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Small Angle Neutron Scattering Studies on Polypropylene

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ABSTRACT: Previous SANS studies have been concerned with isotropic samples in which the macromolecule on crystallizing from the melt retained approximately the same disposition in space. The examples discussed are concerned with the effect on the conformation of the macromolecule of crystallizing in the presence of nuclei obtained from polymer in which the lamellae had been thickened by prolonged annealing. It is observed for the first time that the $(I(\kappa))^{-1}$ vs. κ^2 curves are not simple straight lines and evidence is advanced to show that the behavior is due to the molecules crystallizing in such a way as to give regions of high scattering intensity approximately 150 Å apart. These are connected by fragments of tagged molecules which scatter neutrons very little. A similar separation occurs on cold drawing polypropylene, and SANS measurements at right angles to the draw direction can only recognise parts of the molecules which have the highest scattering intensity.

Polypropylene is a semicrystalline polymer in which ambiguities due to the separation of deuteriopolypropylene (PPD) from protopolypropylene (PPH) on crystallization do not occur. It has therefore been possible to study the conformational changes occurring on crystallization under a variety of conditions with the tagged macromolecules remaining discrete[1,2] by using small angle neutron scattering (SANS). The main conclusions derived from these studies of the conformational changes occurring on crystallization to give isotropic materials are reported in the first two references and the details should be consulted before reading this paper. The main conclusions derived from the earlier work are as follows:

1. Provided the crystallinity is high (>60%), which is the situation with all the samples described in this paper, the scattering of neutrons from the tagged molecules is dominated by that fraction of molecules contained within the crystalline regions. This has been demonstrated experimentally. The well-established chemical etching technique used removes the noncrystalline fraction preferentially leaving the stems of the tagged molecule in their original position in the crystal matrix. If the etched plaque is dissolved in an organic solvent, molecular weight measurements show that all the stems are now discrete entities. The effect of removing the amorphous contributions gives a value for the radius of gyration 0.82–0.9 times the value measured in the unetched plaque.[2]

2. Crystallization does not require the macromolecule to fold into a single lamella, rather the conformation consists of a three-dimensional array of stems of length l_n arranged around the center of mass. Each lamella of thickness d consists of stems derived from many macromolecules.[2] The radius of gyration (R_w) of such a system is given by:

$$R_w{}^2 = \frac{l_n{}^2}{12} + \beta^2 M_w \qquad (1)$$

3. The value of l_n, the neutron scattering stem length, is approximately twice the lamellar thickness (d) determined by SAXS. The latter is therefore the fraction of the chain which tranverses two lamellae. The number of these stems present is a significant fraction of the total and it is estimated that 1 in 3 to 1 in 5 stems is a connective stem.

In this paper we extend these studies of polypropylene to systems in which the conformation of the macromolecule is fundamentally different from that of the simple isotropic system.

Experimental Section

Polypropylene samples were prepared and characterized by using techniques described in previous publications.[1,2]

The isotropic samples of polypropylene used in these studies were obtained by crystallization in the presence of nuclei derived from the melting of polypropylene in which the lamellae had been thickened by prolonged annealing. In order to differentiate between these samples and those which have been studied previously,[1] the crystallization is described as occurring in the presence of "extended chain nuclei". Polypropylene plaques (30 mm × 15 mm × 1 mm) obtained by rapidly quenching molten polymer had an initial crystallinity (X) of 54% and d = 120 Å. These were annealed for 24 h at 139 °C and then cooled to room temperature. Previous studies have shown (Table I, ref 1) that this process increases the crystallinity beyond 60% and this is accompanied by a doubling of the thickness of the lamellae. The plaques were finally melted by heating them to just above the melting point for a short period so as to retain submicron size crystallites derived from the thickened lamellae to act as nuclei for the final crystallization process. This was accomplished by cooling at a rate of 6 °C/h to give samples with crystallinities of 83% and average values of d of 305 Å.

Cold drawn samples of polypropylene were prepared by drawing rapidly quenched polypropylene (d = 120 Å, X = 54%) at 21 °C with the use of an instron tensiometer. Dumbbell shaped specimen gauge lengths of 3.5 cm were drawn at their natural draw ratio with a constant load and at a rate of 1 cm min^{-1}. Values of d increased from 120 to 145 Å and the crystalline fractions from 54 to 58%. The surface of the parallel section of each dumbbell was marked at 0.5-cm intervals and the draw ratio determined by measurement of each section before and after drawing. Samples for the spectrometer were prepared by mounting, in parallel, several pieces of the drawn section in square metal frames 3 cm × 3 cm.

SANS, SAXS, and chemical etching experiments were carried out in the manner described in previous experiments.[1,2]

Results and Discussion

Polypropylene Crystallized with the Use of Extended Chain Nuclei. In the isotropic systems previously studied the radius of gyration and the molecular weight of the PPD molecules in a PPH matrix are obtained by plotting $1/I(\kappa)$, the reciprocal of the intensity per unit solid angle, against κ^2 ($\kappa = 4\pi \sin(\theta/\lambda)$ where θ is half the angle

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Table I
PPD Molecules (3%) Dispersed in PPH Matrix of Similar Molecular Weight and Crystallized as Described in the Text[a]

	PPD soln measurement		SANS, small κ		SANS, intermediate κ			
sample	$M_w \times 10^{-3}$	M_w/M_n	$(M_w)_S \times 10^{-3}$	$(R_z)_S$, Å	$(M_w)_I \times 10^{-3}$	$(R_z)_I$, Å	$(M_w)_S/(M_w)_I = N_B$	Δ, Å, from eq 14
SCPP1	69	3.30	73	144				
SCPP2	179	1.67	226	321	98	150	2.3	154
SCPP5	508	3.90	415	377	144	171	2.9	149
SCPP8	654	1.49	660	442	152	177	4.3	149
SCPP9	1191	1.48	1325	616	302	252	4.3	162

[a] Values of R_z and M_w obtained from the slopes and intercepts of curves of the type shown in Figure 1. X-ray scattering gives $d \simeq 305$ Å as an average value.

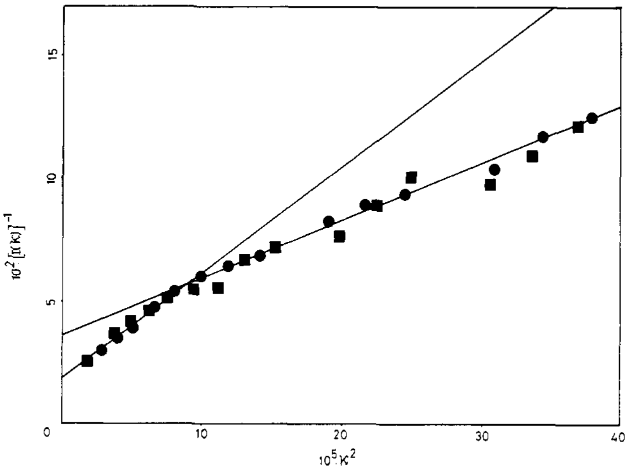

Figure 1. Typical plot of $(d\Sigma/d\Omega\ (\kappa))^{-1}$ vs. κ^2 for isotropic polypropylene crystallized in such a way that fragments of the chain are widely separated (sample SCPP2).

subtended at the detector at which the intensity is measured). With the well-known equation

$$\lim cK_N/I(\kappa) = \frac{1}{M_w}\left[1 + \frac{R_z}{3}\kappa^2\right] \qquad (2)$$

c is the concentration of PPD molecules and

$$K_N = \rho\left[\frac{2X(b_D - b_H)}{M}\right]^2 N$$

where ρ is the density of the polymer, X is the degree of deuteration, N is Avogadro's number, M is the molecular weight of the repeat unit of the tagged molecules, and b_D and b_H are the scattering lengths of deuterium and hydrogen. In all cases a simple straight line relationship was obtained. Crystallization in the presence of "extended nuclei" produces curves of the type shown in Figure 1 which consists of two intersecting lines. Application of eq 2 to the intercept and slope of these gives values for the molecular weight and radii of gyration corresponding to each line. These are summarized in Table I.

A comparison of the values of the molecular weight of the PPD molecules measured in solution with those determined by SANS at small values of κ in the solid state shows that the scattering in this domain of κ space is dictated by the configuration of the macromolecule as a whole. The molecular weights obtained from intermediate values of κ show that in this domain of κ space the scattering is dictated by an entity which is 3–4 times smaller. The macromolecule has therefore crystallized in such a way that parts of the chain are separated sufficiently and scatter the neutron radiation as independent entities.

In Figure 2 is shown a possible conformation of the macromolecule in the solid state which would show this scattering behavior. The main characteristic required is that the chain folds into a lamellae giving regions of relatively high scattering intensity. These are connected by fragments of unfolded chain of much lower scattering ability and therefore of much smaller cross section.

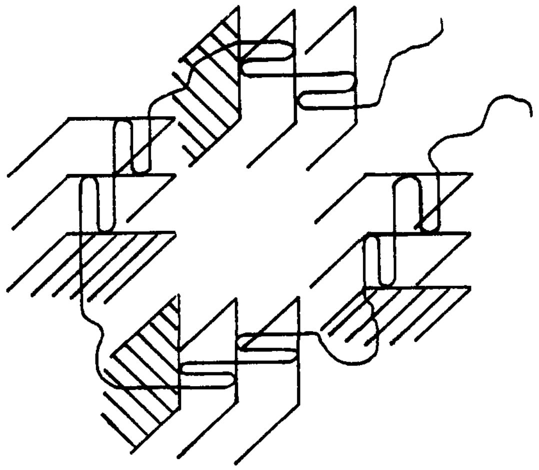

Figure 2. A possible conformation for polypropylene crystallized in such a way that parts of the chain are widely separated.

It might be argued that the crystallization procedure used leads to a fractionation of the polymer producing regions in which tagged molecules of much lower molecular weight are separated from those of higher molecular weight. If this were the case, however, it would be expected that in Table I values of $(M_w)_S$ would be greater than those measured in solution which is not the case. Moreover, polymers with narrow molecular weight distributions would not be expected to show the effect so markedly as those with broad distributions. Variation in the ratio of M_w/M_n 1.5 and 3.9 does not lead to any significant difference. We therefore consider that there has been no separation of tagged molecules of different molecular weight. It can also be shown by a simple calculation that the proportion of tagged molecules of low weight required to give the scattering intensity observed is not possible with the molecular weight distributions quoted.

Sample SCPP1 only gave a single line suggesting that the molecule was too short for fragments of the chain to crystallize in discrete regions.

We wish to emphasize the uniqueness of the curves obtained of which Figure 1 is typical. All systems we have so far studied, including polypropylene and polyethylene crystallized by quenching, annealing, and slow cooling and anisotropic samples obtained by cold drawing quenched polypropylene, give curves which fit a single straight line closely. Curvature toward the κ^2 axis at intermediate κ values has not previously been observed. This is the first example where SANS studies have indicated that parts of the same molecule have crystallized in discrete regions. The distance between these scattering regions diagram-

Table II
PPD (3%) of Differing Molecular Weights Dispersed in a PPH Matrix (homopolymer)[a]

sample no.	PPD soln measurements $M_w \times 10^{-3}$	PPD soln measurements M_w/M_n	SANS/SAXS data before drawing R_w, Å	SANS/SAXS data before drawing $M_w \times 10^{-3}$	SANS/SAXS data before drawing d, Å	draw ratio	SANS data at right angles to draw direction $M_w^{\perp} \times 10^{-3}$	SANS data at right angles to draw direction $R_z^{\perp}$, Å	$M_w/(M_w^{\perp})$	d, Å, after drawing
OPP 1	116	1.9	126	98	140	6.0 to 1	32	47	3.1	145
OPP 2	165	1.5	167	143	140	6.1 to 1	38	51	3.8	145
OPP 3	389	1.6	241	336	140	6.1 to 1	55	61	6.1	145

[a] Polymer samples were heated above the melting point, quenched, and then drawn at room temperature.

matically represented in Figure 2 can be computed by application of scattering theory. The structure can be described as a solid string of disks; the disk represents a cluster of stems and the string the connecting fragment of the molecule.

If R_i is the distance of the center of mass from the ith disk and R_j that from the jth then

$$\frac{d\sigma}{d\Omega}(\kappa) = \langle|F_B(\kappa)|^2\rangle\cdot\langle\sum_{i,j=1}^{N_B} e^{i\kappa(R_i-R_j)}\rangle \quad (3)$$

where the angle brackets denote averaging over different disks, different arrangements of disks, and different orientations. It follows therefore that:

$$\langle\sum_{i,j} e^{i\kappa(R_j-R_i)}\rangle = N_B + \langle\sum_{i,j} e^{i\kappa(R_j-R_i)}\rangle \quad (4)$$

and N_B denotes the number of disks per macromolecule.

We now define the probability of finding one disk within a distance R from another as $g(R)$ and it must follow that:

$$\int_0^{\infty} g(R)\cdot 4\pi R^2\, dR = 1 \quad (5)$$

Combining eq 5 and 4 gives the expression:

$$\langle\sum_{i,j} e^{i\kappa(R_j-R_i)}\rangle = N_B\left[1 + (N_B - 1)\int g(R)e^{i\kappa R}\cdot 4\pi R^2\, dR\right] \quad (6)$$

This is equal to N_B^2 if $\kappa = 0$ or N_B if κ is very large.

We assume that the probability function is Gaussian, that is

$$g(R) = g^{-1} \exp(-R^2/2\Delta^2) \quad (7)$$

and Δ is the mean distance between disks.

$$\frac{d\sigma}{d\Omega}(\kappa) = |F_B(\kappa)|^2 N_B[1 + (N_B - 1)G(\kappa)] \quad (8)$$

where

$$G(\kappa) = \int g(R)e^{i\kappa R}4\pi R^2\, dR \quad (9)$$

The scattering derivable from the differential cross section per cubic centimeter is

$$\frac{d\Sigma}{d\Omega}(\kappa) = K_N C M_w \frac{|F_B(\kappa)|^2}{|F_B(0)|^2}\,\frac{1 + (N_B - 1)G(\kappa)}{N_B} \quad (10)$$

It is evident from Figure 1 and eq 10 that if $\kappa = 0$, $G(\kappa) = 1$ and the intercept is given by

$$E_s = K_N C M_w \quad (11)$$

On the other hand if $G(\kappa)$ tends to zero, eq 10 gives the extrapolated intercept:

$$E_I = K_N C M_w/N_B \quad (12)$$

In Table I values $(M_w)_S/(M_w)_I = N_B$ are given.

From the ratio of intensities we have:

$$\frac{[I(\kappa)]_s}{[I(\kappa)]_I} = [1 + (N_B - 1)G(\kappa)] \quad (13)$$

An estimate of $G(\kappa)$ can be made and therefore the mean distance Δ between the disks determined. It may be shown that:

$$G(\kappa) \bumpeq \exp[-{}^3\!/_2(\kappa\Delta)^2] \quad (14)$$

By plotting $l_n G(\kappa)$ vs. κ^2 an estimate of Δ can be found. These results are summarized in Table I.

The scattering theory therefore indicates that provided the regions of highest scattering intensity are approximately 150 Å apart then models of the type described in Figure 2 are consistent with the behavior observed. This analysis is further supported by comparing values of the radius of gyration for the whole molecule $(R_z)_S$, at a given molecular weight, with those previously obtained with samples in which $1/I(\kappa)$ vs. κ^2 curves were simple straight lines. Comparison with the values obtained for molten polypropylene for example with the values of $(R_z)_S$ in Table I shows that the latter are some 60% larger. The macromolecule must therefore be further removed from the center of mass and arranged in a much less compact way than in the melt.

Finally we have carried out measurements in the high κ region and typical Kratky plots are shown in Figure 3. It is a feature of such plots for isotropic polypropylene that whereas the initial part of the curve shows that the intensity is markedly dependent on the molecular weight, the latter parameter subsequently approaches an asymptotic value independent of molecular weight. It is evident that in this region the values of $I(\kappa)\kappa^2$ differ little from those obtained with isotropic samples with less complex chain conformations.[1] A theoretical treatment by Yoon and Flory[4] of the origin of the shape of these curves identifies the distance between stems of the same macromolecule within the lamellae as a critical dimension in these scattering curves. This suggests despite the abnormality in the conformation of the chain in these isotropic samples that the distance between stems within lamellae is not reduced.

Anisotropic Polypropylene. SANS studies of anisotropic systems in the solid state are relatively uncommon. The most important is the effect of stretching of amorphous polystyrene.[5] In this study the radii of gyration at right angles and parallel to the direction of drawing were determined for extension ratios up to 1.7. The deformation was affine with a small contribution from a nonaffine component as the draw ratio approached 1.7. At higher draw ratios void scattering prevents further meaningful measurements.

We have studied the conformational changes occurring on cold-drawing polypropylene. The data obtained are summarized in Table II. Only information at right angles to the direction of drawing is given because void scattering parallel to this direction makes measurements difficult.

The need to study anisotropic samples raises several problems in scattering theory which are not encountered with the isotropic systems previously described. For ex-

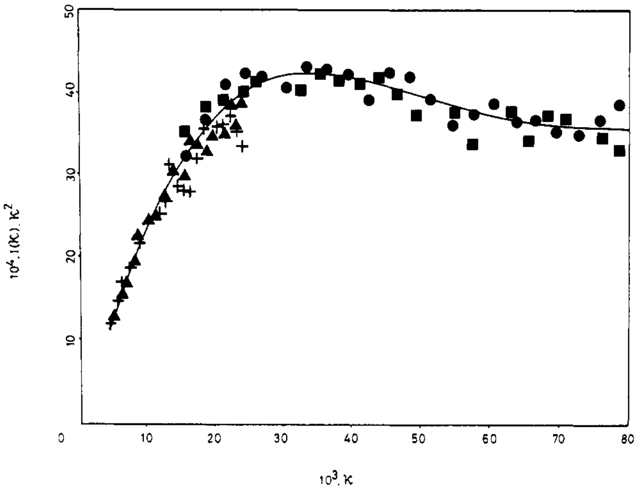

Figure 3. Kratky plot of polypropylene crystallized in such a way that parts of the chain are widely separated (sample SCPP5).

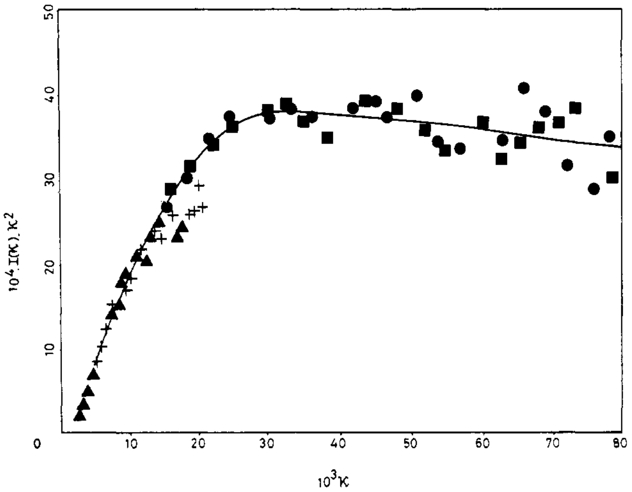

Figure 4. Kratky plot of polypropylene crystallized by quenching the same as for sample no. OPP2.

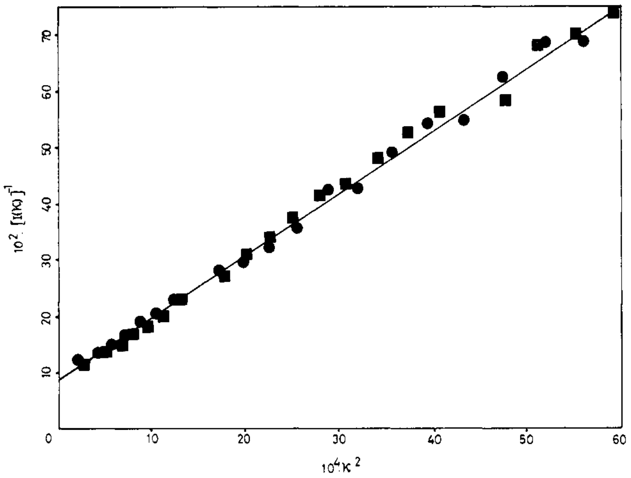

Figure 5. Typical plot of $[I(\kappa)]^{-1}$ vs. κ^2 for cold drawn polypropylene. Measurements made at right angles to the direction of drawing PPD 3% dispersed in a PPH matrix. Samples quenched then drawn at room temperature (sample no. OPP2).

ample, in eq 2 the factor $^1/_3$ occurs in the exponential form from which this equation is derived and assumes a spherically random array. It arises from the value of $\cos^2 \theta$ averaged over a sphere:

$$\langle \cos^2 \theta \rangle = \frac{1}{4\pi}\int\int \cos^2 \theta \sin \theta \, d\theta \, d\theta \tag{15}$$

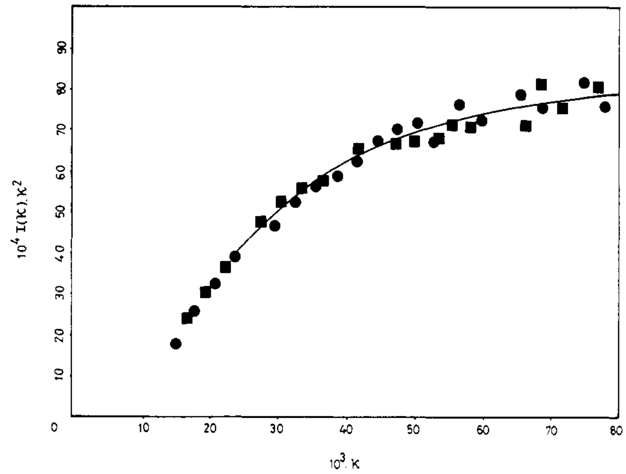

Figure 6. Kratky plot of cold drawn polypropylene (sample no. OPP2).

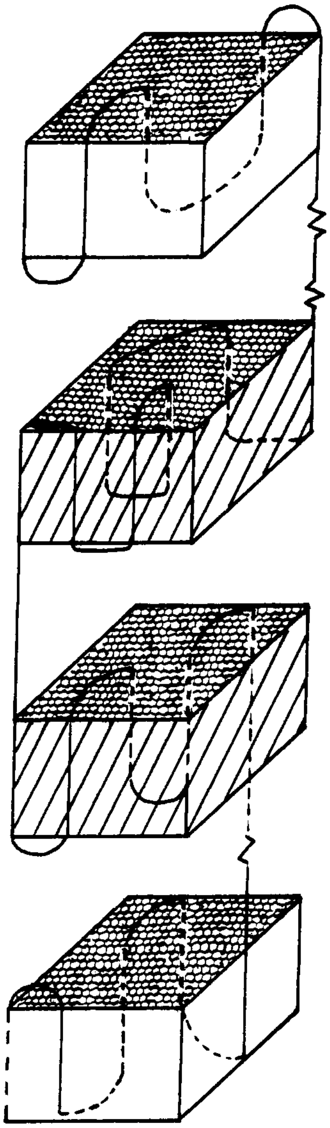

Figure 7. Diagrammatic representation of a possible conformation for cold drawn polypropylene showing the arrangement of stems from the same molecule within each lamellae and how each lamellae is connected to its neighbor. The stems are an average 40 Å apart but could be arranged in pairs. Stems belonging to other molecules are represented by ●.

In uniaxially drawn samples this situation does not exist and we are dealing with a cylindrically random system.

$$\langle \cos^2 \theta \rangle = \frac{1}{2\pi}\int_0^{2\pi} \cos^2 \theta \, d\theta \tag{16}$$

In measuring $R_z^{\perp}$ the equation to be used is:

$$I(\kappa) = I(0)\exp[-\kappa^2(R_z^{\perp})^2/2] \tag{17}$$

Similarly for $R_2^{\parallel}$, if we have complete orientation:

$$I(\kappa) = I(0)\exp[-\kappa^2(R_z^{\parallel})^2] \tag{18}$$

However, in the samples discussed in Table II orientation was not complete and our principal discussion relates to values of $R_z^{\perp}$. However, approximate values of $R_z^{\parallel}$ obtained by curve fitting of data derived from measurements parallel to the drawing axis, using known values of M_w to fix the value of the intercept, led to the conclusion that $(R_z^{\parallel}/R_z^{\perp}) \simeq 3$. One explanation for the results in Table II is that the molecules have separated into discrete domains with molecular weights ($M_w^{\perp}$) in the region 32000–55000. These domains are connected by fragments of the macromolecule which are too few in number to contribute significantly to the scattering at right angles to the direction of drawing. It is due to the lower limit of κ accessible to the Julich spectrometer that, for these highly anisotropic scatterers, one obtains the molecular weight of the separated fragment of the macromolecule. Similarly values of $R_z^{\perp}$ give information of the total cross section of the molecules contained within these domains.

Etching experiments[2] show that only discrete lamellae are present with similar *d* spacing to that measured in the undrawn samples. A possible model consistent with the data obtained for sample OPP2 is that the molecule is folded between four lamellae as shown in Figure 7. Each lamellae contains 10 or more stems and these are connected by 2 to 3 tie fragments. This supports the observation made on the isotropic system that a macromolecule in crystalline polymers can inhabit more than one lamellae. The values of $R_z^{\perp}$ also give information concerning the average distance between stems. Adjacent re-entry or close packing of the stems would lead to a value of $R_z^{\perp}$ approximately a quarter of the value observed. It is concluded from these measurements therefore that the stems are widely spaced either separately or in pairs of undetermined distance apart.

It should be noted that etching gives values for the stem length close to the SAXS value for the *d* spacing and only one stem was identified in the etching system. Similar studies on biaxially oriented polypropylene show only the presence of one stem, and this also is equal in length to the SAXS value of the *d* spacing.

It is interesting to compare the Kratky plot at right angles to the direction of drawing (Figure 6) with that of isotropic polypropylene shown in Figure 4. The unusual feature is that the asymptotic value for the Kratky function, $I\kappa^2$ where $I = d\sum(\kappa)/d\Omega$, is nearly twice the value observed for the isotropic polymer. The reasons for this are not clear and more drawn systems need to be studied. It may not be due to the anisotropy of the system but to the fact that the molecule has contracted in this direction.

Finally, a comparison of the structure of the isotropic quenched polymer with the cold drawn samples shows that the latter is not merely an extension of the former. In fact the molecule has undergone a large reorganization in which some of the original lamellae have been fractured.

References and Notes

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Model Networks of End-Linked Poly(dimethylsiloxane) Chains. 8. Networks Having Cross-Links of Very High Functionality[‡]

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ABSTRACT: Elastomeric networks were prepared from poly(dimethylsiloxane) chains having vinyl groups at both ends. The chains were end-linked with the use of a series of cross-linking agents, including some containing a large number of reactive $Si(CH_3)H$ groups. The resulting networks had values of the cross-link functionality ϕ covering the approximate range 3–37. They were studied with regard to their stress–strain isotherms in elongation at 25 °C and their degree of equilibrium swelling in benzene at room temperature. The values of the modulus in the limits of large and small deformations, the degrees of equilibrium swelling, and the dependence of these properties on ϕ were found to be in satisfactory agreement with the recent molecular theory developed by Flory. The elastic constant $2C_2$, which characterizes the dependence of the modulus on elongation, was found to approach zero as ϕ increased to very large values. This important result is also in agreement with the Flory theory, which interprets the decrease in modulus with an increase in elongation as resulting from a continuous change from a nearly affine deformation to the highly nonaffine deformation characteristic of a "phantom" network.

Elastomeric networks consist of chain molecules joined at junctions (cross-links) which have a functionality ϕ of three or higher. As would be expected, the elastomeric properties of such materials strongly depend on the number density of such junctions in the network or, equivalently, on the average molecular weight between such junctions. There have, in fact, been an exceedingly large number of studies addressed to the problem of relating elastomeric properties such as the elongation modulus or equilibrium degree of swelling to this particular structural feature of a polymer network.[1,2]

In contrast, relatively little is known about the dependence of the elastomeric properties of a network on the *functionality* of its junction points. The desired relationships have been predicted in a number of molecular

[‡] It is a particular pleasure to dedicate this paper to Professor Paul J. Flory on the occasion of his 70th birthday.

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