POSSIBILITIES OF X-RAY SMALL ANGLE ANALYSIS IN THE INVESTIGATION OF DISSOLVED AND SOLID HIGH POLYMER SUBSTANCES

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INTRODUCTION

In diffuse diffraction processes the product of the linear dimension $D$ of the diffracting particles and the angle of scattering $2\theta$, up to which diffraction essentially occurs, is given by the wavelength $\lambda$. Thus, the size of the diffracting particles and the diffraction angles are inversely related. In this way with the normally used CuKa line of $\lambda = 1.54$ Å we shall get diffraction effects on colloidal objects at very small angles; in fact, X-ray small angle scattering occurs. By studying this phenomenon information on particles up to several thousand Ångstroms can be obtained since, with modern devices measurements to fractions of minutes of arc are often possible. On the other hand, the short-wave X-ray light is also capable of clarifying extremely delicate structural details. The information which can be deduced from light scattering in the whole range from zero angle to $180^\circ$ is equivalent to the information of the X-ray small angle scattering in a range which is smaller by a factor given approximately by the quotient of both wavelengths. The range is therefore of the order of magnitude of a few minutes of arc (i.e. about 1/1000 radians). All the information which small angle scattering gives at larger angles can no longer appear in the scattering of visible light. So we understand that with the increasing improvement in experimental technique small-angle analysis is constantly receiving a large number of new applications.

In this paper on high polymers in the dissolved and solid state we shall confine our remarks to diffuse small angle scattering and exclude the study of sharp small angle reflexes on the meridian of solid, stretched high polymers. We may suitably subdivide the discussion as follows:

(i) investigation of solutions by means of which we receive information regarding the “mean” properties of individual high polymer molecules;

(ii) study of the “loosened up” solid high polymers which bring about a “particle-scattering” of the supermolecular micellae or micellar-strands;

(iii) study of solid high polymers in the dense form which corresponds to the state in which these materials are usually technically applied. In this case we receive definite general figures connected with the composition ( pores, crystalline and amorphous fraction), the internal surfaces and the mean dimensions of the zones of uniform electron density.

* For summaries concerning the method and applications of the X-ray small angle scattering in general, see Guinier and Fournet¹, Beeman, Kacsberg, Anderegg and Webb², Kratky³, Porod⁴, Hosemann and Bagchi⁴ and Statton⁴.
HIGH POLYMER MOLECULES IN SOLUTION

According to the fundamental work of W. Kuhn and H. Kuhn, H. Mark and E. Guth, W. Haller and others we have to imagine that, as a result of the free rotation around the main bonds of the molecular skeleton, the linear high polymer molecules in solution behave like movable coils. At sufficiently small angles the shape of the scattering curve will approximate a Gaussian curve in the limit towards zero angle, as does every curve of a diluted system containing any particles of the size of the coils. This result can be understood as a general consequence of the Guinier theory of small angle scattering and of theories of light scattering on dissolved high polymer molecules (Debye, Zimm, Stein and Doty, and others). An exact treatment from the viewpoint of small angle scattering had been given by Peterlin.

With increasing scattering angle the sections of the molecule which co-operate interferentially become continually smaller and smaller, and the Gaussian zone will thus go over to a course which depends upon the geometry of the coils in smaller zones. In accordance with the present state of research we are going to study two types of coils for which detailed calculations of the scattering are already available. The first type is the statistically coiled chain molecule with persistence of direction; the second mode, which was only recently taken into consideration, is the coil with persistence in curvature.

But before entering into the details of the two types, we will discuss the general determination of two numbers which are very important in the characterization of every coiled macromolecule: the radius of gyration and the molecular weight.

The Radius of Gyration

With a sufficiently diluted macromolecular solution the equation for scattering of dissolved particles* in the range of very small angles, corresponds to a Gaussian distribution:

\[ I = I_0 e^{-KR^2\theta^2} \] (1a)

\( K \) is a universal constant \( ( = 16\pi^2/3\lambda^2) \), \( \theta \) is half the scattering angle and \( R \) is the radius of gyration, i.e., the square root of the average square distance of all scattering particles (electrons) from the centre of gravity. In the \( \ln \) form the equation reads:

\[ \ln I = \ln I_0 - KR^2\theta^2 \text{ or } \log I = \log I_0 - 1/2\cdot30 \cdot KR^2\theta^2 \] (1b)

\( \log I \) plotted as a function of \( \theta^2 \) ("Guinier-plot") with decreasing angles approximates a straight line; the slope in this zone, according to (1b), equals \( -1/2\cdot30 \cdot KR^2 \) so that we have

\[ R = [3 \times 2\cdot30 \left( -\tan \alpha/\lambda \right)]^{1/2} \lambda/4\pi \] (1c)

* One never obtains the scattering-curve of the dissolved particles as such; what is obtained is their superimposition with that of the solvent. The usual (if not completely correct) way is to take the difference of both curves, in other words, one has always to take a blind exposure or a blind measurement of the sample container filled with the pure solvent.
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These relations hold when a primary beam with point-shaped cross-section is used. For the sake of higher intensity a primary-beam with line-shaped cross-section is preferred. Here the scattering is modified by the collimation influence, which we have to eliminate*. When this has been completed the scattering curve, in the limit of very small angles, follows equation (1).

In order to obtain a correct result several points need particular attention:

(i) In the Guinier plot scattering curves of coiled high polymer molecules show a shape strongly curved convex towards the abscissa but, with sufficiently small angles, a straight lined zone must always appear which admits the determination of the limiting slope. As a hint for the highest angle up to which equation relation (1c) can be assumed to be valid, we can state that it corresponds to about a Bragg's value of 10 times the radius of gyration. When, for instance, \( R = 50 \, \text{Å} \), then the upper limit of the zone within which a linear scattering curve will occur is given by the equation

\[
\lambda = 500 \times 2\theta
\]

So \( 2\theta = \lambda/500 = 1.54/500 \approx 1/300 \text{ radians} \approx 0.2 \text{ degrees of arc} \).

(ii) There must be no fine particle contamination capable of influencing the zone of the smallest angles of the scattering curve. Very coarse particle contaminations ("dust"), which must at any rate be removed when the scattering of visible light is measured, are hardly a disturbing factor here because their scattering lies at extremely small angles which are not normally covered.

(iii) The solution must be sufficiently diluted otherwise interparticle interference effects appear leading to a reduction of the slope. Since a dilution in which there is complete freedom from interference effects is virtually unattainable, the only method is to study a concentration series down to the smallest possible concentration and to extrapolate \( \tan \alpha \), and the apparent radius of gyration \( R \), respectively, towards zero concentration.

(iv) The scattering contribution of the solvent in such diluted solutions is as a rule much larger than the scattering of dissolved macromolecules which is obtained by subtraction. Accordingly, the precision of both measurements must be much higher than the accuracy wanted for the difference. This fact, together with the extension of the measurements to low concentrations (according to iii) and the necessary fine collimation (according to i), makes such measurements often time consuming and it sometimes causes difficulties unsurmountable at present.

The molecular weight

With a sufficiently diluted solution, when the collimation error has been eliminated and the scattering curve in the Guinier-plot has been extrapolated to zero angle, the zero intensity \( I_0 \) can be obtained. This is the basis for the determination of molecular weight. From light scattering it is well known that, with a diluted colloidal solution of a given concentration, the

* The method of Guinier and Fournet\(^1\) for a primary beam of "infinite" length is often not applicable with dissolved coiled high polymer molecules. Normally we have to use the generalized method applicable for a primary beam of finite length\(^1\). The readers are referred to a summary of all questions pertinent to the collimation influence\(^1\) and to methods in our group\(^1\) for doing this work with the help of an electronic computer.

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scattered intensity extrapolated to the zero angle is proportional to the molecular weight. This also holds for X-ray small angle scattering and, from the absolute intensity, i.e. the relation of the scattered intensity to the intensity of the primary beam, the molecular weight can be directly calculated. We gave the general quantitative formulae in 1951 and demonstrated on various examples, especially protein molecules, the practicability of such measurements and the reliability of the results.

The following equation is valid:

\[ M = 21.0 \frac{I_0 r^2}{\sum P_0 d c (z_e)^2} \]  

where

- \( I_0 \) = scattered intensity extrapolated to the zero angle (after elimination of the collimation influence);
- \( \sum P_0 \) = the energy corresponding to 1 cm of the primary-beam;
- \( d \) = thickness of the sample in cm;
- \( c \) = concentration in g/cm³ solution;
- \( r \) = distance between sample and plane of registration in cm;

The constant signifies: 21·0 = 1/\( \eta e N \);

- \( \eta e \) = Thomson's constant, i.e. the scattering of the electron;
- \( N \) = Loschmidt's number;
- \( z_e \) = number of mole excess electrons per g of the solute;

And

\[ z_e = z_1 - v_1 \rho_2 \]  

where

- \( z_1 \) = mole electrons in 1 g of the solute;
- \( v_1 \) = partial specific volume of the solute;
- \( \rho_2 \) = electronic density of the solvent = electrons/cm³.

In order to get correct values the same measures have to be taken as with the determination of the radius of gyration. An essential point is the determination of the primary energy \( \sum P_0 \).

As will be shown later there is, under certain suppositions, the possibility that the molecular weight can be determined without absolute intensity measurements, but by a comparison of \( I_0 \) and the intensity of the tail end of the scattering curve.

The two quantities, \( R \) and \( M \) can also be determined by the aid of the scattering of visible light. We will see that the X-ray small angle method yields valuable additional information.

**Coils with persistence of direction**

We will discuss only those models, which are in a direct connection with the calculation of the small angle scattering.

The W. Kuhn model—W. Kuhn approximates the molecule by a zigzag chain with freely joined segments of equal length. The directions of the segments are given by pure chance (random flight model) and their number \( n \) and length \( A \) are determined in such a way that an accurate value of the
mean squared end-to-end distance \( \overline{r^2} \) is obtained. Furthermore, both model and real molecule show the same length \( L \) when stretched ("hydrodynamic length"). When these conditions are fulfilled we call \( A \) the statistical chain element and the following equations hold:

\[
\overline{r^2} = An^\frac{1}{2}\quad (\text{random flight formula})
\]

\[
L = An
\]

From (3) and (4) it follows immediately that

\[
A = \frac{\overline{r^2}}{L}
\]

The generalized link chain and the persistence model—Let us begin by approximating a coiled chain by means of several straight segments of length \( z \) which do not succeed each other according to "random flight", but show a persistence in direction. If we call the angle of direction of two successive segments \( \alpha \), then length \( z \) and \( \cos \alpha = k \) are the characterizing numbers for the coiling of the chain. Eyring\(^{16}\) has treated this model in his well-known paper in which his idea was to study the behaviour of the skeleton atoms of a chain molecule, with \((180 - \alpha)\) as the valence angle and \( z \) as the bond length with perfectly free rotation around all bond axes. We can understand this model in a wider sense, namely as an approximation of any coiled chain and without restriction as to the magnitude of \( \alpha \) and the azimuth \( \theta \) (Figure 1). Similarly to W. Kuhn’s model, end-to-end distance and length in the completely stretched state are presupposed to be the same in the real molecule and the model chain. The scattering masses are supposed to be located at the junctions as illustrated in Figure 1. There now arises the question

\[\text{Figure 1. Three links of a link-chain}\]

of how, with the approximation of one and the same real coil once by means of the W. Kuhn model and then by means of a link chain with fixed \( \cos \alpha = k \), the length of the statistical chain element \( A \) is related to the length \( z \) of a
The result is the simple relation:

\[ \frac{A}{z} = \frac{1 + k}{1 - k} \]  

(6)

This expression thus gives the number of straight elements which together replace one statistical chain element. With \( k = 0.8 \) (Figure 2 represents such a chain with 100 links), a statistical chain element corresponds to nine such straight lines.

Let us go one step further. If we join \( n \) straight elements with a direction change corresponding to a given \( \cos \alpha = k \) but with a purely random azimuth, the entire direction change, measured by the mean cosine with the initial direction, is given, according to Smoluchovsky, by \( k^n \). With the length of the stretched chain \( L \) we can also write

\[ k^n = k^{L/z} \]  

(7)

It is at once apparent that in order to obtain a better approximation of a continuously curved coil the straight segments \( z \) must converge towards zero and at the same time \( k \) must tend towards 1. In the limiting case, \( k^n \) becomes a quantity which changes continuously with \( L \), that is to say, it is a proper exponential function which we can write as a power of \( e \); since \( k < 1 \), it must, of course, have a negative exponent:

\[ k^{L/z} = e^{-L/a} \]  

(8)

When we advance along the coil the cosine of the angle with the initial direction drops down according to (8), i.e., in an exponential manner; along the path "\( a \)", which we call the "persistence length", it has diminished from 1 to \( e^{-1} \). This magnitude \( a \) is thus a measure of the tendency to maintain direction. The mean cosine with the original direction thus fades with
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the path along the molecule exactly as, for instance, the intensity of a ray of light in an absorbent medium as a function of the path, or the mass of a radioactive substance as a function of time. A simple consideration, which we will not repeat here, also permits the calculation of the mean square of the distance of two points \( \overline{r^2} \) between which a path \( L \) measured along the molecule axes exists. The following equation applies:

\[
\overline{r^2} = 2a(L - a + ae^{-L/a})
\]  

The application of these ideas signifies the replacement of the coiled molecule by a continuously crooked line, which we call the "persistence model" or the "worm-like chain". It is easy to see that equation (9) also fulfills expectations in respect of limiting cases. For very small \( L \) values we have:

\[
\lim_{L \to 0} \overline{r^2} = L^2
\]

that is to say, a perfect straight form. For very large \( L \) values, on the other hand, we have:

\[
\lim_{L \to \infty} \overline{r^2} = 2aL
\]

Comparison with the random-flight formula (5) of W. Kuhn applied over great distance shows that

\[
2a = A
\]

This equation together with (6) immediately shows that with substitution of a link chain by a worm-like chain of the same end-to-end distance and length in the stretched state, the persistence lengths will correspond to

\[
\frac{a}{z} = \frac{1}{2} \times \frac{1 + \cos a}{1 - \cos a}
\]

links.

The relation between the hydrodynamic length, the persistence length and the radius of gyration—The important question now arises as to how the radius of gyration of the coiled chain is connected with the hydrodynamic length \( L \) when the degree of coiling—the persistence length—is known. From the molecular weight \( M \), the weight \( M_m \) and length \( l \) of the monomer we immediately find \( L \)

\[
L = l \times M/M_m
\]

The number \( x \) of persistence lengths "\( a \)" of which the molecule is built up is

\[
x = L/a
\]

For very long chains equation (11) gives the end-to-end distance. Division \( 6^\frac{1}{2} \) gives the radius of gyration.

\[
R = (2aL)^{\frac{1}{2}}/6^\frac{1}{2}
\]

For short chains the problem has been treated by Peterlin and our group. The relationship between the number of persistence lengths and the radius of gyration is shown in Figure 3.
So far we have supposed that the short range order continues unlimited to long ranges. It is well known, however, that the radius of gyration will change if a not indifferent solvent is used. In a “good” solvent or, quite generally, above the $\Theta$-temperature it can amount to twice and more of the value it has at the $\Theta$-point. There are now two possible limiting interpretations of this effect with respect to the statistic of the shape. Either (a) a change in persistence lengths causes a corresponding change in radius of gyration without disturbance of the statistic, or (b) the short range order and, therefore, the persistence length is unchanged, but the long range order no longer corresponds to the Gaussian statistic. G. V. Schulz et al. have studied this question and have come—by indirect experimental evidence, however—to the conclusion that the latter assumption is much more probable. According to them the increase of the radius of gyration in good solvents (as compared with indifferent ones) comes about by the fact that a statistical exclusion occurs for those configurations where sections which are distant from each other within the molecule come near each other.

Now the small angle method offers a way of deciding between these two possibilities. Measurements currently available are in favour of a persistence length independent of the solvent [compare measurements of Kirste and Kratky on poly(methylmethacrylate)]. On the one hand, it is obviously not permissible to generalize this result but, on the other hand, a relationship between persistence length and radius of gyration according to Figure 2 for a high molecular weight is only to be expected with certainty at the $\Theta$-point. Finally, if the relationship according to Figure 2 holds, then it is proved that the behaviour of the solvent is at least near to an indifferent one. It is plausible to assume that this case will occur preferentially the stiffer the molecules are.

But there is a second reason for a difference between the calculated radius of gyration (from $M$ and $a$) and the directly measured value: the polydispersity. The latter is caused by the fact that the averaging is done differently for $R$ (z-average) and $M$ (weight-average). As a rule, the average $R$ will
always be larger than $R$ corresponding to the averaged $M$ and $I_0$ respectively. The calculated radius of gyration will therefore lag behind that which is obtained by direct measurements. In order to use such a comparison for getting a characteristic measure for polydispersity, it will be necessary to use $\Theta$-solvents. So far, practically no work has been done in this direction.

The small range order—Many attempts have been made\textsuperscript{16, 21–25, 27, 28} to relate the persistence length (cf. W. Kuhn’s statistical chain element) with bond lengths, bond angle and the short range interaction, e.g., free rotation, independent hindered rotation, interdependent hindered rotation. This problem will not be treated here in detail as the very small angle method normally makes no direct contribution to it; it leaves open the interpretation of measured persistence lengths in terms of the above mentioned bond properties.

Nevertheless, we will give some hints as to possible lines of study. We start from ideas put forward by the author and Worthmann\textsuperscript{29}. We were aiming at measuring the intramolecular distance of two iodine atoms in dissolved low molecular compounds. For this purpose we subtracted from the scattering of the di-iodine compound solution that of the solution of the corresponding monoiodine compound, so that the same number of iodine atoms were in both solutions. It is obvious that scattering due to iodine atoms is eliminated by this subtraction. The same holds for all interference effects between the iodine atoms and their surroundings since it is practically the same in both solutions. What remains is the interference effect originating from the two iodine atoms in a fixed distance within the solution of the di-iodine compound. Dividing this by the iodine form factor we get a scattering of $\sin x/\lambda$ where $x = 4\pi l \sin/\lambda$, where $l$ is the mutual distance of the atoms. This method was successful in measurement of the end-to-end distance in different compounds\textsuperscript{29, 30}.

In the same way, the interference effect and, therefore, the mutual distances of heavy atoms (iodine or bromine) substituted in a high polymer chain can be found by subtracting the scattering of the two solutions: the high polymer and the substituted monomer, both containing the same number of heavy atoms. The only two papers—known to the author—based on this idea are those of Brady \textit{et al.}\textsuperscript{31, 32}. They will be discussed later.

The four sections of the scattering-curve—Let us recall the statement that the scattering curve at very small angles has the shape of a Gauss curve. As already proved by Debye's\textsuperscript{8} theory of light scattering for statistically coiled high polymer molecules, the Gauss branch is followed by a $1/\lambda^2$ branch. Its appearance may be seen as an expression of the random arrangement of scattering masses. The scattering at still larger angles will be caused by the behaviour of still smaller sections of the molecule, which can be considered as more and more stretched. As they will occupy all possible directions the scattering effect will correspond to that of a gas of thin needles, which is given by $1/\lambda^4$. There are, of course, transitional zones between the three branches, as shown schematically in Figure 4a. Finally, the periodicities arising from the succession of monomers or strongly scattering atoms along
them can be observed when the molecules are not too strongly coiled. This is discussed in the preceding section. However, this zone no longer belongs to the very small angle scattering.

The position of the transition point between the $1/\theta^2$ and the $1/\theta$ branch—The greater the mean length of the segments of the polymer molecule which can still be called stretched, the smaller are the angles to which the $1/\theta$ branch is extended. In a plot of $1/\theta^2$ towards $\theta$ (Figure 4b) the situation becomes particularly clear. The $1/\theta^2$ branch then becomes a horizontal line; the $1/\theta$ branch becomes an ascending line which, in its leftward extension, goes through the origin; and, finally the Gauss branch becomes a zone which descends towards the origin. By means of extrapolation of the two straight line branches in a direction towards their transition zone we get a characteristic point. It can be directly concluded from the principle of reciprocity in diffraction processes that, between any figures measuring the degree of coiling and the abscissa $\theta^*$ (to be exact: $\sin \theta^*$) of this characteristic point, there must be an inverse proportional relation:

$$a = K 1/\theta^*$$  \hspace{1cm} (17)

The persistence length can thus be deduced from the position of the characteristic point if we succeed in determining the proportionality constant in (17). We arrive at an answer to this important problem by extrapolation of the $1/\theta^2$ and $1/\theta$ branches bearing in mind, of course, their relative intensities. Passing over the calculation given by Porod35, we content ourselves with the result:

$$a = \frac{2\pi^2}{3} \times \frac{1}{\theta^*} = \frac{\lambda}{6.57} \frac{1}{\theta^*}$$  \hspace{1cm} (18)

The relation can be clearly formulated as follows: from the abscissa of the transition point a “net plane distance” $D = \lambda/2\theta^*$ is purely formally calculated. By insertion in (18) we then have

$$a = D/3.29$$  \hspace{1cm} (19)

Division of the Braggs value by 3.29, therefore, gives the persistence length $a$. By substituting $s = 4\pi \theta/\lambda$ and $s^* = 4\pi \theta^*/\lambda$ into (18) we find

$$u^* = as^* = 6/\pi \approx 1.91$$  \hspace{1cm} (20)
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It may be mentioned, however, that a derivation of the complete scattering curve by a statistical method, to be discussed later\textsuperscript{19}, yielded the following result:

\[ u^* = \frac{a \times 4\pi \beta^*}{\lambda} = 2.3 \]  

(21)

We will give preference to the latter value with respect to certain experimental results. With this number we get the relation

\[ a = D/2.73 \]  

(22)

This result is independent of the exact shape of the scattering curve in the transition zone.

The exact calculation of the scattering curve on the basis of the persistence model and the link-chain—The first calculation of a scattering curve was given in cooperation with G. Porod\textsuperscript{18} by means of the persistence model. In a refinement Porod\textsuperscript{35} used a link chain with \( \cos \alpha = 0.8 \) (Figure 2). Figure 5 shows the comparison of the two results for chains of infinite length; in Figure 6 the

\[ u = a \times \frac{4\pi}{\lambda} \sin \theta \]

\[ u = a \times \frac{4\pi}{\lambda} \sin \theta \]

Figure 5. Scattering curves of coils of infinite length; (1) persistence model, first approximation (Kratky–Porod\textsuperscript{18}); (2) link chain, \( \cos \alpha = 0.8 \) (Porod\textsuperscript{35})

\[ u = a \times \frac{4\pi}{\lambda} \sin \theta \]

\[ u = a \times \frac{4\pi}{\lambda} \sin \theta \]

Figure 6. Plot of \( I \beta^2 \) towards \( \theta \) of the curves of Figure 5

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$Iq^2$ curves are shown. The Gauss branch, of course, is missing and it can be seen that the two straight-line zones appear very distinctly. It is also noteworthy that, particularly in Porod's better approach, the transition point in fact lies very close to the value which was to be expected from the foregoing consideration of the intensity, namely at $u^* = a_s^* = 2.00$. In this way the general calculation also leads to a result which, even after further refinement, has suffered no alteration. Deviating from the behaviour to be expected according to the theory of light scattering, an ascending branch in the $Iq^2$ representation appears. Its zone of transition into the horizontal branch makes a direct calculation of the persistence length possible.

An improvement has been suggested by J. J. Hermans and R. Ullmann and, in a more recent paper, J. Hermans and J. J. Hermans succeeded in treating the scattering of the worm-like chain continually covered with masses. There is no essential deviation from the results discussed above. Without going into details we refer to further contributions of Daniels, Stockes and Volkenstein.

So far we have dealt with chains of infinite length. Chains of finite length become interesting from the viewpoint of X-ray small angle scattering insofar as we succeed, by means of a sufficiently high resolution, in measuring the Gaussian branch at smallest angles, and insofar as sufficiently dilute solutions (dispersion of the molecules felt into individual molecules) can be depicted.

Figure 7. Dependence of the scattering curve of a chain with 250 links, $\cos \alpha = 0.8$, on the number $q$ of individual configurations: $q$ equals $\times 50$; $\Delta$, 72; $\bigcirc$, 100; $\square$, 150; $\nabla$, 250; $\bigcirc$, 350 (Heine-Kratky-Roppert)
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investigated. Analytical calculations of the scattering curve have been given in successive approximations by Peterlin, and using the calculations of J. J. Hermans and R. Ulman of $\frac{r^2 n}{\nu}$, by Heine, Kratky, Porod and Schmitz. According to Heine's discussion of these calculations it is difficult to see at the moment what approximation we should have to go to in order to get completely accurate results by analysis.

A statistical method suggested by Peterlin is free from the mathematical difficulties of the analytical method. A link-chain is constructed according to the requirements of statistical shape with the azimuth, which an additional chain-link occupies on the rotatory cone around the direction of the preceding, determined with the aid of a chance number given by an electronic computer. After a certain number of links have been joined a particular configuration of a coiled chain (Monte-Carlo method) is arrived at. If scattering masses are assumed to be localized at all junctions the scattering curve of this chain can be calculated if it occupies all spatial positions with equal frequency. The basis of this calculation is offered by the Debye formula for the scattering of a gas. This may be applied directly because, for this one special configuration, all intramolecular distances between scattering masses are known. It is then possible to produce further configurations with the aid of random numbers, by allowing the machine to calculate the scattering curve in every case and superimpose all curves.

Figure 7

Figure 8. Scattering curves of link chains $\cos \alpha = 0.8$ in the plot of $s^2 I$ towards $s$ calculated by the Monte Carlo method with the number of persistence lengths as parameter (at the margin). (Heine-Kratky-Roppert)
demonstrates how, as the number of the individual configurations increases, curves arise which are more and more smoothed out, so that we finally have a curve which is characteristic of a coiled chain with the corresponding number of links and the given cosine of the angle between two successive links.

Peterlin has calculated curves up to 40 persistence lengths. We have increased the accuracy and calculated the scattering-curves for a sufficient number of chain lengths, up to chains of 100 persistence lengths (Heine, Kratky and Roppert\textsuperscript{19}; Figures 8 and 9). The agreement with earlier curves of this type is quite reasonable but, in detail, there are also deviations from the curves calculated in the same way by Peterlin, namely:

(i) the transition point between the second and third branch is clearly defined for chains which are not too short and lies at $u^* = 2.3$ (instead of 2);

(ii) The middle branch is not horizontal even for relatively long chains but rises slightly with increasing angle.

To substantiate these results a further refinement has been carried through in our group by S. Heine\textsuperscript{20}. He investigated the effect of an excluded volume by arranging spheres along the links and excluding all configurations where a mutual penetration of spheres belonging to different links occurs. The result was that the influence on the scattering curve is practically negligible.

Finally, Heine\textsuperscript{20} studied the problem of whether scattering masses on the link chains are arranged close enough to correspond in a practical way to a
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continuous distribution of matter. He was able to ensure that scattering masses along the links of chains with $\cos \alpha = 0.8$ or 0.9, in addition to those at the junctions, have nearly no effect on the scattering within the three branches under discussion.

With respect to these results, we consider the curves in Figures 8 and 9 (and similar curves we have for $\cos \alpha = 0.9$) as the most exact ones available so far, the more so as they coincide with recent experimental findings of high accuracy.

A study by Benoit and Luzzati [47] investigates a more complicated model. Here, chain crossings, branchings and any number of ends within a coil are admitted. These peculiarities cause a $1/\theta^2$-zone in the scattering curve. Benoit and Luzzati conclude from this that, for the appearance of this zone in experimental curves, the above mentioned phenomena alone are responsible and that the simpler pattern which we ourselves have used cannot explain this species of scattering curve. When crossing and additional free ends are missing the Gauss zone must, accordingly, go over directly into the zone of the rigid rod. In general, however, the theoretical results discussed above demonstrate convincingly that the flexible chain, as well as the link chain without additional ends, crossing etc., yield the characteristic curve shape. It must, of course, always be borne in mind that additional crossings or ends not given by the statistical coiled chain contribute to the intensity of the $1/\theta^2$-branch and can cause a shift of the transition point to larger angles. This fact is particularly noticeable in analysis of the scattering behaviour of strongly branched molecules or unrinsed coils and of highly concentrated systems.

The cross-section factor and the mass per unit length—We have mentioned repeatedly that a gas of needles of infinitely thin cross-section yields a scattering curve according to $1/\theta$ and that the same holds for the tail end of the small angle curve of coiled thin macromolecules. However, if this cross-section is of finite area, we have (as well with a gas of needles as with coiled macromolecules)

$$I = I_q \times 1/\theta \quad I_q = I \theta$$

(23)

Here $I_q$ is the so-called cross-section factor which is determined by the dimension of the cross-section [38]. For its dependence on the scattering angle those general relations nearly hold which are valid for the intensity $I$ scattered by particles. Therefore, by plotting $\ln I_q \equiv \ln I \theta$ v. $\theta^2$ and extrapolating to zero angle (cf. Figure 10), we obtain on the one hand $(I_q)_0 \equiv (I\theta)_0$ and, on the other, the value $- KR_q^2$ from the slope $\tan \alpha$ of the terminal tangent; from this the radius of gyration of the cross-section can be calculated:

$$R_q = [2 \times 2.30 (- \tan \alpha)_0]^{1/2} \lambda / 4\pi$$

(24)

Analogous to the determination of the molecular weight is that of mass per unit length obtained from the quotient of zero intensity of the cross-section factor $(I\theta)_0$ and the primary intensity. After the elimination of the collimation error the following formula applies:
This relation was first reported in 1953\textsuperscript{48} and first applied in 1955\textsuperscript{49} and 1958\textsuperscript{50}. The extrapolation described is necessary when the rods are relatively thick, for instance, with nucleic acids. In the case of high polymers consisting of single chains the situation will mostly be simpler however. As a result of their small spatial dimension the radius of gyration of the cross-section amounts to only a few Å and thus the cross-section factor will fall only very slowly. Therefore, in the $I_\theta$ plot a practically horizontal zone will be found as a rule (Figure 11), and extrapolation to the zero angle is not necessary.

\begin{equation}
\frac{M}{\AA} = 27.3 \left( \frac{I_\theta}{\theta^2} \right) \frac{2}{\sum P_{0dc}(z_0)^2} \tag{25a}
\end{equation}

\begin{equation}
27.3 = \frac{2}{i_0 N \lambda (\text{CuK}_\alpha)} \tag{25b}
\end{equation}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure10.png}
\caption{Scheme of the cross-section factor ($I_\theta$) in the Guinier-plot}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure11.png}
\caption{Scheme of the cross-section factor ($I_\theta$) for very thin coiled molecules}
\end{figure}

At small angles here a steep ascent is superimposed, originating from the $1/\theta^2$ branch. Proceeding to really large angles we will of course, find a decrease in cross-section factor. When the spatial dimensions are of the same order of magnitude as the persistence length the matter gets more complicated. We refer to a paper of Kirste\textsuperscript{51} which deals with this problem.
SMALL ANGLE ANALYSIS OF HIGH POLYMERS

When weight $M_m$ and length $l$ of the monomer are known a degree of association $f$ can be calculated which, however, will normally be $f = 1$. Then the following formula applies:

$$M/A = f M_m/1$$  \hspace{1cm} (26)

It is useful to introduce the number of excess electrons $n_e$ for the monomer

$$n_e = z_e M_m$$ \hspace{1cm} (27)

(27) and (26) inserted in (25) gives

$$f = \frac{27 \cdot 3 (I\theta)_0 M_m l^2}{\Sigma P_0 d(n_e)^2 c}$$  \hspace{1cm} (28)

In most cases we will be sure that $f = 1$ and, therefore, from the chemistry and geometry of the monomer we can easily calculate the mass per unit length $M/A$. In this case the comparison of (2) and (25) opens the possibility of determining the molecular weight from the ratio of $I_0$ to $(I\theta)_0$; according to these equations we can obtain directly (O. Kratky and G. Puchwein, unpublished work):

$$\frac{M}{M/A} = L = \frac{\lambda I_0}{2 (I\theta)_0} = 0.77 \frac{I_0}{(I\theta)_0}$$ \hspace{1cm} (29a)

So we overcome two essential difficulties normally connected with the determination of the molecular weight. First, we need no absolute intensity measurements, i.e. the measurement of the primary energy $\Sigma P_0$ and, secondly, we avoid the determination of the excess electrons $z_e$ by extremely careful density measurement of the solution, which yields the partial specific volume $v_1$ and with (2b) gives $z_e$. We also prevent inaccuracies brought into the result by $r$, $d$ and $c$. We can write equation (29a) with the help of (26) in a modified form:

$$\frac{M}{M_m} = P = 0.77 \frac{1}{l} \frac{I_0}{(I\theta)_0}$$ \hspace{1cm} (29b)

Measurements on coiled molecules with persistence of direction

The first measurements undertaken in 1942\textsuperscript{52} were carried out on cellulose nitrate dissolved in acetone. While neither the pure solvent nor the dry film of cellulose nitrate showed appreciable small angle scattering, a scattering of the solution was discovered which was roughly proportional to the concentration and which increased greatly in intensity as the angle decreased. In this way proof was obtained that colloid molecules produce an easily measurable small angle scattering even when they have a colloid dimension in one direction only and low molecular dimensions in the others. We continued these investigations after the war.

High molecular weight nitrated cotton of $P = 3500$, with $N = 14$ per cent in acetone solution, shows the typical course expected for every large coils\textsuperscript{43} (Figure 12). In these measurements the innermost Gauss zone could not be observed. The intensity of the tail end yielded with the help of (28) exactly the degree of association $f = 1$; this means that the scattering curve can be understood as the effect of a coiled macromolecule. As concentration decreases, the transition point between the $1/\theta$ and the $1/\theta^2$ branch is shifted.
to smaller angles. As the tail end recalculated to equal concentration has always the same intensity, this result can be described by stating that, with increasing concentration, the intensity of the horizontal zone, also recalculated to equal concentrations (i.e. of the $1/\theta^2$ branch in the normal plotting), is growing. The higher the concentration, the greater the mutual penetration of the molecular coils. It is entirely conceivable that the resultant crossings, which exceed those caused by the statistics of the individual molecule, may give rise to an additional contribution to the intensity of the $1/\theta^2$ branch in the sense of Benoit and Luzzati\textsuperscript{47}. Also, of course, by the compression which the coils exercise on each other, there could result a real diminution of the persistence length, which in the scattering curve would cause the same effect. The problem must be left unsolved for the time being.

If we calculate the persistence length in all measurements purely formally according to (21) and extrapolate it on the concentration zero, we obtain the value of $a = 110 \, \text{Å}$. However, this dependence is not a linear one, so that the given value is not completely ensured. An extension of these measurements to smaller concentration is therefore desirable. However, the result is in good agreement with the findings of light scattering measurements. It seems obvious that there is a strong dependence of the coiling on the $N$ content, since with a lowering from 14·14 per cent to 13·83 per cent ($P = 1640$), $a$ falls by about 20 per cent\textsuperscript{43}.

The same tendency is also shown by the measurements in Figure 13\textsuperscript{*}) on four samples of low molecular cellulose nitrates with $N$-contents of around 12 and 11 per cent. The persistence lengths, based on measurements with 0·5 per cent acetone solutions, are found in the first case to equal 58 Å on the

\* O. Kratky, H. Leopold, and G. Puchwein, unpublished measurements, carried through on suggestion by and under the sponsorship of Du Pont de Nemours Comp., Explosive Dept. We wish to use the occasion to express our sincere thanks for this help.
SMALL ANGLE ANALYSIS OF HIGH POLYMERS

Figure 13. \( I^{2}\)-curves of low molecular cellulose nitrates \( c = 0.5\% \); \( a \): solutions in acetone; \( p \): solutions in poor mixed solvents; the numbers refer to Tables 1 and 2 (Kratky-Leopold-Puchwein)

average, and in the second to equal 52 Å using \( \lambda^* = 2.3 \) as demanded by the results of the “Monte Carlo method” (Table 1); solutions in poor solvents give average values of 50 Å and 41 Å respectively (Table 2). In these \( I^{2}\)-curves (Figure 13) we see for the first time an increase of the intermediate branch markedly deviating from the \( 1/\theta^2 \) course, as demanded by the calculation based on the Monte Carlo method for chains of finite length. The transition point is clearly marked. The degree of polymerization is calculated for acetone solutions according to equation (29b) by comparison of the intensity at zero angle (Figure 14) and the value \( (I\theta)_0 \) of the \( 1/\theta \)-branch (Figure 12), together with the known mass of the monomer. Then the radius of gyration \( R_{\text{ealc}} \) obtained according to Figure 3 from the degree of polymerization and the persistence length can be compared with that deduced from

Table 1. Low molecular cellulose nitrates in acetone solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>( N ) (%)</th>
<th>( P )</th>
<th>( a )</th>
<th>( x = L/a )</th>
<th>( R_{\text{exp}} ) (Å)</th>
<th>( R_{\text{ealc}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.08</td>
<td>78</td>
<td>54.3</td>
<td>7.4</td>
<td>83.5</td>
<td>72.2</td>
</tr>
<tr>
<td>2</td>
<td>11.19</td>
<td>145</td>
<td>49.5</td>
<td>15.2</td>
<td>115.5</td>
<td>101.5</td>
</tr>
<tr>
<td>3</td>
<td>11.96</td>
<td>90</td>
<td>56.5</td>
<td>8.2</td>
<td>89</td>
<td>80.8</td>
</tr>
<tr>
<td>4</td>
<td>12.09</td>
<td>157</td>
<td>59.5</td>
<td>13.6</td>
<td>133</td>
<td>113.0</td>
</tr>
</tbody>
</table>

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Table 2. Low molecular Cellulose nitrates in poor solvents

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (%)</th>
<th>P</th>
<th>a</th>
<th>x = L/a</th>
<th>R_{exp} (Å)</th>
<th>R_{calc} (Å)</th>
<th>Cluster (%)</th>
<th>R_{exp} cluster (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.98</td>
<td>78</td>
<td>36.9</td>
<td>19.95</td>
<td>71</td>
<td>62.7</td>
<td>17</td>
<td>204</td>
</tr>
<tr>
<td>2</td>
<td>11.19</td>
<td>145</td>
<td>44.2</td>
<td>16.95</td>
<td>110.5</td>
<td>97.1</td>
<td>13.4</td>
<td>212</td>
</tr>
<tr>
<td>3</td>
<td>11.96</td>
<td>90</td>
<td>49.6</td>
<td>9.3</td>
<td>83</td>
<td>77.0</td>
<td>13</td>
<td>198</td>
</tr>
</tbody>
</table>

Figure 14. Guinier-plot of the scattering curves of the low molecular cellulose nitrates in acetone solution, c = 0.5% (Kratky-Leopold-Puchwein)
SMALL ANGLE ANALYSIS OF HIGH POLYMERS

Guinier's plot $R_{\text{exp}}$ (Table 1, Figure 14). The latter is higher by about 15 per cent on the average, obviously due to polydispersity.

On the one side it may be stressed that the inclination of the middle branch varies in an irregular manner and there is no dependence on the number of persistence lengths according to the tendency of Figures 8 and 9. We conclude from this behaviour that the inclination of the middle zone is very sensitive to influences of a yet unknown type (perhaps due to inhomogeneities of the nitration along the chain); and similarly it depends strongly on the method of the calculation of the scattering curve. A quantitative evaluation of the inclination of the middle branch is, therefore, not possible at present.

The transition point, on the other hand, is very clearly defined. As expected, the persistence lengths for the two samples of about 11 per cent nitrogen content are shorter (average $\approx 52\,\text{Å}$) than those of the two samples of about 12 per cent nitrogen content (average $\approx 58\,\text{Å}$). This difference, however, is not very impressive since the differences between the samples of the same nitrogen content are of the same order of magnitude.

For three of these samples measurements in a poor mixed solvent are available (Table 2, Figure 15). As compared with the $1/\theta$ branch the zero intensity is much higher than is expected according to equation (29b) when using the degree of polymerization found in acetone. Obviously the substance is partly forming clusters which cause a steep increase at smallest angles. In Figure 15 the intercept of the end tangent (full line) with the ordinate give the experimental zero intensity, the points marked on the ordinate (double circles) correspond to the calculated values. It has been taken into account (by a calculation which we can skip here) that by the formation of clusters (Table 2 gives their portions) the concentration of the single molecules is correspondingly lowered. Now it is easy to split off the scattering curves of the single molecules. They start at zero angle from the marked points, follow the broken lines and finally make a smooth transition to the experimental curve. The slopes of the end tangents (broken lines) yield the values $R_{\text{exp}}$ of Table 2. The difference between $R_{\text{exp}}$ and $R_{\text{cal}}$ (from $P$ and $a$) is of the same order of magnitude as in acetone solution. The position of the transition point is unaffected by this operation and so, therefore, is the persistence length. The calculated figures, given in Table 2 are definitely smaller than those in acetone. It may be mentioned that the formation of clusters, as taking place here in poor solvents (Figure 15) is obviously caused by ageing of the samples. Recently studied samples which were prepared freshly showed this effect in poor solvents only in those cases in which optically distinctive "hazes" were observed too.

Obviously we have here the case where a poor solvent reduces the persistence length. This changed short range order, with unperturbed (= Gaussian) long range order, yields a correspondingly smaller radius of gyration. This result need not contradict the ideas of G. V. Schulz$^{24, 25}$ since, for so extremely stretched molecules like cellulose nitrate in sufficiently dilute solution, there will be almost no mutual long range influence of distant parts of the molecule. Thus the short range order is simply continued according to random walk statistics. The constancy of the persistence length in different solvents, as predicted by G. V. Schulz and others obviously

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needs to be valid only for indifferent and "good" (i.e. better than indifferent) solvents. In our case, however, the deviation occurs in solvents being so poor that even clusters partly form.

If cellulose nitrate is an example of a comparatively stretched (stiff) molecule, rubber represents a particularly strongly coiled molecule. Investigations have been carried out by the author and Sand53.

We will now discuss the preparation of solutions. Purified crêpe of very low protein content, further ameripol NS and buna 150 were investigated. Suitable solvents for crêpe and ameripol are hexane and di-isopropylether while toluene is used for buna. Solutions of crêpe centrifuged at about 15000 g for 15 min, exhibit an irregular behaviour in the range of angles corresponding to Bragg's values of 50–500 Å—obviously a result of cluster scattering. Contributions made by these effects in the neighbourhood of 100 Å, present in all samples, can be eliminated by boiling. The clusters are probably residues of the better ordered aggregates of the solid state. Ultracentrifugation (1 hour at 100,000 g) eliminates the remaining disturbances. As this effect was

Figure 15. Guinier-plot of the scattering curves of low molecular cellulose-nitrates, dissolved in poor mixed solvents, \( \epsilon = 0.5\% \) (Kratky–Leopold–Puchwein)
found with natural rubber only it seems to be of native origin. Probably the particles are connected or identical with the supermolecular ones found by Schoon and Grasenick by electromicroscopical investigations. The solutions are invariant with continued ultracentrifugation, boiling and dilution and exhibit a scattering from the smallest angles up to about 10 Å corresponding exactly to $1/\beta^2$. This limiting behaviour is obviously due to molecules, which have not clustered, so that the small angle scattering experiment seems to be an excellent method for proving the absence of clusters, for homogeneity and purity.

Due to the poor scattering intensity as compared with the solvent, a precise determination of the persistence length was difficult. The most reliable measurements of hexane solutions give values in the neighbourhood of 6 Å. But the concentration was rather high (1·3–4 per cent), so that a repetition of these measurements applying the improved techniques of today is desirable.

One more interesting effect found with crêpe solution in hexane may be reported. By storing the purified solution at 0°C for several weeks it developed a peak superimposed on the $1/\beta^2$ branch, very similar to that which can be removed by boiling the unpurified solution. We assume that on cooling, ordered aggregates are built.

Measurements on polystyrene have been described in three short communications by Wada and Okano. In the first one (1963) preliminary results on two high molecular samples are reported. In two $\Theta$-solvents (cyclohexane at 34°C and methylcyclohexane at 67°C) a persistent length of $\approx 10$ Å was found; in three other solvents (methyl ethyl ketone, toluene and acetone at 22°–34°C) values mainly between 10 and 13 Å (with one exception of 16·5 Å) are found. In the second paper (1964), the persistence lengths are given for samples of different molecular weight in four solvents. The same values are found obviously within the limit of error, lying in the range from 8–10 Å. The concentrations of solutions under investigation are rather high (in most cases 5 per cent) and no concentration series have been measured. Nevertheless, the findings coincide within the limits of error with the values of the persistence lengths derived by the authors under the assumption of a statistical coil from $M$ and $R$ measured with other methods. So the results as a whole seem to justify neglecting any influence the solvents might have on the long range order.

In the third paper (1965), two measurements on oligostyrene are reported. They correspond to the type of the theoretical curves of Peterlin for short chains.

An interesting contribution to the short range order of polystyrene is that of Brady et al. with the help of introduction of iodine atoms, based on the ideas developed with low molecular compounds. A comparison of $p$-iodopolystyrene solution with a substance practically corresponding to the monomer, namely $p$-iodotoluene was negative, insofar as there was no difference. From this it could be concluded that there cannot be established a periodicity of iodine atoms; their arrangement along the chain is essentially equivalent to that of the monomer solution. The result demonstrates directly that a random coil conformation of very short segment length characterizes the structure. It is not the tacticity but rather the conformation...
of the backbone itself, which causes the absence of characteristic mutual
distances of the iodine atoms within the chain. This result is in agreement
with that reported above of Wada and Okano who found a persistence
length of about 10 Å.

In a second paper Brady et al. investigated in the same way, the short
range order in 3,5-dibromo-L-tyrosine dissolved in dimethylformamide, by
comparison with 2,6-dibromophenol in the same solvent. Interbromine
spacings measured in a right-handed α-helix with side groups restricted to
rigid positions of maximum fluctuation give moderate agreement with
experiment. Very good agreement with observation is obtained by allowing for
a small oscillation of the phenyl rings.

**Coils with persistence of curvature**

In the calculation given earlier it was the intention to find out the typical
scattering function of the coiled molecule. There should thus be only one
series of curves: one for each number of persistence lengths (viz. the correspon-
ding number of links), being broader or smaller depending inversely on
the absolute value of the persistence length. Indeed most of the measure-
ments corresponded in fact to this concept of a uniform theory, notwithstanding the fact that it was always clear that the various chemical struc-
tures must lead to individual differences in small zones. However, as long
as no clear divergencies from the theory of the wormlike chain could be
found, there was no occasion to introduce new concept or further parameters
into the theory. It was discovered a few years ago that the scattering curve
of atactic poly(methyl methacrylate)* diverges significantly from the known
type: namely in that as a maximum in the increasing branch of the $I\theta^2$-plot
appears (Figure 16). In that paper the preliminary explanation has been

![Figure 16](image_url)

* It is true as Kirste stated at a later stage, that 80 per cent of the sample corresponded
to the syndiotactic form.

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given that the forces of the substituted groups acting along the chain on short distances favour the development of a helical structure in small zones, without being able to bring about a corresponding long range order. The result, however, is that the radii of curvature corresponding to this helical structure occur more frequently than is allowed by statistics of random walk. The weak maximum can be brought into a reasonable connection with this assumption. A similar interpretation of this maximum has later been given by Fedorow and Ptitsyn. These measurements have been difficult, as the difference between the scattering of the solution and that of the solvent is, at medium and large angles, only a small fraction of both (Figure 17).

Referring to these results, Kirste and Wunderlich have investigated the dependence of the scattering curve upon the tacticity of the same substance. The essential point is that the isotactic form behaves according to the worm-like chain, while the syndiotactic form diverges strongly therefrom. An interpretation for the latter curve could indeed be given by the assumption of a perturbed helical structure. In an attempt to obtain a quantitative interpretation Kirste and Wunderlich introduced the concept of curvature persistency besides that of the direction persistency. We can best understand its nature if we refer back to the construction of a statistically coiled chain made of links. Hitherto we have assumed that the azimuth of a link lying on the cone described around the preceding is given purely statistically. Now we assume that the azimuth can vary only within an interval; then the average positions of successive links will form a helical line. The size—or, to put it more accurately, the smallness—of the interval is a measure for the curvature persistency. Kirste and Wunderlich were then able, by means of superposition of scattering curves of direction persistency and curvature persistency, to approximate the actual conduct in a convincing fashion. Further efforts along these lines are highly desirable and likely to prove of great interest.
O. KRATKY

This expansion constitutes an appreciable enrichment of our ideas on the conduct of coiled molecules in solution.

Although the number of measurements of dissolved high polymer molecules is as yet small it should be possible to conclude from the above that theoretical foundations and experimental methods constitute a sound basis for successful further studies in this field.

### HIGH POLYMERS IN THE SOLID STATE

#### Basic relations

The absolute value of the invariant—The volume fractions of the phases which build up a system and their electron densities give the first overall characterization of a system. Now, according to the theories of Debye\(^5\) and Porod\(^8\), an invariant quantity can be defined by:

\[
Q = \int_0^\infty \hat{I} m^2 dm \\
m/r = 2 \theta
\]  
(30a)

and

\[
\hat{Q} = 2Q = \int_0^\infty \hat{I} ndm
\]  
(30b)

Here \(\hat{I}\) means the measured intensity affected by the collimation error, caused by using a primary beam with line-shaped cross-section. The absolute value of \(Q\) and \(\hat{Q}\), i.e. \(Q/\Sigma P_0\) and \(\hat{Q}/\Sigma P_0\), does not depend on the geometrical structure of the system—the degree of dispersion—but only on the mean square fluctuation of the electron density \(( \Delta \rho )^2 \)

\[
\frac{Q}{\Sigma P_0} = K dr \overline{( \Delta \rho )^2} \quad K = \frac{i_0}{4\pi} \lambda^3 N^2 = 8\cdot34 \times 10^{-3}
\]  
(31a)

\[
\frac{\hat{Q}}{\Sigma P} = 2 K dr \overline{( \Delta \rho )^2}
\]  
(31b)

It is reasonable to designate \( \overline{(\Delta \rho)^2} \) as the scattering power of the sample. For the most important case of a two-phase system the following holds:

\[
(\Delta \rho)^2 = (\rho_1 - \rho_2)^2 w_1 w_2 = (\Delta \rho)^2 w_1 w_2 ; w_1 + w_2 = 1
\]  
(32a)

\(\rho_1\) and \(\rho_2\) are the electron densities of the two phases and \(w_1\) and \(w_2\) are the volume fractions. We see that \(w_1\) and \(w_2\) can be calculated if \(\overline{(\Delta \rho)^2}\) and \(\overline{(\Delta \rho)^2}\) are known.

For a three-phase system we can easily derive\(^6\)

\[
(\Delta \rho)^2 = (\rho_1 - \rho_2)w_1 w_2 + (\rho_1 - \rho_3)w_1 w_3 + (\rho_2 - \rho_3)w_2 w_3
\]

\[
w_1 + w_2 + w_3 = 1
\]  
(32b)

The practical difficulties of the determination of both the low angle portion and the large angle portion of the invariant—The complete, precise experimental determination of the invariant is, however, often rendered more difficult by the fact that the scattered portions at the smallest as well as at very large angles are to be measured.
SMALL ANGLE ANALYSIS OF HIGH POLYMERS

The scattering curve cannot be measured down to zero angle. However, when the scattering curve does not rise too steeply with decreasing angle, an extrapolation to zero angle of the $I m^2$ or $I m$ curve is possible without a serious error. With strongly polydisperse systems, such as fibrous materials, for which the distribution of particle sizes or voids often ranges from colloidal to microscopic dimensions, the scattering intensity often rises with decreasing angles so steeply that $I m^2$ or $I m$ does not decrease on approaching zero angle. Then, an extrapolation to zero angle is not possible, and the omission of the innermost portion of the invariant causes an error, the magnitude of which is difficult to estimate. In such cases, there is a definite need to proceed to extremely small angles.

Other complications have to be met in measuring the tail end of the curve at large angles. Although the value of $I$ or $I$ is small in this range, multiplication by the large value of $m^2$ or $m$, as well as integration over a wide range, causes the portion of the invariant originating from the tail of the curve to weigh heavily as a whole. The exact measurement of a weak scattered intensity is certainly possible as such, since the flat course at large angles allows the application of a broad primary beam, which counteracts the decrease of intensity. Aggravating this, however, is the fact that there is always some background radiation present, which cannot be accounted for by the ideal picture of an object consisting of two or more homogeneous phases.

Now there are regularities of a general kind, which render possible a correction of the tail end of the scattering curve. The most important finding of this kind is the relation, following from the theory of Porod\textsuperscript{58}, that if we are allowed to assume a homogeneous electron density within each phase, the tail follows a course obeying $1/m^3$ in the scattering curve not corrected for the length collimation error, and obeying $1/m^4$ in the corrected one. It is actually often found for the scattering curve of a system consisting of particles and voids or with dissolved particles that the curve does not end up approximating the final value of zero, but, especially with exposures affected with collimation error, rather approximates a constant final value. So far, all authors seem to have separated this effect caused by the "liquid structure" within the particle or removed automatically during the elimination of the collimation error, as the scattering curve has to be differentiated in the course of this operation. Luzzati, Witz and Nicolaeff\textsuperscript{59} have studied this question in more detail and came to the conclusion that fluctuations of electron density in small ranges lead, indeed, to an additional constant term in the scattering curve affected with collimation error. If in addition, we assume Porod's rule of the decrease according to $1/m^3$, then the tail end of the curve obeys the relationship:

$$\tilde{I} = \frac{k_1}{m^3} + k_2 \quad \text{and} \quad \tilde{I} m^3 = k_1 + k_2 m^3$$ (33)

It is seen at once, then, that a plot of $\tilde{I} m^3$ v. $m^3$ must result in an ascending straight line whose slope represents this constant term $K_2$. This has to be subtracted from the scattering curve.

According to our experience, the tail end often shows, however, in a
Im³ v. m³ plot a course as demonstrated in Figure 18 where there is a pure 1/m³ course and a rising branch. In such cases, we think it is correct to continue the pure 1/m³ branch. Actually, the pure 1/m³ branch extends over a very much larger range than the rising branch—to appreciate this, the distortion of the plot must be considered. A more complete theory on this correction has been given by Stuhrmann and Kirste.

Figure 18. Typical example for the tail end of the small angle scattering in the Im³ towards m³ plot (Kratky-Pilz-Schmitz-Oberdorfer).

The inner surface and the transversal length—As mentioned above, the tail end portion of the scattering curve, after subtraction of a constant part, varies according to $k/m^4$ and $k/m^3$. According to Porod, the quotient of $k$ and the invariant $Q$ as well as $\bar{k}$ and $\bar{Q}$ is for a two-phase system proportional to the inner surface. The actual relation for the specific inner surface (in Å² per Å³ of the sample) is given by

\[
\frac{O}{V} = \frac{2\pi^2}{\lambda r^3} w_1 w_2 \frac{k}{Q} = \frac{12.82}{r} w_1 w_2 \frac{k}{Q} \text{ Å}^{-1}
\]  

(34a)

\[
\frac{O}{V} = \frac{8\pi}{\lambda r^3} w_1 w_2 \frac{\bar{k}}{\bar{Q}} = \frac{16.32}{r} w_1 w_2 \frac{\bar{k}}{\bar{Q}} \text{ Å}^{-1}
\]

(34b)

By inserting (31a) resp. (31b) and (32a) into (34a) resp. (34b) we obtain directly:

\[
\frac{k}{\sum P_0 \, dr^2} = 6.50 \times 10^{-4} \frac{O}{V} (\Delta \rho)^2
\]

(35a)

\[
\frac{\bar{k}}{\sum \bar{P}_0 \, dr^2} = 1.020 \times 10^{-3} \frac{O}{V} (\Delta \rho)^2
\]

(35b)
By normalizing the numbers $k$ and $\tilde{k}$ characterizing the intensity of the tail end to unity of primary energy and sample thickness and distance from the sample to the plane of registration we get a value which depends only on the area of the surface and the change of electron density occurring in it. It is easy to understand that for a system with more than two phases we have to substitute on the righthand side of (35a) and (35b) a corresponding sum instead of $O(\Delta \rho)^2$, which has to be extended over all surfaces.$^{63}$ For a three-phase system in particular we have e.g. for a curve affected with the collimation error:

$$\frac{\tilde{k}}{\sum P_0 \, dr^2} = 1.020 \times 10^{-3} \times \frac{1}{V}$$

$$\left[ O_{1,2} \left( \Delta \rho \right)_{1,2}^2 + O_{1,3} \left( \Delta \rho \right)_{1,3}^2 + O_{2,3} \left( \Delta \rho \right)_{2,3}^2 \right]$$ (35c)

The internal surface is a correct measure for the fineness of a colloid. However, more vivid is a characteristic number introduced by Porod$^{58, 64, 65}$, the transversal length. In Figure 19 we have sketched a quite irregular two-phase system, which is rather spongelike, so that we cannot define the average particle size. Let us now shoot arrows through the system in all directions and measure the average intersection lengths of the arrows with first one and then the second phase. We call them the transversal lengths and they are given for the phase 1 and 2 respectively by the relations:

$$\bar{l}_1 = \frac{4w_1}{O/V} \quad \bar{l}_2 = \frac{4w_2}{O/V}$$ (36)

**Shape and area of the cross-section in loosened up systems of rodlike particles**—In solid high polymer systems it is known that rodlike structure elements play an important part, and we now want to supplement what has been said on
the determination of the cross-section. Having determined its radius of gyration from the end tangent according to (24), we derive the axis ratio from the convex curvature the curve has towards the abscissa. This is best done in the log-log-plot (cf Figure 21). In addition, according to Porod, the area \( F \) of the cross-section can be determined from the ratio of \( (Im)_0 \) with \( Q \) and \( \bar{Q} \) respectively. In a sufficiently diluted system the following relations hold:

\[
F = 0.378 \, r^3 \, \frac{(Im)_0}{Q}; \quad 0.378 = \frac{\lambda^2}{2\pi} \quad (37a)
\]

and

\[
F = 0.755 \, r^2 \, \frac{(Im)_0}{Q}; \quad 0.755 = \frac{2\lambda^2}{2\pi} \quad (37b)
\]

**Measurements on loosened up regenerated cellulose**

A very dense system will yield a small-angle scattering, which, according to the law of reciprocity of optics, can be interpreted as the scattering of the more-or-less randomly distributed voids. When we are not attempting a pore analysis, but an evaluation of particle size, the system must be loosened up in such a way that an extensive separation of the particles is accomplished as is necessary in the preparation of samples for electron microscopic investigations. We will report on the regenerated cellulose which can be loosened up sufficiently by a preparation pioneered by P. H. Hermans et al. It is the method of making a porously dried, the so-called "air-swollen", cellulose. The X-ray small angle investigation of such materials has been reported already thoroughly in this journal (Kratky and Miholic); therefore, we will give here only a short survey.

We were aiming at obtaining information concerning size and shape of the supermolecular aggregates. With extremely elongated particles, the form in which they are doubtlessly present in these samples, interparticle interference effects practically completely disappear when neighbouring particles are not parallel but in a random orientation. The manner of preparation is in favour of a mutual disorientation which occurs the better the higher the degree of air swelling. We succeeded in getting \( q = 6 \), which can be considered as quite satisfactory.

First, we studied the cross-section factor. From the limiting tangent in the Guinier-plot (Figure 20) we get \( R_q = 46.6 \), from the shape in the log-log-plot (Figure 21) an axis ratio of about \( B/A = 0.4 \) can be derived. By introducing both numbers in:

\[
R_q^2 = 1/12 \, (A^2 + B^2)
\]

we find

\[
A = 150 \, \text{Å}, \quad B = 60 \, \text{Å}
\]

This means that ribbon-like particles are present—micelles or micellar strands. Qualitatively we arrived at this result of an anisotropic cross-section many years ago from the anisotropy of the small angle scattering of stretched and rolled regenerated cellulose films, when irradiating parallel to the direction of stretch.
For a control of the above result we are aiming at measuring the area of the cross-section, the internal surface and the mass per unit length of the elongated particles. The cross-sectional area is calculated from (37); \((Im)_0\) was found by extrapolation in the Guinier-plot of Figure 20. For the determination of the invariant we use Figure 22, but we neglect the peak at the smallest angles and refer to the broken line, which corresponds to the straight-line extrapolation in Figure 20. Obviously, the peak at the smallest angles is originating from clusters and need not be taken into account for the determination of the cross-section of the single particles. But we must include the tail end into the determination of the invariant. From Figure 23 we see that its course is in agreement with the theory, so that the contribution of the tail can be calculated easily and gives \(F = 9360\ \text{Å}^2\). The shape determination gives \(AB = 9000\ \text{Å}^2\), which must be considered a satisfying agreement.

For the determination of the mass per unit length according to equation (25a) we need the ratio \((Im)_0/\sum P_0\). But this relation holds only if we can be sure that 100 per cent of the substance is elongated particles of the same type, that is, no clusters are present contributing to scattering at angles below the limit to which the measurement can be extended. A control is given by the invariant (Figure 22) and we have already learnt that there is an appreciable contribution from clusters. From an evaluation we easily find that only
Figure 21. Log-log-plot of the theoretical cross-section curves for the axial ratio $B/A$ of 0.2, 0.3, 0.4, and 1 with experimental values for regenerated, "air-swollen" cellulose with $q = 5.98; \times : 2.2$ and $\div : 1.16$. The curve $\bullet-\bullet$ corresponds to the tangents of the Guinier-plot in Figure 20 (Kratky-Miholic67). The fraction 0.88 of the substance is present in form of the elongated particles, while the rest obviously forms clusters. With the application of (25a) a corresponding correction must be applied to the concentration. Then we get the result that

$$M/\AA = 8480$$

atomic units again a satisfying match with the other results.

A control for the reliability of the above considerations is the comparison of the absolute invariant measured according to the left hand side of equation (31a), with that one calculated according to the right hand side of the same equation from the known composition. The former value is 5 per cent higher than the latter, a difference lying within the limit of error.

There is one further possibility for control of the given result. When we make the assumption that the surface of the clusters is negligible, we can then calculate the surface of the sample originating only from the micellar strands and, therefore, the intensity to be expected for the tail end. Figure 23 shows that the agreement is very satisfactory.

Corresponding results have been found with less air swollen samples, indicating the same shape for the supermolecular particles. We want to point out that this result is based on five independent findings as shown.
SMALL ANGLE ANALYSIS OF HIGH POLYMERS

Figure 22. \( Iq^2 \) curve for the sample of regenerated “air-swollen” cellulose with \( q = 5.98 \). The dashed line (1) continues the right hand portion of the curve while the dashed line (2) separates the scattering of the disperse fraction from the cluster fraction according to the straight-line extrapolation in Figure 20 (Kratky–Miholic67).

Figure 23. \( k/Q \) plot for the samples of regenerated, air-swollen cellulose with \( q = 5.98, 2.2 \) and 1.16. The dashed lines represent those values derived from the dimensions of the cross-section according the axis lengths (Kratky–Miholic67).

It is remarkable that, obviously for the first time, a complete analysis from the smallest angle (corresponding to 9000 Å Bragg’s value) up to the tail end has been given.

Solid high polymers in the dense state

*Determining of crystalline and amorphous fractions and the transversal length*

- When we measure the absolute value of the invariant and know the densities—and, therefore, the electron densities—of the crystalline and amorphous
state, then with the help of (31) and (32) the volume fractions $w_c$ and $w_a$ of both phases can be determined. However, these relations only apply when the sample represents a two-phase system. When there are air voids as a third phase the scattering power owing to the high electron density difference between air and substance is highly increased: In equation (32b) the squared differences $(\Delta \rho)^2_{12}$ and $(\Delta \rho)^2_{13}$ are greater by about two orders of magnitude than $(\Delta \rho)^2_{12}$. So even with values of the volume fraction of the air voids, $w_a$, as small as some tenths of a percent the scattering can be increased to a multiple of that of the polymer free of air. When the relations (31) and (32a) are applied without taking care of an eventual air void content, one often gets a value higher than 0.25 for $w_1w_2$; such a result is obviously nonsense since, because $w_1 + w_2 = 1$, the maximum of $w_1w_2$ equals 0.25. When we are aiming to determine $w_1$ and $w_2$ we must therefore remove the air voids. With synthetic high polymers this is normally possible by thermal treatment.

With polyethylene samples of different mechanical and thermal pretreatment, the scattering power has been measured (together with Schwarzkopf69) over the whole range beginning at 20 seconds of arc so that a completely determined invariant is available. Table 3 shows some results of samples with and without air voids; for the latter the calculation of $W_c$ and $w_a$ is possible. The range of the values found is in agreement with the results of other methods. The tail end follows the expectations of the theory (Figure 24) and the transversal lengths of the crystalline zone show an obvious connection with the period of the sharp small angle reflexions on the meridian (Table 3).

Similar measurements have been performed on nylon (Brumberger, Kratky and Mittelbach70). In the course of this investigation an idea has been developed which perhaps is of some general significance. While the value for the density of the crystalline fraction from wide-angle X-ray analysis is reliable, this is not always the case for the amorphous density value derived from the molten substance; this state is not immediately comparable with the amorphous fraction within the two-phase system. The difficulty can be circumvented in the following manner. The measured macroscopic density of the solid high polymer under investigation is written down as a function of the known density of the crystalline fraction, the unknown density of the amorphous fraction and the unknown ratio of the two fractions. The measured invariant is, according to (31) and (32), a function of the same numbers and so we have two equations with two unknown numbers which can readily be calculated. Working with nylon in this way we found an amorphous density of $da = 1.11$, a value which is about 1 per cent higher than that from the literature. Degrees of crystallinity in the range of 20 to 30 per cent coincide satisfactorily with results from the intensity of the wide angle reflexions.

The pore analysis—for an exact determination of the void content with the help of equation (32b) we need, besides $p_1$ and $p_2$ ($p_3 = 0$), values for $w_1$ and $w_2$. This supposition is practically always given in the case of cellulose. We will confine ourselves to the discussion of the behaviour of this one example in the dry state.
Table 3. Results on linear polyethylene, trade name Marlex-6009 (melt index 0.9)

<table>
<thead>
<tr>
<th>Sample type and elongation (%)</th>
<th>A-1100&lt;sup&gt;a&lt;/sup&gt;</th>
<th>A&lt;sub&gt;1&lt;/sub&gt;-1100</th>
<th>A&lt;sub&gt;2&lt;/sub&gt;-1100</th>
<th>B-1100</th>
<th>C-1100</th>
<th>A-500</th>
<th>B-500</th>
<th>C-500</th>
<th>B-250</th>
<th>C-250</th>
<th>A-0</th>
<th>B-0</th>
<th>C-0</th>
</tr>
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<tbody>
<tr>
<td>Meridian reflections</td>
<td>225</td>
<td>391</td>
<td>391</td>
<td>207</td>
<td>186</td>
<td>225</td>
<td>207</td>
<td>190</td>
<td>246</td>
<td>228</td>
<td>329</td>
<td>302</td>
<td>238</td>
</tr>
<tr>
<td>Crystalline (%)</td>
<td></td>
<td>76</td>
<td>89</td>
<td>81</td>
<td>81</td>
<td>82</td>
<td>77</td>
<td>80</td>
<td>68</td>
<td>80</td>
<td>69</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>[A] unoriented&lt;sup&gt;b&lt;/sup&gt;</td>
<td>148</td>
<td>148</td>
<td>201</td>
<td>154</td>
<td>204</td>
<td>148</td>
<td>207</td>
<td>148</td>
<td>188</td>
<td>188</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[A] oriented&lt;sup&gt;c&lt;/sup&gt;</td>
<td>188</td>
<td>188</td>
<td>256</td>
<td>196</td>
<td>260</td>
<td>188</td>
<td>264</td>
<td>188</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

<sup>a</sup> A-samples were heated up to 160°C, very slowly cooled to room temperature and elongated at 70°C;
<sup>b</sup> B-samples were not subjected to a thermal pretreatment, elongation at 70°C;
<sup>c</sup> C-samples were heated up to 160°C, quenched by throwing into iced water and elongated at 70°C.
<sup>d</sup> The assumption is made that the internal surface between the crystalline and the amorphous phase is not oriented<sup>b</sup> or is oriented<sup>c</sup> parallel to the direction of the elongation.
<sup>e</sup> This sample contains air voids.
Absolute measurements of this kind have been performed by P. H. Hermans et al. From a number of dry fibres of regenerated cellulose investigated, only one, namely fibre 662 (Figure 25) shows a scattering power in accordance with calculations on the basis of the two-phase crystalline-amorphous model. (For the crystalline portion the value 40 per cent, as obtained from the wide angle analysis, is taken). For all other fibres the scattering power was higher up to the fivefold. Quite obviously we are dealing here with voids, which increase the scattering power considerably. A qualitative confirmation of this assumption is found by comparison of the scattering power with the density of the fibres. As Figure 25 shows, there exists a clear correlation in the sense that scattering power and density vary inversely. Therefore, the density difference is without doubt caused by different void fractions. The latter has to be assumed to be 3.5 per cent for sample 641 with the smallest density (and the highest scattering power). If, however, the scattering power is interpreted on the basis of a three-phase system
consisting of crystalline cellulose, amorphous cellulose and voids, a volume fraction of 0.78 per cent is obtained (i.e., only 1/5 of the value calculated from the density). From this we must conclude that only in this fraction are the voids so small that they become effective in the scattering range investigated (down to an angle corresponding to 300 Å).

Figure 25. Scattering power of dry fibres of regenerated cellulose compared with the density (Hermans-Heikens-Weidinger71)

We carried out absolute measurements* of a similar kind with about 60 types of rayons. The length direction of the primary beam was parallel to the fibre axis so that scattering along the equater was measured. The investigated scattering range was extended down to an angle corresponding to 2000 Å. Figure 26 shows the tail ends in the log-log-plot for a number of curves. A response exactly according to $1/\theta^2$ is in agreement with Porod's58 theory. The scattering power varies within nearly one order of magnitude; an evaluation in terms of equation (31) and (32b), under the assumption of 30 per cent crystalline portion, yields a pore content from 0.04 per cent (practically zero) (one example) up to 0.7 per cent.

Much work has been devoted to a discussion of the connections between the X-ray wide angle diagram and the textile properties of fibres. A similar line of enquiry should be explored with respect to the small angle scattering. It is obvious from our findings, particularly with regenerated cellulose, that the small angle diagram with respect of the shape of the scattering curve is untypical for diverse fibres. The only difference is in the intensity of the tail end which varies appreciably. For this reason $k$ from equation (35) recommends itself for use as a characterizing number. The question then arises as to which textile properties could have a reasonable connexion with it. Many attempts to find correlations of this sort gave, finally, the result shown in Figure 27 (upper part). Here we have plotted the loop tenacity against intensity of the tail end at an angle corresponding to a Bragg's value of 1000 Å, which is of course proportional to $k$. At a first glance one gets the impression

* O. Kratky and A. Sekora, unpublished measurements, carried out under the sponsorship of Chemiefaser Lenzig, Ober-Österreich.
that the latter varies in an irregular manner. Nevertheless, what is seen is the fact that samples with poor scattering intensity have poor loop tenacities, while with increasing intensity the interval increases within which the loop tenacity varies. The poorest loop tenacities in each section of the scattering intensity are more or less the same, while the qualities of the best fibres within each section increased with the intensity.

We can look at the problem in a slightly different way. The ascending line in Figure 27 (upper part) is the average of the loop tenacities. In the bottom part we have plotted the deviations of the individual loop tenacities from this average curve against the intensity. Two facts are now clear:
first, the middle curve is ascending, and, secondly the deviations from the middle curve increase with increasing intensity. This result is qualitatively unchanged when the average curve is drawn a little differently so that the arbitrariness in the achievement of this curve does not influence the result. Summing up we can say that fibres without holes have, on the average,

poor loop tenacities. Fibres with higher void content can be equally poor, but they need not: with higher void content, there is at least, the chance of getting a higher loop tenacity; or the void content is the prerequisite for a good loop tenacity, but it is not a guarantee of its attainment.

The situation is obviously complex. But the measurements so far give the impression, that a reserve of space is necessary for obtaining a high resistance against this special form of strain so that, in general, it is useful to make fibres with a certain void content.

Remarks to the experimental technique

So far measurements of the type described above have been performed in very few laboratories only. We will, therefore, confine our references to the instrumentation developed in our group during the last decade (this instrumentation is, in fact the same as that used by Kirste). Devices used by other schools of small angle research are to be found in papers by Guinier, Bee-man et al. and Luzzati.

The camera used had a collimation system practically free of parasitic scattering. The last improvement together with Leopold may be especially referred to. For automatization of the measurements a step scanning device adapted to the camera is saving much time and allows for work around the clock.
For intensity measurements we prefer a commercial proportional counter with pulse height discriminator. An important problem is the absolute intensity measurement. Here the difficulty arises that the primary energy to be measured is, by several orders of magnitude, higher than the scattering. We solve this problem by weakening the primary energy in a quantitatively defined way to such a degree that its measurement is possible with the same equipment which serves for the scattered radiation. The device developed for this purpose is a rotating perforated diaphragm, which is able to catch the quanta, so to say, individually. It is not necessary to use this device for each measurement. We have samples of polyethylene which are calibrated with respect to their scattered intensity on the absolute scale. Then the scattering of the sample under investigation has simply to be compared with the scattering of the calibration sample.

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* For a summarizing presentation concerning absolute intensity measurements compare ref. 77.
† As absolute intensity measurements are performed as a matter of routine in the laboratory of the author, he is willing to distribute such calibrated samples on demand to all colleagues interested in small angle research.

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