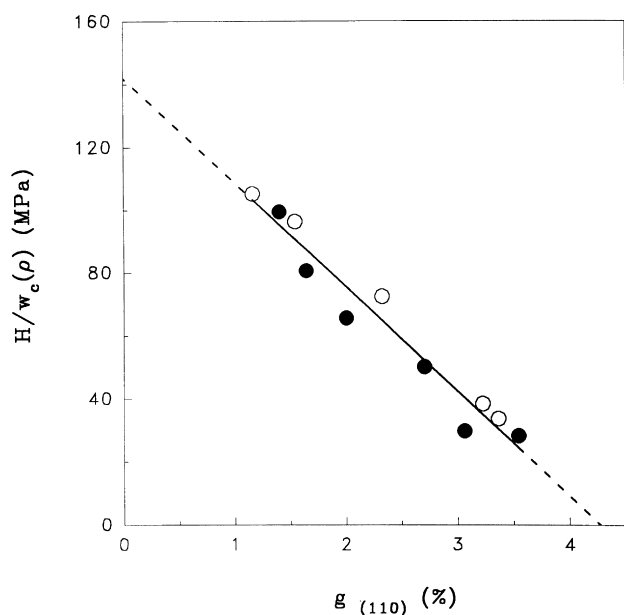

Fig. 7. Dependence of microhardness of fully crystalline branched PE $H/w_c(\rho)$ on the paracrystalline lattice distortions parameter $g_{(110)}$ for samples crystallized from the melt at $\Delta T = 10°C$ (○) and $\Delta T = 68°C$ (●) containing no more than four side-chain groups per 100 C (Table 1).

values taken from Table 1 for comparison. Again two groups of values for H_c are obtained in each groups of samples, between 125.4 and 136.5 MPa for the lower-branched (up to three side groups per 100 C) PE and between 43.2 and 59.4 MPa for the higher-branched (above three side-groups per 100 C) PE regardless of the crystallization conditions (Table 2). What is more striking, the H_c values in the two groups seem to be almost insensitive to the lamellae thickness l_c which changes in the first group between 100 and 250 Å and between 35 and 100 Å for the second group of samples (Table 2).

At first glance this observation seems to contradict the well-documented [14,22] strong influence of the crystal sizes on H, clearly demonstrated in the present study as well (Figs. 5 and 6). In order to understand this finding one has to assume that the lower-branched samples form more or less uniform crystallites with respect to perfection (regardless of the undercooling) and/or the hardness differences observed are encountered by variation of the degree of crystallinity but not of the lamellae thickness. The same holds for the second group, the higher-branched samples. This suggestion is supported by the following consideration: it is well known that for chemically uniform homopolymers the l_c depends only on the undercooling, in contrast to multiblock copolymers. In the second case l_c depends also on the length of the crystallizable blocks when they are too short in order to build up lamellae with thickness determined only by the thermodynamic requirements. Such a situation has been observed in a series of poly(ether ester) multiblock copolymers differing in the crystallizable block length [26,27].

Obviously, one has the same situation in the present case since completely different l_c values (ranging from 50 up to 250 Å) for one and the same crystallization condition ($\Delta T = 10$ or $68°C$) (Table 1) are obtained. In other words, the lamellae thickness is determined exclusively by the concentration and way of distribution of "defects" in the main chain and the lamellae do not differ so strongly in their perfection (particularly for the lower branched group of samples).

The strongest support in favour of the statement that the crystal sizes reflect rather the crystal perfection, provided they are determined by the crystallization conditions but not by the chemical composition and/or structure of the samples, are the results plotted in Fig. 7. They reflect the dependence of H on the paracrystalline lattice distortions parameter g_{110} orthogonal to the (110) planes [2] for some samples listed in Table 1 (except the samples with the highest degree of branching). The values of paracrystalline lattice fluctuations $g_{(hk0)}$ and the size of the coherently diffracting domains, D_{hk0} normal to the chain axis have been obtained according to the paracrystal theory [28], from integral width of the reflections $\delta\beta_{hk0}$:

$$\delta\beta_{hk0} = \frac{1}{D_{hk0}} + \frac{(\pi g)^2}{\bar{d}_{hk0}} m^2 \tag{5}$$
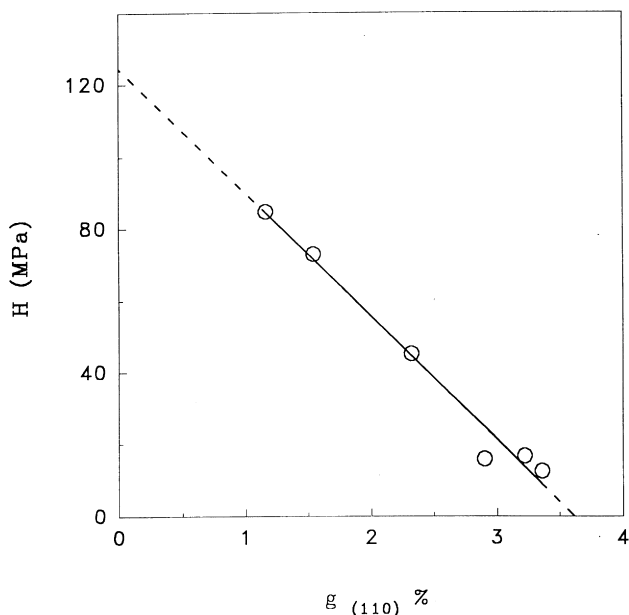
Fig. 8. Dependence of microhardness H of branched PE on the paracrystalline lattice distortions parameter $g_{(110)}$ for samples crystallized from the melt at $\Delta T = 10°C$ and containing no more than four side-chain groups per 100 C (Table 1).

where m is the order of the reflection, $\bar{d}_{hk0}$ the average lattice spacing and $g = \Delta d / \bar{d}_{hk0}$, where Δd, is the mean statistical fluctuation between the lattice planes. This expression assumes that the lattice distortions and the shape factor are Lorentzian and is approximately valid for other profiles [2].

One can see that the extrapolation of the experimental data referring to the two crystallization conditions ($\Delta T = 10°C$ and $\Delta T = 68°C$, Table 1) result in the H values for the "defect free" crystals of 142 MPa. Similar extrapolation to "infinite" large crystals from l_c (Fig. 5) and from D_{200} (Fig. 6) data yield in $H_c^{c\infty}$ of 133 and 141 MPa, respectively. This very good agreement with the data obtained from the two approaches confirms the suggestion that H is very sensitive to crystal perfection but not necessarily to the crystal sizes. The latter reflect the crystal perfection in case it is not accounted for by other structural parameters, i.e. the degree of crystallinity as is the case is with Figs. 5 and 6.

At this point it should be emphasized that a good linearity is also observed if one plots non-normalized with respect to crystallinity H values as a function of $g_{(hk0)}$ as shown in Fig. 8. This plot comprises samples only from series A ($\Delta T = 10°C$, except the last two samples characterized by the highest side-groups content, Table 1). This selection is done in order to be closer to the unbranched PE. The extrapolation of the straight line in Fig. 8 yields $H_c^{id} = 124.4$ MPa. This value is lower in comparison to the previous case (Fig. 7), for obvious reasons (lack of normalization). But what is more important—the linear relationship is preserved.

This strong effect of crystal perfection on the

microhardness allows one to evaluate the "ideal" or equilibrium H value H_c^{∞} by means of extrapolation to infinitely large crystals (Figs. 5 and 6, curve a or to the "defect-free" crystals (Fig. 7) in analogy with equilibrium melting point T_m^{∞} (Figs. 1 and 2). In the same time, using samples with poor crystallinity (straight line b of Figs. 5 and 6 in the present study), it is possible to determine the crystal size characterized by microhardness approaching the zero value. From lines b (Figs. 5 and 6), one can conclude that crystallites having sizes less than around 25 Å do not show experimentally measurable (at least using the technique applied in the present work) microhardness values.

There are at least two reasons for this observation. The first one is related to the crystalline phase. Assuming that low molecular weight paraffins (C_{18}–C_{25}) have crystal sizes in c-direction of the magnitude of the order of their chain length of around 23–32 Å and taking into account their melting points (for C_{20} $T_m = 37°C$ [29]), it becomes understandable why these crystals have to be rather soft at room temperature at which the measurements are carried out. The second factor leading to the result $H = 0$ is the fact that in the PE samples containing such crystallites dominates the amorphous phase (up to 80 wt% and more) which is even softer because of its very low T_g values as will be demonstrated in the subsequent section.

In discussing the crystal sizes, characterized by the microhardness measurable at room temperature, it should be mentioned that realistic H values of a few MPa have been obtained on crystalline paraffins (C_{20}–C_{32}) having similar crystal sizes (between 25 and 40 Å) [5]. This finding does not contradict the present conclusion about the minimal l_c value of 27 Å for the following reason. The low-molecular-weight paraffins are completely crystalline in contrast to the present samples characterized by poor crystallinity (Table 1). For this reason, they exhibit proper microhardness since their crystallites do not float in a liquid-like matrix amounting to 80% of the total mass as is the case with the PE samples showing poor crystallinity (Table 1).

4.2. Effect of crystal perfection on microhardness

Let us come back to Figs. 7 and 8 where the dependence between microhardness and the paracrystalline lattice distortions is presented. In both cases a fair amount of linear relationship is observed.

In the case where the structure of the polymer crystals can be conveniently described by means of the one-phase paracrystalline concept, the plot in Figs. 7 and 8 offer the opportunity for relating analytically the microhardness with crystal perfection.

The straight line in Fig. 8 allows one to derive a very simple equation relating the microhardness H of a crystalline polymer with its paracrystalline lattice distortions g_{hk0}:

$$H = H_c^{id} - kg_{(hk0)} \text{ (MPa)} \tag{6}$$

where for the case of PE $H_c^{id} = 124.4$ MPa and $k = -34.4$ (the regression coefficient is 0.990).

This equation seems to be rather universal, i.e. one can easily calculate the microhardness H of any crystalline polymer using the paracrystalline lattice distortion $g_{(hk0)}$ as determined by WAXS measurements for a particular sample, provided H_c^{id} and k have been once determined for the same polymer. One has to stress again that this equation holds only for crystalline polymers which can be structurally described by means of one-phase paracrystalline model.

In the cases where the structure data indicate the presence of a second, i.e. amorphous phase (as can be for example concluded from a DSC trace where clear evidence for both the glass transition and the melting of crystals exist) one has to use another equation for the calculation of the overall H. Such an equation which accounts for both the crystalline and amorphous phases, was recently proposed [7]:

$$H = \varphi H_c + (1 - \varphi)(1.97T_g - 571) \text{ (MPa)} \qquad (7)$$

where φ and H_c are the mass fraction and the microhardness of the crystalline phase or component, respectively, and $(1 - \varphi)$ is the mass fraction of the amorphous phase or component with glass transition temperature T_g.

The last Eq. (7) was shown [7] to be particularly useful for complex multiphase and/or multicomponent systems with one or more phases and/or components which are liquid-like at room temperature and deviations from the additivity law were observed if one assumes for the soft phases and/or components $H_a = 0$.

In conclusion, the overall microhardness of semicrystalline polymer with known T_g value of the amorphous phase can be expressed by combining Eqs. (6) and (7):

$$H = \varphi(H_c^{id} - kg_{(hk0)}) + (1 - \varphi)(1.97T_g - 571) \text{ (MPa)} \qquad (8)$$

4.3. Evaluation of T_g of PE

In the introductory part it was mentioned that PE is not commonly available in a completely amorphous state and for this reason its T_g value is not known exactly. The recently derived simple analytical expression relating the H of completely amorphous polymers and their T_g (Eq. (1), [7]) holds for polyesters and polyamides and their copolymers provided the main-chain comprises mostly single chemical bonds. Taking into account these two considerations it looked challenging to use Eq. (1) for evaluating of T_g of PE by applying the H value for the completely amorphous PE obtained by extrapolation.

The extrapolation of the data of the present study to completely amorphous material (Figs. 3 and 4) leads to H values without any physical meaning as already mentioned above. Nevertheless, the use of these values for the purpose of Eq. (1) results in T_g values being between -23 and $-25°C$. It is important to note that in the same temperature interval are the highest reported T_g values for PE [23], i.e.

$-30 \pm 15°C$. The latter value is reported for the T_g of commercial PE, which is also the case in our study.

Noteworthy in this respect is also the report of Pereña et al. [30] who studied microhardness using dynamic mechanical (DMTA) measurements at low temperatures (between -60 and $25°C$) with five commercial samples of PE, two of them of high density (HD) and another three of low density (LD). The experimental data for H show clear transition around $-30°C$ (for LD samples) and around $-10°C$ (for HD) samples). The data from DMTA show this transition only for the LD samples in agreement with the observation [31] that β-relaxation is clearly detected by DMTA only in branched PE and has been not detected at all in linear PE of medium molecular weight. Taking into account the fact that the PE studied in the present work is also a branched one it should be emphasized that there is very good agreement between the experimentally observed transition temperatures (between -20 and $-30°C$) [30] and that predicted by means of Eq. (1) (-23 and $-25°C$).

Serious support in favour of the T_g values for PE between -23 and $-25°C$ can be found in the recent review of Boyd [32] on the glass transition temperatures obtained from molecular dynamics simulations. Comparing the calculated from simulation T_g values with the experimentally reported ones Boyd pointed out that for PE there are two distinct observable amorphous-phase relaxation processes, called in the literature β and γ. It is consistent to consider the β process to be the glass transition region. However, since the γ process is better resolved and is more prominent, some workers have preferred to consider this process to be connected with T_g. The β and γ values (for the β it is around $-25°C$ and for γ in the vicinity of $-120°C$) and ranges here refer to measured values for these two processes: they come from a variety of low frequency dynamic mechanical and dielectric measurements. When allowance is made for an upward shift in the experimental value of T_g in the semicrystalline environment compared with an unconstrained amorphous phase, the agreement of the molecular dynamic value appears to be better with the β process interpretation [32].

In summary, taking into account the various values of T_g depending on the technique used [23] as well as the results from the molecular dynamic simulations [32] one can conclude that microhardness is also a technique which can be used for indirect evaluation of T_g of polymers not accessible in a completely amorphous state [33].

References

[1] Boyer RF. Transitions and relaxations Supplement. In: Bikales NM, editor. Encyclopedia of polymer science and engineering, 2. New York: Interscience, 1977. p. 811.

[2] Baltá Calleja FJ, Martinez-Salazar J, Čačkovic H, Loboda-Čačkovic J. J Mater Sci 1981;16:739.

[3] Baltá Calleja FJ, Kilian HG. Coll Polym Sci 1985;263:697.

[4] Baltá Calleja FJ, Kilian HG. Proceedings of the International Discussion Meeting Polymer Science and Technology, Rolduc, 1985.

[5] Ania F, Kilian HG, Baltá Calleja FJ. J Mater Sci Lett 1986;5:1183.

[6] Martinez-Salazar J, Baltá Calleja FJ. Mater Sci 1983;18:1077.

[7] Fakirov S, Baltá Calleja FJ, Krumova M. J Polym Sci Polym Phys Edn 1999;37:1413.

[8] Rueda DR, Baltá Calleja FJ, Hidalgo A. Spectrochim Acta 1974;30:1545.

[9] Martinez-Salazar J, Baltá Calleja FJ. J Cryst Growth 1980;48:283.

[10] González Ortega JC, Baltá Calleja FJ. Ann Fis 1974;70:92.

[11] Vonk CG. J Appl Cryst 1973;6:148.

[12] Baltá Calleja FJ, Rueda DR, Porter RS, Mead ZT. J Mater Sci 1980;15:765.

[13] Flory PJ, Vrij A. J Am Chem Soc 1964;85:3548.

[14] Baltá Calleja FJ. Adv Polym Sci 1985;66:117.

[15] Volmer M. Kinetik der Phasenbildung, Dresden: Theodor Steinkopff Verlag, 1939.

[16] Hoffman JD. Private communication.

[17] Hoffman JD, Weeks JJ. J Res Natl Bur Standards 1962;66A:13.

[18] Fakirov S, Avramova N. Acta Polymerica 1982;33:271.

[19] Fakirov S, Avramova N. J Polym Sci, Polym Lett Ed 1982;20:635.

[20] Avramova N, Fakirov S. Polym Commun 1983;24:19.

[21] Fakirov S, Avramova N, Tidick P, Zachmann HG. Polym Commun 1985;26:26.

[22] Baltá Calleja FJ. Trends Polym Sci 1994;2(12):419.

[23] Brandrup J, Immergut EH. Polymer handbook, New York: Wiley, 1989.

[24] Baltá Calleja FJ, Fakirov S, Roslaniec Z, Krumova M, Ezquerra TA, Rueda DR. J Macromol Sci, Part B: Phys 1998;B37(2):219.

[25] Baltá Calleja FJ, Vonk CG. In: Jenkins AD, editor. X-ray scattering of synthetic polymers, Amsterdam: Elsevier, 1989.

[26] Fakirov S, Apostolov A, Fakirov C. Int J Polym Mater 1992;18:51.

[27] Apostolov A, Fakirov S. J Macromol Sci, Part B: Phys 1992; B31(3):329.

[28] Hosemann R, Bagchi SN. Direct analysis of diffraction by matter, Amsterdam: North Holland, 1962 p. 239.

[29] Lide DR, editor. Handbook of chemistry and physics 76. Boca Raton, FL: CRC Press, 1995. p. 6–64.

[30] Pereña JM, Martin B, Pastor JM. J Mater Sci Lett 1989;8:349.

[31] Popli R, Glotion M, Mandelkern L, Benson RS. J Polym Sci Polym Phys Edn 1984;22:406.

[32] Boyd RH. Trends Polym Sci 1996;4:12.

[33] Fakirov S, Krasteva B. J Macromol Sci Part B: Phys 2000; in press.