Some comments on chain dimensions in the semi-crystallized state

Jean Michel Guenet
Centre de Recherches sur les Macromolécules (*CNRS*), 6 *Rue Boussingault*, 67083
Strasbourg, Cédex, France
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In view of recent experimental and theoretical work on the conformation of semicrystalline polymers analytical calculations of the mean chain dimensions are performed for models containing short crystalline sequences and alternating amorphous sequences. The results are analysed and illustrated by means of the parameters for polyethylene and isotactic polystyrene. The invariance of the radius of gyration with crystallinity can only be explained by introducing chain folding in the crystalline sequence. The number of folds required is discussed considering the data obtained both in the Guinier and intermediate ranges of scattering vectors.

INTRODUCTION

A large body of neutron scattering data has been gathered[1-4] on the chain conformation of semicrystalline polymers. In the case of polyethylene, experiments performed by different teams have shown that labelled chains have the same dimensions in the bulk-crystallized state as in the melt. This result as well as the behaviour of the scattered intensity in the intermediate range have been used by Yoon and Flory[5] to propose a conformational model wherein regular folding does not take place. These authors draw additional support[6] for their model based on considerations of the long relaxation time τ_m in the melt. For polyethylene, they show that this relaxation time τ_m is much longer than the time τ_p needed for the crystalline growth front to cover a distance comparable with the chain dimensions. Thus thermal motions can only affect local arrangements, excluding the possibility of adjacent re-entry. However, this criterion has not been universally accepted. Recently, Klein[7] and DiMarzio *et al.*[8] have suggested that the diffusion rate of chains in the melt must be taken into account, since the existence of isotopic segregation has shown this effect to be comparable to that of the rate of spherulitic growth[1]. Their estimates of the time scale for the disentanglement of polymers from the melt during crystallization is about three orders of magnitude greater than the estimates given by Flory and Yoon. They conclude that chain folding is not proven but neither is it disproven by kinetic considerations. Guttman *et al.*[9] have pointed out nonphysical characteristics in the Yoon Flory model. Thus, if no re-entry occurs, the density of the amorphous material located at the crystal surface would be close to 2, which is clearly impossible. Furthermore, they claim that experimental curves obtained in the intermediate range can be fitted, within experimental error, to scattering functions for conformational models containing folded sequences[9].

Alternatively, in the case of isotatic polystyrene, we have effectively shown[4] that the conformation in the semicrystallized state is strongly dependent on the chain mobility in the medium. In contrast with polyethylene, the radius of gyration varies as $M^{0.78}$ and for the highest tagged chain molecular weight increases drastically with crystallinity within a matrix of medium molecular weight ($M_w = 4 \times 10^5$). It must be mentioned that no isotopic segregation occurs in these experiments. From these results we have proposed a conformation called ACA[10] which contains a large crystalline sequence incorporated along the 330 plane with two amorphous wings. By increasing the molecular weight of the matrix ($M_w = 1.7 \times 10^6$), the same results as published for polyethylene have been found[4] (invariance of mean dimensions with crystallinity).

The purpose of this paper is to present some analytical calculations of the radius of gyration for conformational models made of short crystalline sequences in order to complete a previous paper[10] devoted to models possessing large crystalline sequences. Two models are considered with simple arguments:

(i) The garland model (*Figure* 1*a*) with N_s identical subunits made of a short crystalline sequence containing f rods and an amorphous sequence which is the simplest scheme frequently envisaged;

(ii) A central core model, where the core contains f_1 rods and each crystalline sequence in the wings contains f_2 rods (*Figure* 1*b*). This conformation has also been proposed by Guttman *et al.*[9] to explain the results for polyethylene. However, they have performed numerical calculations for only two different molecular weights of the labelled chains. In this paper, an extension of the calculation to any molecular weight is attempted.

The theoretical relations will be illustrated and discussed in relation to the parameters for polyethylene and isotactic polystyrene.

THEORETICAL

Here, calculations are performed by considering the medium as completly crystalline morphologically. This means that pure amorphous domains are non-existent. Consequently, the equations given will only be useful for substantial degrees of crystallinity.

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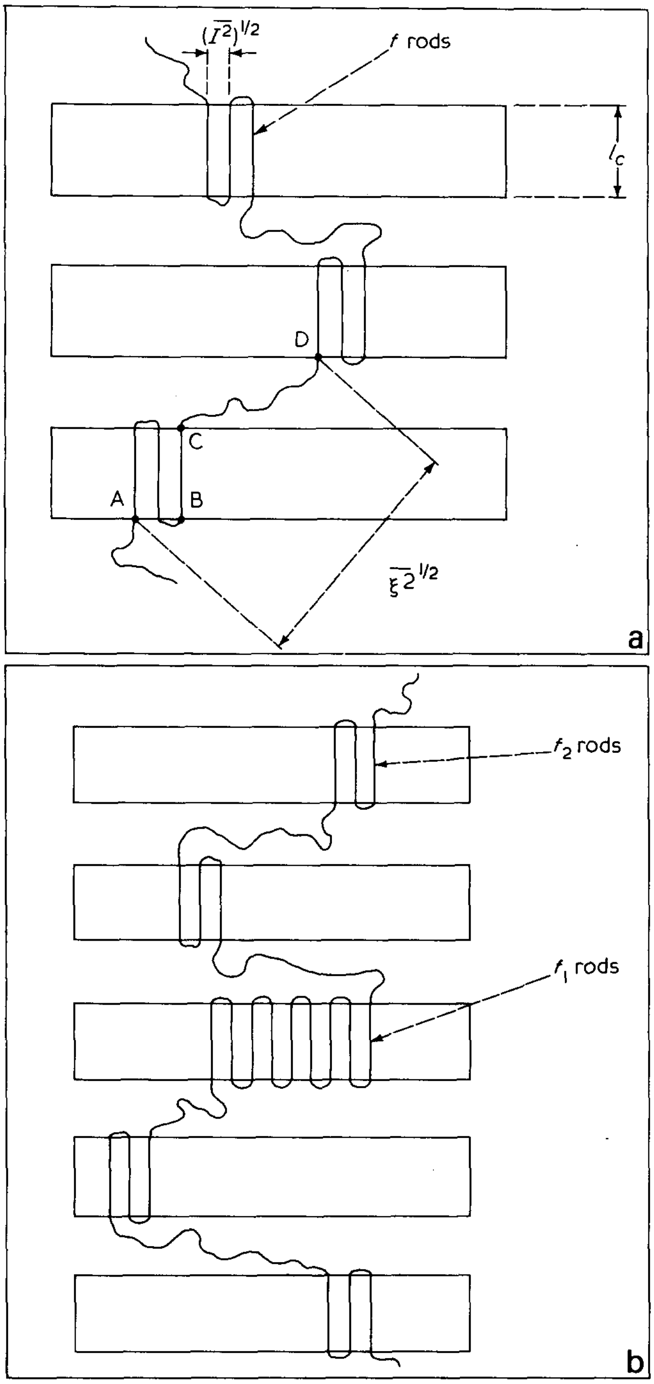

Figure 1 (a) Garland model; (b) central core model

Garland model (*Figure* 1*a*)

We assume N_s equivalent subunits of end-to-end distance $(\overline{\xi^2})^{1/2}$. Without considering orientation correlation[11] we are allowed to express the radius of gyration as:

$$\overline{R_G^2} = \frac{N_s \overline{\xi^2}}{6} \tag{1}$$

Considering f rods per crystalline portion separated by a distance $(\overline{l^2})^{1/2}$, and taking l_c as the lamellar thickness equation (1) is only valid for $l_c > (\overline{l^2})^{1/2}(f-1)$.

In *Figure* 1*a*, ξ can be calculated according to:

$$\xi = \mathbf{AB} + \mathbf{BC} + \mathbf{CD} \tag{2}$$

which leads to:

$$\overline{\xi^2} = \overline{\mathrm{AB}^2} + \overline{\mathrm{BC}^2} + \overline{\mathrm{CD}^2} + \overline{\mathbf{AB}.\mathbf{CD}} + \overline{\mathbf{BC}.\mathbf{CD}} \tag{3}$$

The two last terms in relation (3) can be written:

$$\overline{\mathbf{AB}.\mathbf{CD}} = \overline{\sum_i^{n_a} \mathbf{AB}.\mathbf{b}_i} \tag{4}$$

where b_i is the vector defined by the ith statistical segment of a Gaussian chain having n_a segments. Since we can assume that there is no correlation of orientation between **AB** or **BC** with any $\mathbf{b}_i$ (except for $i=1$ and $i=n_a$), we can approximate equation (4) by:

$$\overline{\mathbf{AB}.\mathbf{CD}} = 0 \quad \text{and} \quad \overline{\mathbf{BC}.\mathbf{CD}} = 0.$$

Introducing the different parameters, $\overline{\xi^2}$ becomes:

$$\overline{\xi^2} = (f-1)^2\overline{l^2} + l_c^2 + n_a\overline{b^2} \tag{5}$$

or

$$\overline{\xi^2} = (f-1)^2\overline{l^2} + l_c^2 + 6\overline{r_a^2} \tag{6}$$

where $\overline{r_a^2}$ is the radius of gyration of the amorphous sequence assuming that the end-to-end distance is the same as for a free Gaussian chain. This approximation seems correct since such a model is invoked when the overall chain has no time to rearrange during crystallization. However, a better approximation would be to take into account a perturbation of the end-to-end distance $(\overline{s^2})^{1/2}$ with:

$$\overline{s^2} \neq n_a\overline{b^2}$$

Then, equation (6) must be written:

$$\overline{\xi^2} = (f-1)^2\overline{l^2} + l_c^2 + \overline{s^2} \tag{7}$$

Alternatively, to take into account the existence of junction loops between rods of the same crystalline sequence, we introduce the parameter z expressed as follows:

$$z = \frac{fn_r}{(f-1)n_l + fn_r} \tag{8}$$

where n_r and n_l are respectively the number of monomers in a rod and in a loop. If $n_c = (f-1)n_l + fn_r$, we obtain:

$$x = \frac{zn_c}{n_a+n_c} \quad \text{and} \quad \frac{n_a}{n_a+n_c} = \left(\frac{z-x}{z}\right) \tag{9}$$

where x is the degree of crystallinity.

Considering the definition of the number of subunits N_s

$$N_s = \frac{N}{n_a+n_c} \tag{10}$$

where N is the total number of monomers in the chain, we arrive at:

$$N_s = \frac{Nx}{fn_r} \tag{11}$$

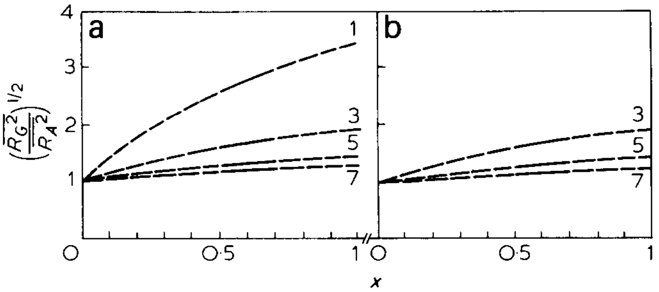

Figure 2 $(\overline{R_G^2}/\overline{R_A^2})^{1/2}$ as a function of crystallinity x in the case of polyethylene for different numbers f of rods in the crystalline sequence (limited to $f = 7$ in order to apply equation (1) without significant approximation). Full lines define experimental regions for which equation (13) pertains. (a) Adjacent re-entry along 220 plane $(\overline{l^2})^{1/2} = 4.93$ Å; (b) second neighbour re-entry along 220 plane $(\overline{l^2})^{1/2} = 9.9$ Å

Applying equation (1) $\overline{R_G^2}$ reads:

$$\overline{R_G^2}=\frac{z-x}{z}\overline{R_A^2}+\frac{Mx}{M_rf}\left[(f-1)^2\frac{\overline{I^2}}{6}+\frac{l_c^2}{6}\right] \qquad (12)$$

where M and M_r are respectively the molecular weights of the chain and of the rod, and $\overline{R_A^2}$ the radius of gyration of the chain in the completely amorphous state. This last parameter may be measured by SANS experiments[1,11]. In the discussion the following relation will preferentially be used:

$$\left(\frac{\overline{R_G^2}}{\overline{R_A^2}}\right)^{1/2}=\left[\frac{z-x}{z}+\frac{Mx}{6M_rf\overline{R_A^2}}\left((f-1)^2\overline{I^2}+l_c^2\right)\right]^{1/2} \qquad (13)$$

If now an end-to-end perturbation in the amorphous sequence is considered, we obtain:

$$\left(\frac{\overline{R_G^2}}{\overline{R_A^2}}\right)^{1/2}=\left[\frac{Mx}{6\overline{R_A^2}fM_r}(6s^2+(f-1)^2\overline{I^2}+l_c^2)\right]^{1/2} \qquad (14)$$

Central core model

Calculations of the radius of gyration for the ACA model have been derived in a previous paper[10]. The result is:

$$\overline{R^2}=(3-2y)\overline{R_p^2}+y\overline{r_e^2}+(1-y)^2\frac{(2+y)}{2}\overline{R_A^2} \qquad (15)$$

where y is the weight fraction of the crystalline sequence and in the case of regular folding along an $hk0$ plane[10]

$$\overline{R_p^2}=\frac{(f-1)^2\overline{I^2}}{12}\quad \overline{r_e^2}\simeq l_c^2/12.$$

$\overline{R_A^2}$ is the mean square radius of gyration in the pure amorphous state. Introducing a small change by replacing the pure amorphous A wings by semicrystalline wings, the conformation becomes identical to the central core model drawn in *Figure* 1*b*. The mean square dimensions $\overline{R_{cc}^2}$ can then be calculated using equation (15) merely by replacing $\overline{R_A^2}$ by $\overline{R_G^2}$ which is the radius of gyration of the chain adopting a total garland conformation with f_2 rods per crystalline sequence. This procedure is possible since, for a Gaussian conformation or the 'garland' model, the mean square dimensions are proportional to the molecular weight of the chain. Consequently, equation (15) must be modified by introducing new parameters: y_1 = the weight fraction of the central core ($y_1 = M_rf_1/M$); y_2 = the weight fraction of crystalline sequence in the wings (with $y_1+(1-y_1)y_2=x$). f_1 and f_2 are respectively the number of rods in the central core and in a crystalline sequence in the wings (*Figure* 1*b*).

We obtain:

$$\overline{R_{cc}^2}=(3-2y_1)(f_1-1)^2\frac{\overline{I^2}}{12}+y_1\frac{1_c^2}{12}+(1-y_1)^2\frac{(2+y_1)}{2}\overline{R_G^2} \qquad (16)$$

in which $\overline{R_G^2}$ may be represented by:

$$\overline{R_G^2}=\frac{z-y_2}{z}\overline{R_A^2}+\frac{My_2}{6M_rf}[(f_2-1)^2\overline{I^2}+l_c^2] \qquad (17)$$

DISCUSSION

From these equations it is clearly impossible to describe the specific behaviour of the two models. Hence the calculations will be illustrated using known parameters for polyethylene and isotactic polystyrene.

Polyethylene

Most discussions of semicrystalline models have been essentially based on an experiment performed by Schelten *et al.*[1]. Their samples of polyethylene, rapidly quenched from molten state to solid state, are characterized by a degree of crystallinity $x = 0.65$ and a long spacing: $L = 250$ Å leading to $l_c = 160$ Å[1]. This method of preparation avoids the formation of isotopic clusters. Experimental results show no variation of mean dimensions after crystallization.

Garland model. For computing the ratio $(\overline{R_G^2}/\overline{R_A^2})^{1/2}$ we will consider two cases:

(i) adjacent re-entry along the 200 plane as suggested by infra-red experiments[12] $[(\overline{I^2})^{1/2} = 4.93$ Å];

(ii) re-entry between second neighbours as proposed to occur in single crystals[2] but along 200 plane $[(\overline{I^2})^{1/2} = 9.9$ Å].

In *Figures* 2*a* and 2*b* equation (13) is plotted as a function of X for the two cases described above from $f = 1$ to $f = 7$ using $\overline{R_A^2} = 0.2$ M^1. The principle remark which follows from this study is that a model without folding leads to an increase of 300% in the radius of gyration for $x = 0.65$. Consequently, the only way to observe an invariance in the mean dimensions for $f = 1$ would be to assume a negative radius of gyration for the amorphous sequence. The case where $f = 3$ is particularly interesting. If we consider regular folding, the invariance of the radius of gyration can only be mathematically obtained by putting $z < x$. This would mean that the crystallinity in the lamella would be smaller than that of the whole sample which is clearly impossible. If we now consider, as proposed by Yoon and Flory[5], an irregular re-entrance with $p_{escape} = 0.3$ meaning that, on average the chain threads three times through the lamella before going to another, we obtain $\bar{f} = 3$.

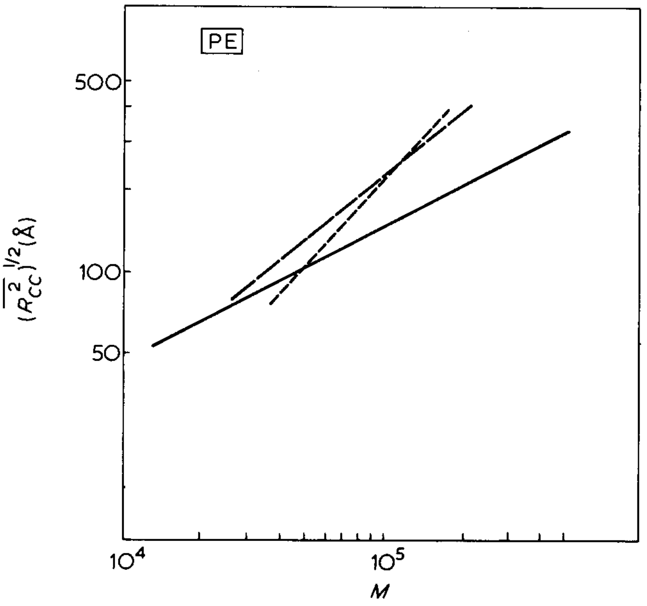

Figure 3 Radius of gyration as function of molecular weight on a double logarithmic scale in the case of the central core model for polyethylene. Full line stands for experimental results[1], broken line $f_1 = 7$ with $f_2 = 3$, dotted line $f_1 = 11$ with $f_2 = 3$

To take this case into account (that the implantation is somewhat at random in the crystal) the term containing $(f-1)^2\overline{l^2}/6$ in equation (13) must be modified and it will have a smaller value than for regular folding. However, the term containing $l_c^2/6$ is always much larger than 1 for $f=3$ so that the only mathematical way to obtain $\overline{R_G^2} \simeq \overline{R_A^2}$ is also by putting $z<x$ in this model, which is a non-physical solution. Furthermore, both for regular and irregular re-entry with $f=3$, it is impossible to account for the invariance of the mean dimensions with crystallinity by taking a mean square end-to-end distance $\overline{s^2}$ for the amorphous sequences smaller than that for a free Gaussian chain. We note that $z<x$ is equivalent to the anomalous density pointed out in the disordered region for the Flory model[5] by Guttman *et al.*[9] from numerical computations.*

In order to observe an invariance of mean dimensions after crystallization, we have to introduce folds in the crystalline sequence. After *Figure* 2, the best fit corresponds to $f=5$ to $f=7$, for which the radii of gyration in the molten state and in the 65% crystallized state differ by approximately 20%. Taking into account the relative accuracy of the SANS measurements performed on polyethylene[1] and the approximations in the calculations, this difference lies within the experimental error. This result is similar to others obtained by Monte-Carlo simulation[9]. However, the distinction between adjacent re-entry and second neighbour re-entry appears impossible. This arises from a large lamellar thickness compared with the width of the crystalline sequence.

Central core model. Calculations for molecular weights of $M = 3.5 \times 10^4$ and 4.9×10^4 have been performed using the Monte-Carlo method by Guttman *et al.*[9]. They suggest a central core with $f_1 = 7$ to $f_1 = 11$ and $f_2 = 3$. Using these values, plots of radius of gyration as a function of molecular weight reported in *Figure* 3 have been obtained from equation (16) for $3.5 \times 10^4 \leqslant M \leqslant 10^5$. These results show that the approximations used in the calculation of R_G have almost no influence since, for $M = 4.9 \times 10^4$, values obtained from the Monte-Carlo simulation[9] are close to those calculated here (see *Table* 1). Returning to *Figure* 3, we see that for $M > 10^5$ theoretical values of $\overline{R^2_{cc}}$ become much larger than those measured experimentally. This result is clear since for large molecular weights the central core represents only a small part of the overall chain and hence we must investigate the behaviour of the garland model again with $f=3$. Consequently, this model seems not to agree with experiment whatever the molecular weight, although the scattering function derived from it fits experimental values of intensity at large angles. However, we have shown[10] that increasing the central core sequence with molecular weight meets the experimental criterion in the Guinier range but no information was obtained in the intermediate range.

In view of these results, the only model which is seen to fit the experimental criterion with regard to invariance of the radius of gyration is the garland model containing 5 to 7 folds per crystalline sequence. Looking at the intensity scattered at large angles, and particularly the experiments of Sadler[2], it is possible to discover whether the re-entry is adjacent or takes place between second neighbours. In this case, the intensity exhibits a crossover from $I(q) \simeq q^{-2}$ to $I(q) \simeq q^{-1}$ suggesting the presence of isolated rods. The crossover scattering vector at which this behaviour occurs is[15]:

$$q^* = \frac{2}{(\overline{l^2})^{1/2}}$$

It follows from the results of Sadler and Keller[2]: $(\overline{l^2})^{1/2} \simeq 8$ to 10 Å. This supports the garland model with second neighbour re-entry. SANS experiments have shown that this occurs in single crystals both of polyethylene[2] and isotactic polystyrene[14] and thus there is no reason for ignoring a similar effect in the bulk.

Isotactic polystyrene. We have shown in a previous paper[4] that isotactic polystyrene chains can exhibit two different conformations in the bulk crystallized state according to the mobility in the medium. The first conformation, corresponding to the ACA model has already been widely discussed elsewhere[4]. The second conformation, obtained by diminishing the mobility, and

Table 1 Values of the radius of gyration for the central core model in the case of polyethylene chains of molecular weight M_W = 4.9×10^4. (a) From equation (16); (b) from ref 9; (c) experimental value from ref (1)

	$(R^2_{cc})^{1/2}$ (a)	$(R^2_{cc})^{1/2}$ (b)	$(R^2)^{1/2}_{exp}$ (c)
$f_1 = 7$ $f_2 = 3$	126	108	102
$f_1 = 11$ $f_2 = 3$	109	101	102

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* Remark. We must here take into account the fact that lamellae of different thickness are present in the medium[13]. Accordingly, calculating the value of l_c for models where $f=1$ or $f=3$ could pertain for polyethylene, we obtain $l_c \sim 10$ A which is of the order of the persistence length in the amorphous state. Thus, whatever the value of l_c, $\overline{R_G^2}$ is always larger than $\overline{R_A^2}$ for these models.

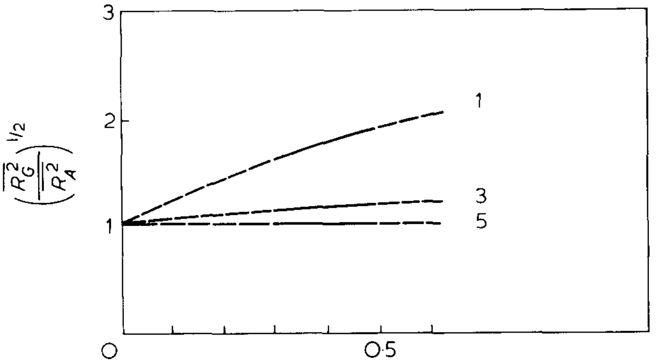

Figure 4 $(\overline{R_G^2}/\overline{R_A^2})^{1/2}$ as function of x in the case of isotactic polystyrene for different values of f, garland model; limited to $f = 5$ in order to apply equation (1) without significant approximation. Full lines define the experimental region

for which the invariance of mean dimensions as in polyethylene has been observed, will be examined here in order to determine whether regular folding occurs in this case. Since a central core type model fits the first conformation[4], only the garland model is considered here.

SANS results have been obtained on samples crystallized at 185°C leading to $l_c = 100$ Å and $x = 0.35$[4]. For isotactic polystyrene, re-entry occurs along 330 plane[16]. This arises from the high energy required to change a right-hand helix into a left-hand helix[17] or *vice versa.* Hence, $(\overline{I^2})^{1/2} = 12.6$ Å, a value much larger than in polyethylene. From measurements on single crystals[16], values of $z = 0.74$ for $l_c = 75$ Å have been obtained. For $l_c = 100$ Å, considering the same number of monomers in the loops, the value of z becomes 0.8.*

The variation of $\overline{R_A^2}$ as function of molecular weight has been measured at 180°C in an atactic matrix. The results available in a previous paper[12] are:

$$\overline{R_A^2} = 5.3 \times 10^{-2}\ \mathrm{M}$$

Plots for different values of f are presented in *Figure* 4. As in the case of polyethylene, the ration $(\overline{R_G^2}/\overline{R_A^2})^{1/2}$ is found to be close to 1 for $f = 5$. A model without re-entry would lead to mean dimensions 50 to 90% higher than those measured in the amorphous state. It is possible to cross check this result ($f = 5$) with the intensity observed at large angles. *Figure* 5 shows the behaviour of the 35% crystallized sample[4] and an amorphous sample, both having the same number of tagged chains. In both cases $I(q)$ varies as q^{-2}. This can be explained by considering the limiting form factor $P(q)$ which is valid for $q(\overline{r_a^2})^{1/2} > 1$ and $ql_c > 1$:

$$\lim P(q) = \frac{1}{N^2}[N_s\, n_a^2 \lim P_a(q) + N_s\, n_c^2 \lim P_c(q)] \tag{18}$$

where $\lim P_a(q)$ and $\lim P_c(q)$ are respectively the asymptotic expressions of the form factors for the Gaussian sequence and the crystalline sequence. Using the same symbols as before equation (18) becomes:

$$\lim P(q) = \frac{z-x}{z} \lim P_a(q) + \frac{fM_r x}{Mz^2} \lim P_c(q) \tag{19}$$

where $\lim P_a(q) = 2/q^2\overline{R_A^2}$ which represents the asymptotic behaviour of the scattered intensity from a chain in the completely amorphous state. The crystalline sequence can be compared with a thin sheet of length l_c and width $(f-1)(\overline{I^2})^{1/2}$. For $q^* = 2/(f-1)(\overline{I^2})^{1/2}$, $\lim P_c(q)$ reads[16,18]:

$$\lim P_c(q) = \frac{2\pi}{q^2 l_c (f-1)(I^2)^{1/2}} \tag{20}$$

Then, $\lim P(q)$ must behave as q^{-2} just beyond $q^* = 4 \times 10^{-2}$ for $f = 5$, which is effectively the case in our experiments (*Figure* 5). For $f = 3$, this behaviour would be reached just after $q^* = 8 \times 10^{-2}$.

Results in the Guinier range and in the intermediate range for isotactic polystyrene are thus consistent with models including the existence of regular chain folding.

CONCLUSIONS

The analytical calculations presented here are easily available and lead to values of the mean dimensions, particularly in the central core model, close to those obtained by sophisticated computation methods[9].

The invariance of the radius of gyration with crystallinity can only be accounted for by introducing regular folding in the crystalline sequence. Such a model is confirmed by considering the asymptotic behaviour of the scattered intensity in the intermediate range, which is consistent with the presence of small sheet-like structures. The data gathered on isotactic polystyrene[4,16,19], for which isotopic segregation does not take place, show clearly that the size of the sheet-like crystalline sequence increases with the chain mobility in the originally amorphous medium. Thus, it seems in the case considered here that a conformational garland type model fits the experimental results and is consistent with viscoelastic considerations.

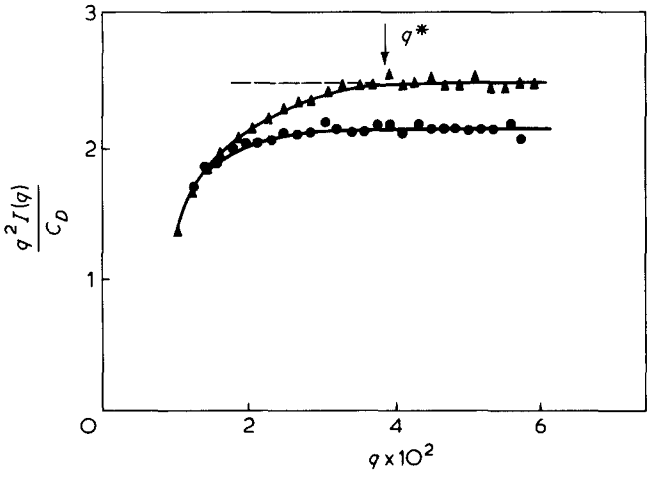

Figure 5 Kratky plot $q^2I(q)/C_D$ as function of q in arbitrary units. ▲, 35% crystallized sample ($M_{\mathrm{WIPSD}} = 5 \times 10^5$ and $M_{\mathrm{WIPSH}} = 1.7 \times 10^6$); ●, amorphous sample ($M_{\mathrm{WIPSD}} = 5 \times 10^5$ and atactic matrix). For the crystalline sample q^{-2} behaviour is reached for $q^* \sim 4 \times 10^2$

Remark. For $l_c = 100$ Å and $(\overline{I^2})^{1/2} = 12.6$ Å, tight loops would lead to $z = 0.9$.

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