Steps in the transition of an entangled polymer melt to the partially crystalline state

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New Journal of Physics 1 (1999) 17.1–17.29 (http://www.njp.org/)
Received 11 August 1999; online 10 November 1999

Abstract. For s-polypropylene, three different s-poly(propene-\textit{co}-octene)s, two poly(ethylene-\textit{co}-octene)s and poly(\textit{\epsilon}-caprolactone) we determined the relationships between the crystallization temperature $T_c$, the crystal thickness $d_c$ and the melting peak temperature $T_f$ by carrying out time- and temperature-dependent small-angle x-ray scattering experiments. As a general law, $d_c$ is found to be inversely proportional to the supercooling below a characteristic temperature, $T_c^\infty$, which is always located above the equilibrium melting point following from an application of the Gibbs–Thomson equation. $T_c^\infty$ is not (for the polypropylene-based copolymers) or only weakly (for the polyethylene-based copolymers) dependent on the co-unit content. The ‘crystallization line’ $T_c$ versus $d_c^{-1}$ and the Gibbs–Thomson melting line $T_f$ versus $d_c^{-1}$ limit the range of the accessible partially crystalline states. The occurrence of two well defined independent boundary lines may be understood as indicating that the transformation from the melt into the partially crystalline state is generally, for homopolymers and copolymerized derivatives likewise, a two-step process, beginning with the building up of an initial form of lower order at the crystallization line which then becomes stabilized to end up in the state with layer-like morphology melting at $T_f$. Stabilization is achieved without a change in $d_c$. AFM and TEM observations suggest that the initial structure could be composed of crystal blocks in planar assemblies. The stabilization then would result from their merging into a continuous lamella. It is proposed that the size of the blocks represents the minimum necessary to retain intrinsic stability. As a further result it was found that crystallinities reached at the end of isothermal crystallization processes remain invariant over larger ranges of $T_c$, in contrast to the changing length scales of the structure.

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1. Introduction

Over the last few years we have investigated the crystallization and melting behaviour of syndiotactic polypropylene (s-PP) and two related copolymers, employing time- and temperature-dependent small-angle x-ray scattering (SAXS) experiments [1]. The studies yielded accurate results for the relationships between the crystallization temperature \( T_c \), the crystal thickness \( d_c \), the crystallization time \( \tau \) and the location of the melting peak \( T_f \). In particular, we gained more knowledge about the effects introduced by the co-units. Syndiotactic polypropylene turned out to be especially suitable for this kind of investigation because:

- the crystal thickness remains constant during both the time of isothermal crystallization and the heating up to the melting point and therefore represents a well defined quantity;
- the change of the crystallization time with temperature is slow compared to most of the other polymers, which enables a large range of crystal thicknesses to be included in the analysis.

The total scenario arising from the studies includes some surprising new features. Not surprisingly, the melting peak locations \( T_f \) are found to change with crystal thickness as described by the Gibbs–Thomson law. An increase in the co-unit content leads to a parallel shift of the Gibbs–Thomson line to lower temperatures, and comparable shifts along the temperature axis are observed for curves of \( \tau \) versus \( T_c \). On the other hand, unexpectedly, we found no effect at all of the co-unit content on the crystal thickness. There exists a common temperature dependence for all samples and it is very simple: throughout the large range of \( T_c \)s covered by our experiments crystal thicknesses are inversely proportional to the supercooling below a
well defined characteristic temperature which agrees with or comes very near to the equilibrium melting point of perfect s-PP. The observations demonstrate that crystal thicknesses are not determined by the supercooling below the respective melting point of a copolymer, but depend on the absolute temperature chosen for the crystallization only. For all samples melting starts immediately above the crystallization temperature and then extends up to the melting peak. As already mentioned, we found that there is no change in the thickness of the crystallites throughout the full melting range. Hence, the stability of crystallites is obviously not a function of the crystal thickness only, but is also affected by additional controlling factors. We take the observations on s-PP as a clear indication that the building up of the crystallites is a two-step process. At the beginning there emerges an initial form, which is just stable at \( T_c \). This form then becomes stabilized, at \( T_c \) and during heating, and finally turns into the layer-like crystallites which melt at \( T_f \).

Considering the structural character of the initial state, we found evidence that it may be envisaged as an assembly of crystal blocks. The block dimensions with an edge length along the chain direction equal to the thickness of the final lamellae and values of the same order of magnitude in the lateral directions set them just at the limit of their stability. The lamellae then arise from a merging of the blocks and this provides the observed stabilization at constant \( d_c \). Support for this view came from atomic force microscope (AFM) observations [2]. These show a granular substructure of the lamellae directly after their formation which then disappears on heating.

One has to ask whether the behaviour is specific to s-PP. We therefore carried out an analogous series of experiments on other systems, starting with two poly(ethylene-co-octene)s and poly(\( \epsilon \)-caprolactone). In addition, we further extended the investigations on s-PP to even higher co-units contents. As shown in this communication, the properties of the s-PPs are systematically continued and, more important, the main features of the s-PP scenario are found again for the two other systems.

So far the focus of the studies was on the crystal thickness only. Of the same importance is a knowledge of the degree of crystallinity and its dependence on the crystallization temperature and the co-unit content. We accordingly complemented our studies on s-PP and also determined crystallinity values for the polyethylenes and poly(\( \epsilon \)-caprolactone). As shown in the following, the result is surprisingly simple: while the thickness of the crystallites changes on varying the crystallization temperature, their global volume fraction remains constant, thus constituting an invariant property.

### 2. Experimental

#### 2.1. Samples

The investigations were carried out for three different polymer systems:

- a syndiotactic polypropylene and three derived syndiotactic poly(propene-co-octene)s, synthesized by S Jüngling in the Institute of Macromolecular Chemistry of our university, using a metalloocene catalyst [3]; samples possess a high stereoregularity, including only 3% of meso diads;
- two poly(ethene-co-octene)s of the metalloocene catalyst type, supplied by Dow Chemicals Europe;
- a sample of poly(\( \epsilon \)-caprolactone) purchased from Aldrich Chemical Co.
Table 1. Properties of samples.

| Sample                        | Octene units (%) | Octene units (mol) | \(M_n\) | \(M_w/M_n\) |
|-------------------------------|------------------|--------------------|--------|-------------|
| \(s\)-polypropylene and \(s\)-poly(propene-co-octene) |                  |                    |        |             |
| \(s\)-PP                      | 0                | 0                  | 104.000| 1.7         |
| \(s\)-P(\(co\)-0)4           | 4                | 1.7                | 73.000 | 2.1         |
| \(s\)-P(\(co\)-0)15          | 15               | 6.4                | 94.000 | 1.7         |
| \(s\)-P(\(co\)-0)20          | 20               | 8.5                | 62.000 | 1.6         |
| \(poly\)(ethylene-co-octene)  |                  |                    |        |             |
| \(P(E-co)-0)7                 | 7.5              | 2                  | 36.400 | 2.4         |
| \(P(E-co)-0)14                | 14               | 4                  | 30.200 | 3.0         |
| \(poly(\varepsilon\)-caprolactone) |                |                    |        |             |
| \(PCL\)                      |                  |                    | 42.500 | 1.5         |

Properties of the samples are collected in Table 1.

2.2. Instrumentation

The SAXS experiments were carried out with the aid of a Kratky camera attached to a conventional Cu-K\(_\alpha\) x-ray source, employing a temperature-controlled sample holder. Using a position-sensitive metal wire detector, scattering curves were usually registered within a few minutes counting time. The slit-smeared data obtained were deconvoluted by application of an algorithm developed in our group [4]. Before starting an isothermal crystallization, samples were kept in the melt at a sufficiently high temperature for up to 30 min and then cooled in the sample holder as quickly as possible (within several minutes) to the crystallization temperature. By observation of the intensity it was ensured that crystallization did not start before reaching isothermal conditions.

Complementing the SAXS measurements we followed the kinetics of crystallization and determined the final crystallinities with the aid of a differential scanning calorimeter (Perkin–Elmer Model DSC4) and with a mercury-filled dilatometer. Weight fraction crystallinities \(\phi_w\) were derived from the heat released during the crystallization and the change in the specific volume by calculating the ratio to the ideal values, \(\Delta H_{id}\) and \(\Delta v_{id}\). These were chosen as follows:

- syndiotactic polypropylene: \(\Delta H_{id} = 183\ \text{J g}^{-1}\)
- polyethylene: \(\Delta H_{id} = 293\ \text{J g}^{-1}\), \(\Delta v_{id} = 0.17\ \text{cm}^3\ \text{g}^{-1}\)
- poly(\(\varepsilon\)-caprolactone): \(\Delta H_{id} = 157\ \text{J g}^{-1}\).

The temperature dependences of \(\Delta H_{id}\) and \(\Delta v_{id}\) were at first neglected. The minor errors thus introduced do not affect the main conclusions.

For a direct view on structures we made use of an atomic force microscope (‘Nanoscope III’). We applied the tapping technique, thus probing in particular the viscoelastic properties of the surfaces and edges of the crystallites. We used height, amplitude and phase modes; they yielded consistent results with the best contrast being obtained in the phase mode. Experiments

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were carried out for s-PP, preparing samples with planar surfaces in two ways. First, films 
sandwiched between two glass slides were isothermally crystallized, and then rapidly cooled 
and placed for some days in ice-water. This finally led to a detachment of one of the glasses. 
Alternatively, we also prepared thin films from a spin-coated solution. These were melted after 
extracting the solvent, and then again isothermally crystallized and quenched.

We also had a look at the morphology of s-PP and s-P(P-co-0)20 using a Zeiss LEO 912 
Omega transmission electron microscope (TEM) at 120 kV accelerating voltage. Thin films 
were prepared from a solution which wetted a carbon-coated grid. After evaporating the solvent, 
films with a thickness in the order of 50 nm were obtained. These were isothermally crystallized 
and then stained with ruthenium tetroxide vapour for about half an hour.

2.3. SAXS data analysis

Having determined the primary beam intensity with the aid of a moving slit system, desmeared 
scattering curves were obtained in absolute values, as differential cross sections per unit volume, 
$\Sigma(q)$. With a knowledge of $\Sigma(q)$ the one-dimensional electron density autocorrelation function 
$K(z)$ and its second derivative $K''(z)$, which gives the interface distance distribution function 
[5,6], can be calculated directly by applying the Fourier relations

$$K(z) = \frac{1}{r_e^2} \frac{1}{(2\pi)^3} \int_0^\infty \cos qz \ 4\pi q^2 \Sigma(q) \ dq$$  \hspace{1cm} (1)

and

$$K''(z) = \frac{2}{r_e^2 (2\pi)^2} \int_0^\infty \left[ \lim_{q \to \infty} q^4 \Sigma(q) - q^4 \Sigma(q) \right] \cos qz \ dq.$$  \hspace{1cm} (2)

Here, $q$ denotes the scattering vector $q = 4\pi \sin \theta_B / \lambda$ (where $\theta_B$ is the Bragg scattering angle); $r_e$ is the classical electron radius. In all the measurements the crystal thickness $d_c$ was derived 
from the location of the respective peak in $K''(z)$. Usually this agrees with the values deduced 
in the normal way from $K(z)$, but there were also cases with slight deviations. Just to remain 
consistent, we always used the value following from $K''(z)$.

A useful parameter in kinetical measurements and also the analysis of the continuous melting 
on heating is the Porod coefficient. It generally describes for two-phase systems the asymptotic 
behaviour of the scattering curve as

$$\lim_{q \to \infty} \Sigma(q) = r_e^2 \frac{P}{(q/2\pi)^4}.$$

The Porod coefficient is directly related to the interface area per unit volume, $O_{ac}$, by

$$P = \frac{1}{8\pi^3} O_{ac} (\rho_{e,c} - \rho_{e,a})^2$$  \hspace{1cm} (4)

where $\rho_{e,c}$ and $\rho_{e,a}$ denote the electron densities of the crystals and the fluid phase, respectively. 
This relation is generally valid, for homogeneous as well as heterogeneous structures and therefore, 
for example, also if spherulites fill a sample only partially.

SAXS experiments also enable the crystallinity to be determined. One generally obtains 
the ‘linear crystallinity’, as

$$\phi_l = \frac{B}{Q + B}.$$  \hspace{1cm} (5)
Here, $-B$ denotes the ordinate of the ‘base line’ of $K(z)$ ([7], p 411) and $Q$ is the integral scattering power equal to $K(z = 0)$. $\phi_l$ describes the volume fraction occupied by the crystalline lamellae within one stack. For an estimate $\phi_l$ can also be calculated as

$$\phi_l \approx \frac{d_c}{L}$$

with $L$ as the long spacing. This is an approximation because $L$ represents the most probable rather than the average distance between adjacent crystallites.

When the sample is densely filled with stacks of laterally extended lamellae then $\phi_l$ equals the global volume fraction crystallinity $\phi_v$. Deviations can arise mainly for two reasons, both leading to $\phi_v < \phi_l$. First, one may encounter a heterogeneous situation, for example, when spherulites fill a sample only partially. Second, the lamellae, although existing as laterally extended objects, may include a certain portion of non-crystalline material at the borders and inbetween crystalline blocks. If the thickness of the separating regions is below $\approx 2$ nm there is no scattering effect in the small-angle range. The result is just a decrease in the contrast between the layer-like objects with reduced crystallinity and the intervening fully amorphous regions.

3. Results

For all three systems under study we carried out the same series of measurements.

- We followed the structure changes during an isothermal crystallization and a subsequent heating by time- and temperature-dependent SAXS experiments, thereby obtaining the relationship between the crystallization temperature, the crystal thickness and the melting peak temperature.
- We measured the DSC melting curve subsequent to the isothermal crystallization.
- After completion of the crystallization process at $T_c$, we determined the crystallinity. Values of the linear crystallinity $\phi_l$ were derived from the one-dimensional correlation function $K''(z)$, values for the weight fraction crystallinity $\phi_w$ were deduced from the heat of crystallization or the volume change resulting from the crystallization process.

3.1. s-Polypropylene and s-poly(propene-co-octene)s

Figure 1 shows as an example the result of a time- and temperature-dependent SAXS experiment conducted for s-P(P-co-0)4 for $T_c = 125.5$ °C. The lower part depicts the structure evolution during the isothermal crystallization as reflected in $K''(z)$. The prominent peak with increasing intensity refers to the crystallites. Its location indicates a (most probable) crystal thickness of $d_c = 6.5$ nm. The contributions of the amorphous layers and the intercrystalline distances, i.e. the long spacing, are broadened and much weaker. They give a maximum around 16 nm and a minimum around 23 nm, respectively. Obviously, the crystals do not thicken. Apart from a short initial period the crystal thickness remains absolutely constant.

The upper part depicts the structure changes during the subsequent heating, showing on the right-hand the Porod coefficient and on the left-hand side the changes in $K''(z)$. One observes from the very beginning a decrease in $P$, rather than an increase as expected for constant crystallinity due to the increasing electron density difference. Hence, melting of the sample starts immediately above $T_c$. In correspondence with the DSC measurements, where the melting peak location is normally taken as the ‘melting point’, we chose the

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Figure 1. s-(P-co-O)4: changes of the interface distance distribution function $K^{''}(z)$ during an isothermal crystallization at 125.5 °C (bottom) and a subsequent heating up to the melt (top left-hand side). Curves are vertically shifted by amounts which increase linearly with time or temperature. Change of the Porod coefficient during the heating (top right-hand side).

Temperature with the largest change in the Porod coefficient, i.e. the maximum slope $dP/dT$, as the melting point $T_f$. It is indicated in the figure. The curves $K^{''}(z)$ on the left-hand side demonstrate that the continuous melting extending from $T_c$ up to $T_f$ is not accompanied by any change in $d_c$. We carried out checks comparing the relative changes in the amplitude of the maximum of $K^{''}$, the Porod coefficient $P$ and the crystallinity as derived from the DSC-melting curve. We always found good agreement, provided that the heating rates of the DSC and of the SAXS experiments were similar. These are clear-cut results and they imply, as has already been stressed in the previous papers,
Figure 2. s-PP and s-P(P-co-O)x: crystallization line $T_c$ versus $d_c^{-1}$ (open symbols) and Gibbs–Thomson melting lines $T_f$ versus $d_c^{-1}$ (full symbols) as derived from time- and temperature-dependent SAXS experiments. The dotted line represents the extrapolated melting line of perfect s-PP.

that there are more controlling factors for the stability of the crystallites than just the thickness.

From these experiments we derived the relationships between $T_c$, $d_c$ and $T_f$. The results obtained for all s-PP-based samples are collected in figure 2. It includes in addition to previously reported data the results obtained for the copolymer with 20% per weight of octene units, s-P(P-co-O)20. The data for this new sample fit perfectly into the already established scheme.

The Gibbs–Thomson equation suggests plotting $T_f$ versus $d_c^{-1}$. This results in the series of parallel lines in the figure, with shifts to lower temperatures with increasing content of octene units. In the previous paper [1] we used these lines to determine by an extrapolation the Gibbs–Thomson melting line of perfect s-PP, thereby accounting for the presence of 3% meso diads in all the samples. The dotted line gives the outcome of this expolation and indicates an equilibrium melting temperature of perfect s-PP of $T_f^\infty(0) = 196^\circ$C.

The single line with the higher slope refers to the crystallization process and gives the relation between the crystallization temperature and the crystal thickness, again represented in the form of a temperature, here $T_c$, versus the inverse crystal thickness $d_c^{-1}$. As we see, this line is straight and surprisingly, there is no effect at all of the co-units. The thicknesses found for all four samples, s-PP and the copolymers, which greatly differ in the contents of octene units, are all located on one common curve. Furthermore, the straight form indicates a simple law: the crystal thickness is inversely proportional to the distance from a characteristic temperature, and, as is noticed, the latter coincides or comes very near to the equilibrium melting point of perfect s-PP, $T_f^\infty(0)$.

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Figure 3 shows a selection of typical DSC thermograms for all samples. They were always measured immediately after an isothermal crystallization without an intermediate cooling, in correspondence to the SAXS experiments. Curves start at the respective $T_c$ with a rise in the heat flow to the level given by the heat capacity. Melting begins a couple of degrees above $T_c$, and then increases in rate and reaches a maximum at $T_i$. One observes a clear tendency when varying the content of octene units. An increase leads generally to a more continuous appearance, with a broadening of the melting peak, and for the higher co-unit contents to a more distinct onset of melting, finally leading to the evolution of a second peak near to $T_c$. In the last case of s-P(P-co-O)20 the thermogram may be addressed as showing the melting of two groups of crystallites with different stability. This difference, however, is not based on a difference in $d_c$, as is demonstrated by the SAXS experiments.

Figure 4 shows, as a last result for this system, the crystallinities reached at $T_c$ after completion of the isothermal crystallization processes. Both the linear crystallinities deduced from the SAXS data and the global crystallinities derived from DSC are given. The overall result is very simple: for each sample the crystallinity is invariant over the range of accessed $T_c$'s. This seems to be true for both the linear crystallinity $\phi_l$ and the weight fraction crystallinity $\phi_w$, with the exception of the highest $T_c$'s chosen for the two copolymers with the highest co-unit contents. Comparison of $\phi_l$ and $\phi_w$ shows a clear tendency: there seems to be a perfect agreement for s-PP, but then, rather than finding $\phi_w > \phi_l$ as expected for a sample completely
Figure 4. Crystallinities of s-PP and s-P(P-co-O)x after isothermal crystallizations at different $T_c$s: weight fraction crystallinity $\phi_w$ derived from the DSC signal (open symbols) and linear crystallinity $\phi_l$ deduced from $K(z)$ (full symbols). The $T_c$ dependence of $d_c$ is shown for comparison (right-hand axis).

filled with stacks of laterally extended crystallites, one always observes $\phi_w < \phi_l$. The ratio $\phi_w/\phi_l$ decreases with increasing content of co-units. Figure 4 also includes the temperature dependence of the crystal thickness, just to show the difference in behaviour. While the crystallinity remains constant for each sample one always finds distinct changes in the crystal thickness. The result implies that crystal thickness and long spacing vary proportionally to each other. A change of the crystallization temperature modifies the length scales of the partially crystalline structure, but has no effect on the global fractions of the crystallized and non-crystallized chain parts.

3.2. Poly(ethylene-co-octene)

Figure 5 shows the structure evolution and melting observed for P(E-co-0)7 during and subsequent to an isothermal crystallization at 103 °C. Data indicate a growth of crystals with a thickness of 6 nm which takes place without any detectable thickening. The peak position also remains also unchanged during the melting, with the exception of the highest temperatures around $T_f$. Figure 6 shows the results obtained by this kind of experiments, presented again in plots of $T_c$ and $T_f$ versus $d_c^{-1}$. Measured points are assembled on straight lines. We find two Gibbs–Thomson ‘melting lines’ and, different from the s-PP-based systems, also two ‘crystallization lines’ $T_c$ versus $d_c^{-1}$. The shift between the crystallization lines, however, is much smaller than

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Figure 5. P(E-co-O)7: changes of $K''(z)$ during an isothermal crystallization at 103°C and a subsequent heating up to the melt.

that of the melting lines. Therefore, the crystal thicknesses are, also in this case, not a function of the supercooling below the respective melting points. The thin lines in the drawing which connect $T_c$ on the crystallization line with $T_f$ on the melting line depict the location of the $K''$ maximum as found during the heating. For the higher crystallization temperatures these lines are vertical, indicative for a constant $d_c$. For the lower temperatures they are curved near the end, thus indicating a slight displacement of the peak position when approaching the melting line.

As the co-unit content of P(E-co-0)14 is just twice that of P(E-co-0)7, we obtain the Gibbs–Thomson line of perfect polyethylene by repeating the shift. As shown in the figure by a dotted line, it ends at 145°C for $d_c^{-1} \to 0$, which is indeed the equilibrium melting point of polyethylene.
Figure 6. P(E-co-O)x: crystallization lines \( T_c \) versus \( d_c^{-1} \) (open symbols) and melting lines \( T_f \) versus \( d_c^{-1} \) (full symbols) as derived from time- and temperature-dependent SAXS experiments. The dotted line is the extrapolated melting line of linear polyethylene.

On the other hand, a linear extrapolation of the crystallization lines points to limiting temperatures which are definitely located above the equilibrium melting point of polyethylene. The data of the s-PP-based systems gave us the impression that the characteristic temperature determining the crystal thickness would agree with the equilibrium melting point of perfect s-PP. Obviously this is not generally valid. The results obtained for the PE-based samples show a clear difference.

Figure 7 presents some typical DSC thermograms as measured for the two samples after isothermal crystallizations at different temperatures. Regarding the overall appearance of the thermograms, one finds for both samples two different ranges. Melting always immediately sets in upon heating, leading to a peak located 5–7 °C above \( T_c \). In a first range, ending at \( T_c = 90 \) °C for P(E-co-0)14 and \( T_c = 101 \) °C for P(E-co-0)7, this peak is followed by a second one at an essentially constant location; independent of the chosen \( T_c \) all melting processes are finished at 102 and 113 °C, respectively. In the second range, for higher crystallization temperatures, no second peak appears and the location of the unique peak increases with \( T_c \). Note the corresponding observations in the SAXS experiments as presented in figure 6. One finds in the lower temperature ranges curved connecting lines which all tend to end on the melting line at the same final point. For \( T_c \)'s in the upper ranges the behaviour changes. Here the connecting lines are mostly vertical and the end points \((T_f, d_c^{-1})\) vary correspondingly.

Figure 8 depicts registrations by dilatometry of the crystallization kinetics of the two samples. For the given long crystallization times this was preferable to DSC measurements. The kinetical data show that the change with temperature of the growth rate in the PE-based systems is much more rapid than for the s-PP-based systems. One observes a change of one
Figure 7. P(E-co-O)7 (top) and P(E-co-O)14 (bottom): DSC thermograms measured subsequent to isothermal crystallizations at various $T_c$'s (heating rate 10 K min$^{-1}$).

order of magnitude within 3°C, compared to 15°C in the s-PP case (cf figure 4 in [1]). For this reason experiments on PE can generally cover only a smaller temperature and thickness range.

Figure 9 shows the crystallinities measured after the various isothermal crystallization processes. We observed no effect of the long-time perfectioning processes on $\phi_1$. In the case of the weight fraction crystallinity derived from dilatometry we took the value reached after completion

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Figure 8. P(E-co-O)x: kinetics of isothermal crystallization at the indicated $T_c$ followed by dilatometry.
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Figure 9. Crystallinities of P(E-co-O)x after isothermal crystallizations at different Tcs: weight fraction crystallinity $\phi_w$ derived from the dilatometric curves (open symbols) and linear crystallinity $\phi_l$ deduced from $K(z)$ (full symbols). $T_c$ dependence of $d_c$ (right-hand axis).

of the main part of the crystallization process. Although the values of $\phi_l$ show some scatter there is clearly no tendency for a change with $T_c$, at least when comparing it with the distinct changes in $d_c$. For the sample with the lower octene content the weight fraction crystallinity derived from dilatometry corresponds to the linear crystallinity, for the sample with the higher co-unit content we again find $\phi_w < \phi_l$, as for s-P(P-co-0)20 at the highest crystallization temperatures. The tendency of the ratio $\phi_w/\phi_l$ to decrease with $T_c$ is again similar to s-P(P-co-0)20.

3.3. Poly($\varepsilon$-caprolactone)

Figure 10 presents the structure evolution during isothermal crystallization of the investigated poly($\varepsilon$-caprolactone) during an isothermal crystallization at 40°C and the subsequent heating up to 60°C in the molten state. The dominant peak is again due to the crystallites which have a thickness of 6.8 nm at this temperature, with a distance $L = 15$ nm between neighbours. There is no crystal thickening during the crystallization and only a slight shift of the maximum at the end of the heating process. Experiments therefore provided us again with well defined results concerning the dependences between $T_c$, $d_c$ and $T_l$. These relations are shown in figure 11. Data determine the Gibbs–Thomson melting line and again a straight crystallization line relating $d_c^{-1}$ and $T_c$. One observes a large difference between the limiting temperatures of the two lines. The point of intersection between the two lines, located at 70°C is that which is usually
Figure 10. PCL: changes of $K''(z)$ during an isothermal crystallization at 40 °C and a subsequent heating up to the melt.

quoted as the equilibrium melting point of PCL, as it arises as the limiting temperature from the Hoffman–Weeks plot.

For crystallization temperatures below 40 °C one observes during heating more pronounced peak shifts, as is indicated by the curved connecting lines. For these lower crystallization temperatures the final melting refers to crystallites which all have the same thickness, $d_c = 7$ nm. For the higher temperatures, above 40 °C, $T_f$ increases with $T_c$, together with the thickness. The DSC melting curves again show a corresponding behaviour, as is demonstrated in figure 12.
Figure 11. PCL: crystallization line $T_c$ versus $d_1^{-1}$ (open symbols) and melting line $T_f$ versus $d_1^{-1}$ (full symbols) as derived from time- and temperature-dependent SAXS experiments.

Figure 12. PCL: DSC thermograms measured subsequent to isothermal crystallizations (heating rate 10 K min$^{-1}$).
Figure 13. PCL: kinetics of isothermal crystallization at the indicated $T_c$s followed by the time dependence of the Porod coefficient.

Figure 14. PCL: times of crystallization at different $T_c$s taken from figure 13 (full squares) and determined by DSC (circles).

Variation of the crystallization temperature below 40°C does not lead to any changes in the melting peak position, whereas for higher temperatures an upward shift of $T_f$ with increasing $T_c$ is observed.

Figures 13 and 14 give some selected kinetical curves $P(t)$ measured for PCL and the derived dependence $\tau(T_c)$, respectively. In this case one has a change by one order of
Figure 15. Crystallinities of PCL after isothermal crystallizations at different $T_c$s: weight fraction crystallinity $\phi_w$ derived from the DSC signal (open symbols) and linear crystallinity $\phi_l$ deduced from $K(z)$ (full symbols). $T_c$ dependence of $d_c$ (right-hand axis).

magntitude within 5 °C, intermediate between the polyethylene- and the polypropylene-based systems.

Finally, figure 15 shows the crystallinities achieved after the various isothermal crystallization processes, again in a comparison with the temperature dependence of the crystal thickness. We again find the linear crystallinity $\phi_l$ to be strictly constant. Values of $\phi_w$ were obtained by DSC and therefore only over a limited temperature range. Over this range we have a good agreement with $\phi_l$, as is indicative of a sample densely filled with stacks of laterally extended lamellae.

4. Discussion

4.1. The range of accessible partially crystalline states

The results obtained for the two ethylene–octene copolymers and poly(ε-caprolactone) demonstrate that the main conclusions derived from the previous studies on the s-PP-based materials are not peculiar but generally valid. In all the cases studied, the transformation of the melt into the partially crystalline state looks like a two-step process, beginning with the formation of a well defined initial structure with lower order, which is subsequently stabilized to end up in the final state with a layer-like morphology. The signature of the initial state is the
Figure 16. Schematic of $d_c^{-1}/T$-diagram of partially crystalline states.

Figure 17. Effect of solid state thickening in HDPE: crystal thicknesses after isothermal crystallizations obtained by SAXS (line at 121 °C [9]) and derived from TEM micrographs (chain curves, from [8]), entered into figure 6.

‘crystallization line’ $d_c^{-1}$ versus $T_c$, that of the final state the Gibbs–Thomson melting line $d_c^{-1}$ versus $T_f$. Stabilization is basically achieved without any detectable change in $d_c$. How far it goes varies within a sample. For a larger part the stabilization is complete, which is indicated by a melting at $T_f$, in other regions it remains incomplete as is indicated by an earlier melting. The respective weights change with the co-unit content. The higher the fraction of co-units,
the more the stabilization is hindered, and the higher is the part which remains in the initial stage. The crystallization line and the melting line together determine the range of accessible partially crystalline states. The \( \frac{d^{-1}}{T} \)-phase diagram provides an appropriate description and figure 16 presents the general situation in a schematic drawing. All the accessible states are contained in the shaded range bounded by the two lines. Its extension is determined by the slopes of the two lines and their limiting temperatures \( T^\infty_f \) and \( T^\infty_c \). This statement is not a trivial one. In principle, all states below the Gibbs–Thomson melting lines are thermodynamically stable, but obviously, due to the peculiar mechanism of the transition from the melt into the partially crystalline state, not accessible throughout.

The statement holds true for all the samples investigated, but there is no rule without exception: high-density polyethylene, and thus exactly that system which was most intensively studied in the past, behaves differently. Data can be taken, for example, from structure determinations carried out using an electron microscope by Voigl-Martin and Mandelkern [8], and also from a previous SAXS analysis carried out in our group [9]. Figure 17 shows these data entered in the previous diagram (figure 6). As we see, they fall outside the range of the partially crystalline states found for the ethylene–octene copolymers. The origin of this different behaviour is obvious: it is the thickening in the solid state which accompanies isothermal crystallization processes in linear polyethylene. As reflected in the presence of the \( \alpha \)-process, polyethylene crystals retain a high internal mobility; chains can carry out a sliding diffusion in a longitudinal direction. Consequently, the stabilization processes subsequent to the formation of the initial structure also include for linear polyethylene a thickening and the range below the crystallization line becomes accessible.

In fact, longitudinal diffusive motions within polymer crystallites are the exception rather than the rule and the same holds for the crystal thickening. In addition, the thickening is always suppressed if co-units are included in the chains. This also holds for the PE-based samples of this investigation. As the co-units cannot be transported through the crystallites their presence suppresses a long-range longitudinal diffusion and therefore the crystal thickening.

Of obvious importance for the crystallization behaviour is the characteristic temperature \( T_{cf} \), located at the point of intersection of the crystallization and the melting line. Our experiments concern only temperatures below this characteristic point, for practical reasons: even before reaching \( T_{cf} \) crystallization times were already so long that experiments could not be continued. In principle, crystallization processes should go on also for temperatures above \( T_{cf} \), up to the equilibrium melting point \( T^\infty_l \), but one has to expect a change in the mechanism. There might exist systems which allow the situation to be checked, but so far we have not yet found an appropriate one.

Note that it is \( T_{cf} \) which is usually obtained by the popular Hoffmann–Weeks plots, rather than the equilibrium melting point as is erroneously assumed by many authors. Errors resulting from this incorrect assignment can be drastic. For example, for our PCL sample the equilibrium melting point, as derived from the melting line when extrapolated to \( d^{-1} = 0 \), is located around 100 °C rather than around 70 °C, as would follow from the literature.

4.2. Structure of initial form. Indications from TEM and AFM

While the understanding of the melting line is clear, as representing the melting of lamellar crystallites from their lateral surfaces as described by the Gibbs–Thomson equation, the existence
of the crystallization line with its intriguing properties brings up new questions. To begin with, one has to ask about the structural characteristics of the initial state and about the stabilization processes which transfer it into the final lamellar crystallites. Our tentative answers, already given in the two previous papers, are: the initial state can be envisaged as an assembly of blocks, all of equal size and in a roughly planar arrangement. The stabilization then follows from a merging of the blocks into lamellae.

There are several pieces of evidence leading us to this view. Our studies on the s-PP-based copolymers indicate that stabilization becomes more and more hindered when increasing the number of octene units. For s-P(P-co-0)15 and s-P(P-co-0)20 a large part remains in the initial phase. Therefore, comparing TEM pictures of the morphology taken for s-PP and the latter samples should inform us about the structural character of the initial phase. Figure 18 presents two electron micrographs obtained for thin films of s-PP and s-P(P-co-0)15. After isothermal crystallizations, conducted at 125 and 75 °C, respectively, they were quenched to room temperature and stained with ruthenium tetroxide vapour. For s-PP we observe, as expected, continuous lamellae. On the other hand, the morphology of s-P(P-co-0)15 resembles arrays of blocks, ordered in the picture along lines, which means on planes in the bulk.

The structure agrees with the observed crystallinities $\phi_w$ and $\phi_l$ given in figure 4. We find for s-P(P-co-0)20 a large difference between the two values, with $\phi_w < \phi_l$, as it should indeed be the case if the layer-like objects producing the scattering are blocks being arranged on planes. When including a dilatometric measurement it becomes possible to carry out a rigorous check and a quantitative analysis. After completion of an isothermal crystallization at 58 °C we obtained the following data:

- density increase from dilatometry: $\rho - \rho_a = 0.012$ g cm$^{-3}$
- electron density increase from SAXS: $\sqrt{B} = \rho_e - \rho_{e,a} = 4.4$ nm$^{-3}$
- linear crystallinity from SAXS: $\phi_l = B/(B + Q) = 0.15$
- heat of fusion: $\Delta H = 16$ J g$^{-1}$.

Figure 18. TEM micrographs of s-PP (left) and s-P(P-co-O)15 (right). Samples were isothermally crystallized at 125 and 75 °C, respectively, and then cooled to room temperature.
\( \rho - \rho_a \) and \( \rho_e - \rho_{e,a} \) correspond to each other, since we have generally

\[
\rho_e - \rho_{e,a} = \frac{8N_A}{14 \text{ g mol}^{-1}}(\rho - \rho_a) \quad (N_A \text{ is the Avogadro number})
\]

giving \( \rho_e - \rho_{e,a} = 4.1 \text{ nm}^{-3} \), which means agreement with the SAXS result within the error limits of the measurements. The agreement can be taken as proof that the blocks indeed assemble to set up essentially planar objects, as this is the basis for the data analysis via the one-dimensional correlation function \( K(z) \).

The blocks do not fill the layers densely. This clearly follows from calculating the difference between the mean electron density of the layers, \( \rho_{e,c} \), and the amorphous regions, using

\[
\rho_{e,c} - \rho_{e,a} = \frac{\rho_e - \rho_{e,a}}{\phi_l} = 29.3 \text{ nm}^{-3}.
\]

This is definitely below the value of the electron density difference between crystalline and amorphous regions \([6]\)

\[
\rho_{e,c} - \rho_{e,a} = (29.9 + 0.105T[^\circ\text{C}]) \text{ nm}^{-3} = 36 \text{ nm}^{-3}.
\]

Therefore, the blocks fill the lamellae only to a degree \( \phi_{\text{intra}} = 29.3/36 = 0.81 \), and the global volume fraction crystallinity is \( \phi_v = \phi_l \phi_{\text{intra}} = 0.12 \).

Finally, \( \phi_v \) can be compared to the DSC result. When accounting for the temperature dependence of \( \Delta H_{\text{id}} \) (using \( \Delta H_{\text{id}} = [183 - 0.5(130^\circ\text{C} - T)] \text{ J g}^{-1} \)) and changing from \( \phi_w \) to \( \phi_v \) one obtains \( \phi_v = 0.09 \). This somewhat smaller value could indicate a reduction in the heat of melting due to surface effects and/or internal disorder.

Finding beaded strings as a characteristic feature in TEM micrographs of partially crystalline polymers is, of course, not at all new. They have been frequently observed and reported on, maybe for the first time in an early work by Okui and Kawai \([10]\), and more recently in particular in studies by Minick \textit{et al} on copolymers of polyethylene \([11]\). The new insight arises from the combination of the TEM micrographs and the SAXS results. The bare existence of the crystallization line which includes both commonly, the nearly perfect s-PP and all the copolymers, clearly indicates that the related initial-block-dominated structure is always formed in the first step, for homo- and copolymers likewise, independent of the final structure reached, it may be layer-like, granular or a mixture of both.

More support comes from quite recent AFM studies. Even if lamellae appear continuous in the TEM, they can exhibit, in the AFM, an internal granular structure. Using the tapping technique, which probes the viscoelastic properties of surfaces, it can be clearly resolved. Magonov in studies on polyethylene and poly(vinylidene fluoride) \([12]\] and ourselves when investigating s-PP \([2]\], observed regular variations of the viscoelastic properties along the edges and also at the surfaces of the crystalline lamellae. Figure 19 (left) presents another typical AFM image of s-PP. Edges and surfaces of the lamellae here show a well developed granular substructure, which is in striking contrast to the TEM micrograph presented above. Interestingly, the appearance changes on annealing, as is demonstrated by the image on the right: after the annealing, the substructure has mostly disappeared. We understand the granular substructure as a memory to the building process, the lamellae being created from blocks which form in the first step, and their disappearance as a demonstration of stabilization being accomplished by a merging of the blocks. It appears that the merging processes remains incomplete at the first crystallization temperature and that the full perfectioning is
Figure 19. s-PP, isothermally crystallized at 135 °C (left) and subsequently annealed at 150 °C (right). Tapping mode AFM phase image (frequency, 323 kHz; free and setpoint amplitude, 30 and 18 nm).

only reached later, during the heating up to \( T_f \). For the copolymers, the perfectioning process is hindered. Correspondingly, we observed in an analogous AFM experiment on s-P(P-co-O)15 that annealing just removed many of the beaded strings, leaving only those parts which were able to perfect.

More examples pointing at a block-like substructure of lamellae are found in the literature. Direct evidence is found in a TEM study of Kanig [13] who succeeded in fixing the initial state in the case of HDPE by applying the staining procedure at elevated temperatures. The observed morphology differs qualitatively from the final stacks of lamellae. Layer-like objects with an internal granular structure are seen, which have a low resistance against shear deformations. Kanig calls them ‘smectic’, but ‘hexatic’ would probably be a better name, not in the strict sense, as this would require hexagonal symmetry, but for addressing the main structural characteristics of this phase, which possesses long-range order with regard to the orientation of the unit cells and no positional long-range order. This would exactly be the case for an array of equally oriented blocks. Bassett and Patel [14] observed in an electron microscopic study of the morphology of isothermally crystallized poly(4-methylpentene-1) on heating localized sites of melting within the later grown ‘subsidiary’ crystallites. It very much looks as if individual crystalline blocks would become unstable and melt already shortly above \( T_c \). Another example is included in the work of Petermann and Gohil [15]. They investigated thin films of polyethylene and isotactic polystyrene by electron diffraction and dark-field imaging. The electron diffraction patterns were indicative of a uniform orientational order within the crystalline lamellae. However, the dark-field patterns, when obtained for \( hkl \)-reflections with \( l \neq 0 \), demonstrate that the lamellae are indeed built up by blocks, which were equally oriented, but shifted relative to each other along the chain direction.
Figure 20. s-PP, isothermally crystallized at 122°C. SAXS analysis of the melting-recrystallization process at 150°C indicating a jump-like change of $d_c$.

Finally, as is well known from numerous studies, analysis of the width of the WAXS Bragg reflections observed for semicrystalline polymers always yields coherence lengths in the lateral direction of the crystallites in the order of several nanometres, which is much smaller than those found for low molar mass crystals. Just to cite one recent example, Akpalu et al [16] find in an x-ray investigation of poly(ethylene-co-octene)s a coherence length in the order of 5 nm (corresponding to a halfwidth $\delta q = 0.2 \text{ nm}^{-1}$) which, and this is also typical, increases to about twice this value during the isothermal crystallization process. The coherence length may be identified with the lateral extension of the blocks and the increase may reflect their merging. Hence, in view of all these results, it looks to us conceivable to visualize the structure of the initial phase as being built up of blocks with a certain planar order.

4.3. Selection of crystal thicknesses

Our view implies that the thickness of the final lamellar crystals is already fixed by the size in the chain direction of the blocks. Asking for the selection rule effective for $d_c$ therefore amounts to asking for the criterion which determines the block dimensions. A first straightforward answer follows directly from the observations: it is that size which keeps the blocks just stable, because they have their melting point only a few degrees above $T_c$. It is this stability limit which is included in the schematic drawing figure 16.

One may wonder what happens after melting of the blocks, which occurs if they cannot stabilize by merging. Do new blocks form immediately with a somewhat larger size as given by the crystallization line at the higher temperature? In the s-PP-based samples, which produced the clearest results, we found no indication for such a process. This would lead to a shift in the position of the peak in $\mathcal{K}''(z)$, which was not observed. As it appears, a shift in the peak position
occurs only after complete melting, i.e. above $T^c$, and then it takes place in a discontinuous manner. Figure 20 shows, as an example, corresponding observations on s-PP. As a check shows, the newly formed crystallites have just that thickness which would be predicted from the crystallization line at the temperature of their formation. Therefore, the re-crystallization after a melting again proceeds via the initial block structure, following the phase diagram as shown in figure 16. We find no direct adjustment of the lamellar crystallites without an intermediate step via the initial phase, as this would lead to a continuous, rather than an abrupt thickness change.

4.4. Some speculations about the co-unit independence of crystal thicknesses and the temperature invariance of crystallinities

We thus think we have reasonable answers to the questions about the structural characteristics of the initial phase and the mechanism of their stabilization, but there are more issues.

- Why is the crystallization line not, or only weakly dependent on the content of the co-units? What is the meaning of the limiting temperature $T^c_{\infty}$, which may come near to the equilibrium melting point of the homopolymer, as is the case for the s-PP-based samples, or can also be located above it, not too far away, as for the P(E-co-O)s, or at a larger distance, as for PCL?
- How can the invariance of the crystallinity, simultaneous with the change in the crystal thickness, be understood?

In our last published paper dealing with the s-PP-based samples, we tried to give some answers to the first question [2], and we repeat it here only briefly. Melting of crystallites is normally a process which takes place at their surface. At the melting point we have a dynamic equilibrium between detachment and attachment processes. When increasing the temperature slightly, the detachment processes become dominant and the crystal melts from the surface. The presence of co-units or, in low molar systems, of solvent molecules reduces the attachment rate and a balance between attachment and detachment process is only achieved at a lower temperature, as described by Rault’s law. This is not found exactly in the case of interest, and this is an intriguing observation. We found a suggestion about a possible alternative mechanism of melting from looking into a different field, namely the melting of metal clusters with sizes in the nanometre range [17,18]. For these systems indications exist that melting could represent an intrinsic breakdown rather than a process which proceeds from the surface [19,20]. These melting points also vary linearly with the inverse of the cluster diameter. Therefore, could it not be that the macromolecular blocks also possess and reach an intrinsic limit of stability? Macroscopic crystals always melt from their surface before reaching the limit of intrinsic stability, for nano crystals, however, the order might be inverted. At present, this is just a hypothesis, which needs a closer examination, but the facts are puzzling. This view would give a natural explanation for both observations, the independence of the crystal thickness on the co-unit fraction, and the location of the limiting temperature, lying in general above the equilibrium melting point $T^c_{\infty}(0)$ of the homopolymer, i.e. $T^c_{\infty} > T^f_{\infty}(0)$. It implies that we should consider the formation of a crystal block as a self-organization process taking place in a co-operative manner similar to the formation of a micelle in a solution or to the initial ordering processes observed in block copolymers after a quench from the homogeneous deep into the ordered phase [21], rather than as developing by nucleation and growth.

How can the observed constancy of the crystallinity be interpreted? It holds strictly for s-PP, s-P(P-co-O)4, P(E-co-O)7 and PCL for both $\phi_i$ and $\phi_w$ over the whole temperature range.
covered by the studies. One might feel that the samples with higher co-unit contents, which show a decrease in the crystallinity with increasing temperature, behave in the normal way, in the expected manner. The decrease can be addressed in the spirit of Flory’s treatment of copolymer crystallization, as being due to the decrease in the fraction of sequences long enough to build-up the crystallites, thereby considering, that in order to remain stable crystal thicknesses must increase with increasing temperature. However, as demonstrated by the results, in the central temperature region and for the majority of studied samples, these ideas do not seem to be applicable. As a general statement, observations indicate that the potential of a given polymer system to crystallize is limited and well defined over a larger temperature range. It looks as if the melt would be a two-component fluid, composed of crystallizable and non-crystallizable chain parts with essentially fixed fractions. Indeed, just recently evidence has been accumulating that supercooled polymer melts may micro-separate into regions with variant properties. These regions may differ in density (Terrill et al [22]), in the conformational statistics of chains (Tashiro et al [23]), in the orientational order (Imai et al [24]) and in their mobility (Fukao and Miyamoto [25]), with indications that the less mobile parts set up a network through the sample (Pogodina and Winter [26]). Typically these features are only observable during a short period, before the onset of the main part of the crystallization, i.e. before the rise of Bragg peaks in the WAXS diagram. Authors dealing with these phenomena argue that the establishment of a peculiar kind of order in macromolecular fluids may be due to the high degree of supercooling realized in these systems. Under these conditions one may well envisage spontaneous ‘spinodal-like’ ordering processes, occurring without the need for an activation.

If a preordering really occurs in supercooled melts then crystallization would take place under peculiar conditions. The spherulites would proceed into a preordered melt rather than a normal homogeneous fluid, finding there already clusters of crystallizable segments. Reorientation of these clusters in front of a growing spherulite could be as easy as the reorientation of the domains in a nematic liquid crystal and could be accomplished by the homoeptaxial forces emanating from the blocks at the growth front. Olmsted et al [27], when proposing a theoretical treatment of ordering processes in supercooled polymer melts, point only at possible effects on the primary nucleation. Regarding the observed invariance of the crystallinity, one might think that assuming a quasi two-component fluid could well have a wider significance.

Above we tentatively explained the observed independence of the lamellar thickness on the co-unit content by suggesting that the size of the constituting blocks could represent the minimum required to retain their intrinsic stability. Assuming a preordered melt opens an alternative way to explain the observation. Formation of preoriented crystallizable regions could include a shifting away of the co-units in addition to the entangled chain sequences. If the blocks form out of such an already unmixed state there would also be no effect of the co-units. A decision between the two different explanations is not possible at present and needs more experiments.

5. Conclusion

Finally, we summarize the main findings once again.

- The range of accessible partially crystalline states when described in a $d_c^{-1}/T$-phase diagram is limited by two lines, the ‘crystallization line’

$$T_c = T_c^\infty - C_1 d_c^{-1}$$

(7)
which describes the relationship between the crystallization temperature and the crystal thickness and the ‘melting line’

\[ T_{f} = T_{\infty}^c - C_2 d_c^{-1} \]  

(8)

giving the point of fusion of the lamellar crystallites as described by the Gibbs–Thomson equation. The limiting temperature \( T_{\infty}^c \) of the crystallization line is not, or only weakly dependent on the co-unit content. \( T_{\infty}^c \) is always larger than the equilibrium melting point of a sample

\[ T_{\infty}^c > T_{\infty}^f. \]  

(9)

- Formation of the semicrystalline state in a supercooled polymer melt is apparently a two-step process, beginning with the formation of an initial state of lower order at the crystallization line which then passes over into the final lamellar structure melting at \( T_f \). The passing over occurs in general without a change in \( d_c \).

- Investigations with TEM and AFM in combination with the SAXS experiments indicate that the initial state may be set up by crystal blocks in planar assemblies.

- While crystallite thicknesses vary with the crystallization temperature, crystallinities remain invariant over large temperature ranges.

These findings hold up to a characteristic temperature \( T_{cd} \) given by the point of intersection between the crystallization line and the melting line, for entangled polymer melts with the exception of systems like linear polyethylene where, due to a high intracrystalline mobility, solid state thickening processes take part in the structure formation.

Acknowledgments

Support of this work by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg ‘Strukturbildung in Makromolekularen Systemen’) is gratefully acknowledged. Thanks are also due to the Fonds der Chemischen Industrie for additional help.

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