Recent Developments in Polymer Applications of Small-Angle Neutron, X-ray and Light Scattering*†

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Recent advances in the small-angle scattering of X-rays, neutrons and light by polymers are reviewed. The three techniques are compared, from both experimental and theoretical points of view. Applications are discussed for the study of homophase and heterophase polymers, both in solution and in the solid state, as well as for unoriented and oriented crystalline polymers.

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I. Introduction

A. Comparison of three techniques

The techniques of small-angle neutron (SANS), X-ray (SAXS) and light (SALS) scattering are all manifestations of interference phenomena as described by the equation

\[ E_s = E_0 \sum_i p_i \exp \left( \frac{i k r_i s}{\lambda} \right), \]

where \( E_s \) and \( E_0 \) are the scattered and incident electric field strengths, \( p_i \) is the fraction of the radiation scattered by the \( i \)th scattering element (which could be an atom, molecule or volume element), \( k = 2\pi/\lambda \) (where \( \lambda \) is the wavelength of the radiation within the scattering medium), \( r_i \) is a vector from an arbitrary origin to the element and \( s \) is the vector difference between unit vectors along the incident and scattered rays having magnitude \( 2 \sin (\theta/2) \) (where \( \theta \) is the angle between the incident and scattered rays and is twice the Bragg angle). The differences of the techniques are primarily related to the nature of \( p_i \). For neutron scattering this is associated with the nature of the scattering nucleus, for X-ray scattering with electron densities and for light with polarizabilities or refractive indices. Since these three properties differ for a given system for the different sorts of radiation, various structural elements will be weighted differently through their use. It is well known that, while hydrogen atoms are poor scatterers of X-rays as compared with carbon, they are good scatterers of neutrons. Furthermore, the substitution of deuterium for hydrogen in a structure appreciably affects neutron scattering but insignificantly affects X-ray scattering. Thus, the technique of isotopic labeling has proved of great value in SANS.

In the case of both X-ray and light scattering a common technique is to affect \( p_i \) through use of solvent swelling or immersion. The effect is particularly evident for samples which exhibit high scattering due to their containing microvoids. Filling of these voids with a liquid can appreciably reduce the electron-density or refractive-index fluctuations arising from these voids and substantially reduce scattering. For polyphase systems, use of a swelling liquid which primarily swells one of the phases can be instructive. For example, with a crystalline polymer liquids primarily swell...
amorphous regions so that the electron-density or refractive-index differences and the differences in \( p_i \) can be changed in a predictable manner through the proper choice of solvent. For SANS, similar effects may be brought about through swelling of a protonated polymer with a deuterated solvent.

Because of the higher energies of X-ray compared with visible light photons and because of the involvement of inner electrons in SAXS, chemical bonding has little effect on SAXS and there is negligible influence of the relative directions of radiation polarization and molecular orientation direction. Hence, \( p_i \) is polarization independent. This is not the case for SALS where \( p_i \) depends upon the polarization tensor so that scattering patterns are very dependent upon polarization directions. While this complicates interpretations, it is a mixed blessing in that additional information may be obtained through polarization studies.

Polarization effects are, of course, significant for SANS. However, these are concerned with nuclear spin orientation, and have not, as yet, led to application for polymer studies. A factor to be considered for SALS is the appreciable refractive index of most materials for visible light. This leads to the necessity of correcting wavelengths and angles for refraction effects.

Because of similarity of wavelengths, the sizes of structures studied by SANS and SAXS are similar. With the somewhat longer wavelengths available with SANS, especially with cold sources, diffraction effects often occur beyond the Bragg limit, simplifying interpretation. The very appreciably longer wavelengths of visible light render the SALS technique most suitable for the study of much larger structures. Thus, while SANS and SAXS studies are concerned with molecular dimensions and sizes and spacings of crystals, SALS is concerned with aggregates of these, such as phase separated domains, fibrils and spherulites. Use of the various techniques in a complementary manner is, of course, desirable.

The various techniques have different requirements for sample dimensions. For SANS, low scattering cross sections lead to the desirability of employing large scattering volumes. Practical considerations usually lead to an upper limit of about 1 cm for the incident beam diameter and several millimeters for the sample thickness. For biological samples, a compromise of appreciably smaller samples is often reached. For SAXS, X-ray tube design and multiple-scattering considerations usually dictate a maximum sample area of a few square millimeters and thicknesses of a millimeter or less. While laser beams for SALS usually have diameters of a millimeter or two, they may be focused to much smaller diameters for microbeam studies. It is often desirable to expand the diameter of the laser beam in order to assure a statistically significant number of structures within the scattering beam and to minimize 'speckling'. Thicknesses of samples for SALS may vary, ranging from a centimeter for relatively transparent amorphous systems to a few microns for highly scattering crystalline polymers. For such highly scattering systems, it is difficult to work with samples thin enough to avoid multiple scattering, so that corrections for its effect are applied. Surface roughness can affect SALS measurements and it is desirable to minimize it by immersing or fusing samples between smooth glass plates.

B. Impact of recent developments in SANS

Neutron scattering is the most recent addition to the techniques used. Under the terms of the title of this review, almost all the SANS ever done with polymer samples might be included. The technique was first applied to polymers at the beginning of this decade and most of the publications have only appeared in the last few years. In these circumstances it seems reasonable to take as the starting point of this review the last SAS meeting held in Grenoble in 1973.

At that meeting papers involving neutrons and polymers were concerned almost exclusively with conformation of polymer chains in a bulk amorphous environment. Based on the simple idea of tagging a few molecules in the bulk by deuteration, these experiments confirmed the Flory hypothesis that in bulk samples the excluded-volume effects would be screened out and the chains return to their unperturbed dimensions. Results in both the Guinier and the intermediate \( K \) ranges were reported, which effectively rules out everything but random flight statistics. \([\kappa \text{ is sometimes designated as } q \text{ or } h \text{ and is } (2\pi/q_s) \text{ or } (4\pi/q_s) \sin(\theta/2).]\) Since these experiments, which were almost an anticlimax, confirming as they did results that had been confidently expected, some less anticipated effects have been observed as the technique has been extended to crystalline systems and then to investigation of semi-dilute and concentrated solutions, to copolymers and polyelectrolytes, to networks and uniaxially deformed samples. Many of these results are described in the following sections and for this reason the references have been omitted at this point for brevity.

A particularly interesting feature of the last few years has been the lively interaction between theory and experiment in the domain of semi-dilute and concentrated solutions. The unique possibilities offered by SANS of observing both single-chain and many-chain effects in a many-chain environment have encouraged the development of theoretical descriptions of polymer solutions and, as will be discussed in § III B, the experimental results have posed some new problems for the theoreticians.

Some recent investigations, of model networks, of stretched systems and of polymer mixtures, foreshadow what will certainly be an important application of SANS in the next few years – investigation of technologically important problems such as the extrusion and moulding of polymers, polymer blends and the manufacture of composites and synthetic membranes. In each of these fields the practical empirical approach often adopted at present can be expected to be reinforced by a detailed knowledge of behavior at a molecular level.

II. Experimental techniques

A. X-rays and light

1. Instrumentation

While scattering technology is reviewed elsewhere, it might be emphasized here that the most significant development in experimental techniques during the past few years has been the application of position-sensitive detectors, permitting the acquisition of data in parallel over many angles (Schelten & Hendricks, 1975). In addition to increasing the speed of data acquisition, the use of two-dimensional detectors in SAXS permits the use of pin-hole collimation and avoids the difficult, if not impossible, task of desmearing slit data with oriented systems (Baczek, 1977; Hendricks, 1978).

A similar breakthrough has occurred with SALS, where the use of an optical multichannel analyzer, essentially a vidicon coupled with a multichannel analyzer, permits the acquisition of angular data in two dimensions in short times.
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In both cases it is possible to process data in real time with a dedicated computer, making it possible to study readily time-dependent phenomena. In this way kinetics of crystallization and phase separation and of deformation and relaxation processes have been studied.

Speed of data collection is enhanced through use of more intense radiation sources. For SAXS, use of rotating-anode generators has become more common. The future availability of synchrotron sources appears to have great potential. Light scattering studies have been greatly facilitated by the use of lasers. In addition to their high intensity, lasers have the merits of high monochromaticity permitting the observation of Rayleigh line width and Brillouin phenomena (outside of the scope of this review).

2. Data treatment

Data treatment has been facilitated through the use of high-speed computers. A general computer program for the processing of SAXS data has been published by Vonk (1975). This program (a listing of which is available from the author) is written in Fortran V and can perform many of the operations commonly used in treating SAXS data. Experimental data may be smoothed, and repeat measurements may be scaled and averaged and statistically erratic data may be detected and discarded. Background data may be subtracted, and desmearing may be carried out by a procedure previously described by Vonk (1971). Liquid-scattering subtraction and high-angle extrapolation may be made. The invariant may be obtained and one or three-dimensional correlation functions may be obtained from either the smeared or the desmeared data.

A significant advance in data treatment is the description of a procedure for indirect Fourier transformation of data by Glatter (1974, 1977a, b). This procedure, valid for non-periodic scattering media, permits the simultaneous smoothing, desmearing and Fourier transformation of data. The distance distribution function is approximated by a linear combination of spline functions which, after transformation and smoothing, are used to estimate the radius of gyration. The method is said to be superior to the Guinier approximation in that residual background intensity does not lead to oscillations. Distance distribution functions of the cross sections of elongated particles like cylinders and of the thickness of flat sheets can be computed from unsmoothed smeared experimental data.

B. Neutrons

1. The H–D substitution technique for variation of contrast factors

The principles of the neutron scattering apparatus have been described in another paper at this conference (Schelten & Hendricks, 1978). The existence of only two or three machines in the world has led to a fairly standardized experiment which is not worth re-describing here. However, it is worth re-emphasizing the main factor which influences the increasing use of SANS in polymer problems. As was stated in the Introduction, this is the random variation of scattering lengths from nucleus to nucleus, quite unlike the monotonic increase in electron density through the periodic table. In particular, there is a large difference between hydrogen and deuterium.

The coherent intensity (normalized for the incident flux) in a neutron experiment is described by the cross section dσ/dΩ which is the probability that a neutron will be scattered into solid angle Ω for unit volume of the sample. It should be noted that the cross section, commonly used to express the neutron scattering power of a sample, is identical with the Rayleigh ratio, R, more commonly used for light scattering. For a polymer dilute solution

\[
\frac{d\sigma}{d\Omega} = Z N_p B_p - \frac{V_p}{V_s} B_S S(\kappa) \quad (2)
\]

Z is the number of monomer units in a chain and \( N_p \) the number of polymer molecules per unit volume in solution. \( B_p \) and \( B_s \) are the total coherent neutron scattering lengths of a monomer of polymer and a solvent molecule respectively.

Although neutron scattering is a nuclear process, this ‘smearing’ of the scattering lengths over a molecular unit is valid in the small-angle region where the observations are being made, involving long-range correlations within the sample. \( V_p \) and \( V_s \) are the specific volumes of monomer and solvent and the term \( V_p/V_s \) simply takes account of the replacement volume of solvent molecules by polymer. \( S(\kappa) \) is the molecular structure factor.

The coherent scattering lengths of carbon, oxygen, hydrogen and deuterium are 0.665, 0.580, -0.374 and 0.665 x 10^{-12} cm respectively. Table 1 shows how these values combine to form \( B \) values for some common polymer monomers and solvent molecules and their deuterated analogues.

The table shows clearly how the deuteration of polymer or solvent can be used to change contrast factors for all or part of the chain at will. The factor \( V_p/V_s \) is usually of order unity, so that a good idea of the contrast can be obtained by directly comparing the \( B \) values. Note that a deuterated polymer chain in an hydrogenous polymer has now a contrast factor equivalent to a polymer in a solvent.

These values show that the experiment is reversible in the sense that hydrogenous polymer in deuterated matrix (or solvent) and deuterated polymer in hydrogenous matrix (or solvent) have the same contrast. Other factors however come into play in the choice of system. The first is, of course, the cost of deuteration itself. At face value it would appear advantageous to tag molecules by deuteration in an hydrogenous matrix or solvent. However, the difficulties of working with very small quantities to produce very well characterized samples may argue against this in certain cases.

A more important argument centers around the scattering from the matrix or solvent itself. If this is high, or unstable, it may make observation of the signal from the tagged molecules very difficult. Two effects come into consideration. Firstly, there is the question of incoherent scattering. This scattering arises from fluctuations in the scattering lengths across the sample and is particularly large for hydrogen because of interactions between the neutron and nuclear spins. For hydrogen the incoherent cross section is 81 x 10^{-24} cm², while for most other nuclei including carbon, oxygen and deuterium it is of order 1 x 10^{-24} cm². While the incoherent scattering is essentially isotropic, it forms a flat background to the coherent signal and, if it is very intense, can adversely affect the signal-to-noise ratio \( R \), (Higgins, 1978). This signal-to-noise ratio has been calculated for a number of possible pairs in Table 1. On inspection of these values, the argument would immediately appear to be won in favor of using a deuterated matrix. However, the second point to be considered is that it may be
Table 1. Summed scattering lengths \((B = \Sigma b_i)\) per molecule or monomer unit for some polymers and solvents

For definitions see § II.B.1.

<table>
<thead>
<tr>
<th></th>
<th>Polystyrene</th>
<th>Polymethyl methacrylate</th>
<th>Benzene</th>
<th>Cyclohexane</th>
<th>CS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_8H_8)</td>
<td>2.33</td>
<td>1.5</td>
<td>9.82</td>
<td>1.75</td>
<td>0.5</td>
</tr>
<tr>
<td>(C_8D_8)</td>
<td>10.66</td>
<td>9.0</td>
<td>7.99</td>
<td>0.5</td>
<td>1.22</td>
</tr>
<tr>
<td>(C_9O_2H_8)</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_9O_2D_8)</td>
<td>9.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_5H_6)</td>
<td>7.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_6D_6)</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_6H_{12})</td>
<td>11.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_6D_{12})</td>
<td>1.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[R^*\]

Polystyrene \(h_8\) in benzene \(d_6\) 475
Polystyrene \(d_8\) in benzene \(h_8\) 77
Polystyrene \(h_8\) in CS₂ 1.75
Polystyrene \(d_8\) in CS₂ 51 000
Polystyrene \(h_8\) in polystyrene \(d_8\) 690
Polystyrene \(d_8\) in polystyrene \(h_8\) 69

\(*) R = \text{(Coherent scattered intensity/incoherent scattered intensity) per unit solid angle.}\)

even more annoying to have a \(k\)-dependent signal from the matrix than an isotropic one, however intense. If the ‘matrix’ or solvent has a high value of \(B\), then density fluctuations, voids, and other artifacts can cause an intense small-angle signal, particularly in crystalline or semi-crystalline samples (Ullman, Summerfield & King, 1977). This may be very difficult to separate from the signal of the tagged molecules, especially when it may vary from sample to sample. There appear to be no hard and fast rules about choice of deuteration for the tagged molecules or for the matrix and except in particular examples the final decision seems almost a matter of taste.

2. Problems arising from deuterium tagging

While the assumption that deuteration is a relatively minor perturbation to the system certainly holds in comparison with the problems of heavy-atom tagging necessary for investigation in the same regime with X-rays, it is also necessary to point out that a number of problems have come to light in recent years.

One such problem is discussed in some detail below (see § V D). Polyethylene \(h_6\) and \(d_6\) have a \(6^\circ\) difference in their crystallization temperatures. Apparently associated with this there have been difficulties arising from a sort of aggregation, or at least a fluctuating density of tagged molecules within the sample, which leads to anomalous forward-scattering intensities.

Another effect has been the shift in the \(\theta\) temperature of a polymer–solvent combination if one of the pair is deuterated. It has been found, for instance, that for polystyrene in cyclohexane the \(\theta\) temperature shifts up or down by about \(4^\circ\) if one of the pair is deuterated (Straziell & Benoit, 1975).

Thus, while the use of deuteration and SANS has opened many possibilities in the investigation of polymer systems, it is worth a little caution in the experimental procedures adopted.

3. Summary of typical experimental procedures

The samples are usually of area \(~1\ \text{cm}^2\) and with a thickness calculated to give approximately 50% transmission of the direct beam. Solutions are normally held in quartz cells (quartz has almost no small-angle signal). The neutron diffractometer has a normal configuration with sample-detector distances chosen to cover the desired range of \(k\). The wavelength resolution can be relaxed for measurement in the Guinier range provided that the wavelength distribution is known (for a discussion of this point see for example Cotton et al., 1974).

A measurement on a sample with and without tagged molecules is made. If the matrix or solvent is deuterated, then the hydrogen contents of the ‘background’ and ‘sample’ runs are adjusted so that the incoherent noise signal is the same in both cases. If the molecular weight is to be determined from the absolute value of the extrapolated forward scattering, then the measured intensity is normalized to scattering from an incoherent scatterer - usually vanadium or sometimes water [see Jacrot (1976) for a discussion of absolute measurements].

Such correlation also automatically takes into account both variation in solid angle subtended by the detector at the sample and detector efficiency.

III. Homophase amorphous systems

A. Theory

1. Debye–Bueche

Debye & Bueche (1949) have shown that if the scattering amplitude is squared prior to integration the scattering equation for an isotropic substance may be written in the form

\[ I_s = K \eta^2 \int_0^{\alpha} \sin(\alpha r) \frac{\sin(\alpha r)}{\alpha r} r^2 \, dr, \]  

(3)
where $K$ is a constant whose value depends upon the type of radiation used, $\eta^2$ represents the mean square fluctuation in scattering power,

$$\eta^2 = (\bar{p} - \bar{p})^2,$$

where $\bar{p}$ is the mean scattering power of the medium, and $\gamma(r)$ is an (auto)-correlation function in scattering power defined as

$$\gamma(r) = \langle \eta_i \eta_j \rangle / \eta^2,$$

where

$$\eta_i = p_i - \bar{p}$$

and the symbol $\langle \rangle$, designates averages over pairs of volume elements separated by a scalar distance $r$. This function expresses the probability of correlation of two fluctuations separated by distance $r$.

The quantity $\eta^2$ is related to the invariant and may be obtained by integrating the scattering over all angles according to (Guinier & Fournet, 1955)

$$\eta^2 = 2/(\pi K) \int_0^\infty \kappa^2 I(\kappa) d\kappa.$$

For a two-phase system with sharp boundaries, $\eta^2$ may be given by

$$\eta^2 = \varphi_1 \varphi_2 (p_1 - p_2)^2,$$

where $\varphi_1$ and $\varphi_2$ are volume fractions of the phases having scattering powers $p_1$ and $p_2$. This equation may be generalized to multiphase systems to give

$$\eta^2 = \sum_{i} \sum_{j} \varphi_i \varphi_j (p_i - p_j)^2.$$

If the boundaries between phases are not sharp, $\eta^2$ is reduced. For example, for a two-phase system with a linear gradient of scattering power between phases, equation (III-A-6) becomes (Kambatta, Warner, Russell & Stein, 1976)

$$\eta^2 = (p_1 - p_2)^2 \left[ \varphi_1 \varphi_2 - (1/6) \varphi_3 \right].$$

where $\varphi_3$ represents the volume fraction of interphase region.

Generally the correlation function may be obtained by Fourier inversion of the scattering data. Debye, Anderson & Brumberger (1957) have shown that for a randomly dispersed system, the correlation function is an exponential

$$\gamma(r) = \exp (-r/a).$$

where $a$ is a correlation distance and is a measure of the size of the fluctuation. In this case, equation (3) reduces to the form,

$$I_s = (K/\eta^2) a^3/[1 + \kappa^2 a^2].$$

It is noted that at large $\kappa$, this equation predicts that $I_s$ varies as $1/\kappa^4$ in agreement with Porod's law. A plot of $I_s^{-1/2}$ against $\kappa^2$ should yield a line having a slope/intercept equal to $\kappa^2$. Such plots have been obtained (Kambatta et al., 1976) from SALS and SAXS data. For example, Fig. 1 shows a plot for SAXS from some amorphous blends of poly-e-caprolactone (PCL) with polyvinyl chloride (PVC).

For dilute dispersions of one component in another, $a$ may be taken as a measure of the size of the dilute component. For a more concentrated dispersion, $a$ is best interpreted in terms of the transverse lengths given by Porod and Kratky (Kratky, 1966):

$$l_1 = a/\varphi_2$$

and

$$l_2 = a/\varphi_2,$$

where $l_1$ and $l_2$ are the average lengths of random chords passing through the two phases. Application of this approach to the PCL/PVC blend leads to the results shown in Fig. 2. It is noted that for dilute PCL, the transversal length is of the order of 3-0 nm as compared with a diameter of 4-2 nm calculated from the molecular weight of PCL on the basis of a compact sphere model. Thus, it appears that in dilute solution, the PCL is molecularly dispersed in the PVC.

Further evidence comes from an examination of the value of $\eta^2$. Based upon a sharp interface model, with macroscopic electron densities assumed for the two phases, a value of $3 \times 10^{-3}$ (mole e cm$^{-3}$)$^2$ is obtained for a 30 wt % PCL blend, as compared with an experimental value of 1.28 x
The difference may be reconsidered by using equation (10), which allows the calculated $\eta^2$ to be reduced by an amount dependent upon the thickness of the phase boundary. Such calculation leads to the conclusion that the boundary thickness of the PCL/PVC interface is an appreciable fraction of the phase diameter, suggesting molecular interpenetration between phases. These results, suggesting compatibility of these two polymers at segmental level, may more reasonably be interpreted on the basis of a molecular theory of scattering, as discussed later. The larger values of $I_{pc}$ found at higher concentrations indicate molecular aggregation. The Debye-Bueche theory may be used for SAXS, SANS and SALS for molecular dispersions, aggregated molecules and indeed for phase-separated systems as discussed later.

For oriented systems, equation (3) may be generalized as

$$I_{se} = (K/4\pi)\eta^3 \int_0^\infty \gamma(r) \cos k(r \cdot s) dr,$$

where now $\gamma(r)$ represents an angularly dependent vector-correlation function and $dr$ is an integration over the magnitude and angles of the vector $r$. This equation predicts a dependence of scattered intensity upon azimuthal scattering angles.

For SALS where polarization effects are significant, Stein & Wilson, (1962) have shown that for a special case, equation (3) may be generalized to

$$I_{sp} = K \left( \frac{\eta^3}{2} \right) \int_0^\infty \gamma(r) \sin (kr) r^2 dr + \left( \frac{4}{45} \right) \frac{\eta^6}{2} \int_0^\infty f(r) \sin (kr) r^2 dr,$$  

$$I_{ho} = (1/15)K\delta^2 \int_0^\infty f(r) \sin (kr) r^2 dr.$$

$I_{sp}$ designates the intensity of light scattered when incident and scattered beams are both vertically polarized (perpendicular to the plane of measurement of $\theta$) whereas $I_{ho}$ designates scattering with vertical polarization of the incident polarization and horizontal polarization of the scattered radiation. $\delta^2$ represents the mean square fluctuation of anisotropy of refractive index (assumed uniaxial) where $\delta = n_1 - n_2$ and $f(r)$ is a correlation function for orientation of optic axes defined as

$$f(r) = \left[ 3 \cos^2 \theta_{ij} - 1 \right]/2,$$

where $\theta_{ij}$ is the angle between the optic axes of the $i$th and $j$th volume elements, separated by distance $r$. This extension has proved useful for the description of the scattering from crystalline polymers.

2. Guinier approach

If the $\sin (kr)/kr$ term in equation (3) is expanded in a series, one obtains

$$I_s = K \eta^3 \int_0^\infty \gamma(r) \left[ 1 - (\frac{kr}{3})^2 + (\frac{kr}{5})^3 \right] r^2 dr,$$

$$= K \eta^3 \int_0^\infty \gamma(r) r^2 dr \left\{ 1 - \frac{k^2}{3!} \int_0^\infty \frac{\gamma(r) r^4 dr}{5!} + \ldots \right\},$$

where $I(0^\circ)$ is the zero-angle scattering and $R_g^2$ is the mean square radius of gyration of the scattering object, which for a dilute dispersion may be used to characterize the size of the dispersed scattering particle or molecule. Thus a plot of $I_s$ vs $k^2$ may be used to determine $R_g^2$.

Alternatively, one may recognize that to the approximation of the first two terms, equation (19) is identical with the expansion of

$$I_s = I_0 \exp \left[ -\frac{R_g^2}{3} k^2 \right].$$

so that a plot of $\ln I_s$ vs $k^2$ also gives a line of slope characteristic of $R_g^2$. This Guinier plot has been widely used for the interpretation of scattering data. Non-polymeric applications of this approach have dealt with measurements on such systems as colloidal particles and porous rocks. Polymeric applications have primarily been concerned with dilute solutions in which X-ray measurements have complemented molecular dimension studies obtained by solution light scattering. Recently SANS has allowed determination of dimensions of single chains in bulk samples and concentrated solution.

3. Molecular approach

For dilute solutions, correlation functions may be calculated on the basis of molecular models. For example, for a dilute dispersion of spheres of radius $R$

$$\gamma(r) = 1 - \frac{\delta^2}{6} (r/R) + \frac{1}{12} (r/R)^3,$$

leading to the familiar expression for the scattering from dilute spheres,

$$I_s = K I_0 V_s^2 (p_s - p_o)^2 \left[ \frac{3}{13} \sin U + U \cos U \right]^2,$$

where $V_s$ is the sphere volume, $p_s$ and $p_o$ are the scattering powers of the spheres and their surroundings and $U = \kappa R$.

For polymer chains in dilute solution a Gaussian correlation function leads to the intensity variation,

$$I_s = I(0^\circ) (2/v^2) \left[ v - 1 + \exp(-v) \right],$$

where

$$v = \kappa R^2.$$

Deviations from this prediction are taken as indications of deviation from Gaussian behavior.

The intensity of scattering at zero angle is related to the weight-average molecular weight. For example, for X-ray scattering, Kratky has shown that (Kratky, Porod & Kahovac, 1951)

$$\bar{M}_w = [I(0^\circ)/I_0]^2 \left[ \frac{4}{3} D c \bar{N}_d (z_1 - v_1 g_2)^2 \right],$$

where $t$ is the sample-detector distance (cm), $D$ is the sample thickness (cm), $c$ is the concentration of the dissolved sample (g cm$^{-3}$), $z_1$ is the number of moles of electrons per gram of dissolved substance, $v_1$ is its apparent partial specific volume (cm$^3$ g$^{-1}$), $g_2$ is the electron density of the solvent, $l_n$ is the Thomson scattering factor for a single electron and $N_d$ is Avogadro's number.

The scattering from more concentrated solutions is better treated with thermodynamic fluctuation theory, in which the scattering from a system may be written in terms of the mean square fluctuation in scattering power,
where \( v \) is the number of volume elements constituting the system. It is assumed that \( \Delta p^2 \) may be expressed in terms of fluctuations in (actual) density and in concentration according to

\[
\Delta \rho^2 = \left( \frac{\partial \rho}{\partial d} \right)^2 (4\pi d^2) + \left( \frac{\partial \rho}{\partial c} \right)^2 (4\pi c)^2 .
\]  

(27)

This equation neglects cross-correlations between density and concentration fluctuations. Substitution of this result into (26) leads to the result that the total scattering may be written as a sum of a term arising from density fluctuations and a term arising from concentration fluctuations. For dilute solutions it is assumed that the density fluctuations of the solution are identical with those of the solvent, so that the concentration term may be obtained by subtracting solvent scattering from solution scattering. The limitations of this assumption for SAXS have been considered (Goodisman & Brumberger, 1973).

For one-component systems, the scattering arises entirely from density fluctuations. These may be calculated in terms of the isothermal compressibility \( \kappa \) to give (Wendorff & Fischer, 1973)

\[
\Delta N^2/ N = k_B T \kappa d_x .
\]

(28)

where \( k_B \) is Boltzmann’s constant and \( \kappa \) is in this equation designates the isothermal compressibility rather than the scattering vector and \( d_x \) is the particle density. Comparison of measured and calculated density-fluctuation contributions to scattering has been used to assess the possible contribution to scattering arising from structure within amorphous polymers.

The consideration of the contribution to scattering from concentration fluctuations leads to the equation

\[
\frac{H_C}{R(0^\circ) - R(\text{solvent})} = \frac{1}{M_w} + 2A_2 c .
\]

(29)

where \( R \) is the scattering intensity expressed as a ‘Rayleigh ratio’ as

\[
R = I(\theta) / I(0) ,
\]

(30)

where \( V_x \) is the volume of the scattering system, \( A_1 \) is the second virial coefficient characterizing solute–solvent interaction. The equation is valid for light, X-ray and neutron scattering. The constant \( H \) depends upon the kind of radiation and is, for light scattering,

\[
H = \frac{2\pi^2 n^2 (\partial n/\partial c)^2}{N_A^4} ,
\]

(31)

while for X-ray scattering, it is

\[
H = N_a (\partial q_{\text{e}} / \partial c)^2 ,
\]

(32)

and for neutron scattering (Kirste, Kruse & Ibel, 1975),

\[
H = Z \left[ B_\rho - B_4 V_r / V_x \right]^2 N_a / m^2 ,
\]

(33)

where terms are defined as in equation (2) and \( m \) is the molecular weight of a monomer unit.

This equation is conventionally used for polymer molecular-weight determination by solution light scattering. It has been extended to X-ray scattering, primarily by Kratky and coworkers. While the theory was originally developed for dilute solution, the use of heavy-atom substitution for SAXS and isotopic substitution for SANS has permitted its extension to concentrated solutions and to bulk polymers.

The data obtained at finite angle is commonly extrapolated to zero angle and concentration using the approach of the Zimm plot, where, in its angular dependent form, equation (29) can be written in the form,

\[
\frac{H_C}{R(\kappa)} = \frac{1}{M_w \rho(\kappa)} + 2A_2 c .
\]

(34)

The left-hand side of (34) is plotted as \( \sin^2 (\theta/2) \) for various values of \( c \) and the results are doubly extrapolated to \( c = 0 \) and \( \kappa = 0 \) to give an intercept which is the reciprocal weight-average molecular weight. The value of \( A_2 \) is obtained from the slope of the concentration variation and the radius of gyration from that of the angular dependence.

B. Single-chain correlation functions

1. Bulk polymers

(a) X-rays: A subject of paramount interest in polymer physics in recent years is the nature of the amorphous state. The conventional picture has been that proposed by Flory (1953, 1969) and coworkers of Gaussian chains packed randomly with respect to each other and having dimensions identical with those assumed in a theta solvent. This model has been remarkably successful in accounting for thermodynamic, mechanical and optical properties of amorphous polymers.

More recently alternative models for the amorphous state have been proposed. One of these, advocated by Yeh (1972), proposes the existence of folded-chain domains, somewhat similar to, but more disordered than, those occurring in crystalline polymers. The other, proposed by Pechold and coworkers (Pechold, 1968, 1969; Pechold & Blasenbrey, 1970), is a bundle model involving extended chain meanders containing defect regions referred to as ‘kinks’ and ‘jogs’. Scattering techniques have been brought to bear on this problem. Neutron scattering results are discussed elsewhere in this review.

It has been proposed in an earlier publication by Harget & Siegmann (1972), that the SAXS from polyethylene terephthalate (PET) arose from regions 3-4 nm in size, which they associated with the Yeh-type domains. Critical studies of SAXS from amorphous PET, PVC, polymethyl methacrylate (PMMA) and polycarbonate have been carried out by Wendorff & Fischer (1973), Dettenmaier & Fischer (1973), Fischer et al. (1976), and by Uhlmann and coworkers (Renninger, Wicks & Uhlmann, 1975; Straff & Uhlmann, 1976), who investigated the effect of a large number of variables such as sample treatment, molecular weight, swelling and additive concentration. They conclude that neither the inherent structure of the pure polymer nor microholes are the origin of the scattering and that ‘scattering can be attributed to foreign particles’; and that a very small amount of foreign particle content having an electron density appreciably different from that of the polymer can account for the excess scattering. If the addition scattering is subtracted out, the residual scattering may be understood on the basis of thermal density fluctuations of the homogeneous polymer and it would be unreasonable to associate it with density differences between phases.

The nature of the density fluctuations in amorphous polymers has been studied by Wendorff & Fischer (1973) and Rathje & Ruland (1976), who conclude that above \( T_c \) the density-fluctuation scattering is comparable with that which would occur for a low-molecular-weight liquid and is cal-
culable from the compressibility with equation (28). Below $T_c$ the scattering depends upon the compressibility of the sample at the equilibrium state at $T_e$ and is associated with 'frozen-in' disorder.

The light scattering from amorphous polymers may also be used as a measure of the state of order. Earlier measurements have been reported by Fischer et al. (1974, 1976), and more recent ones by Patterson (1976) who observed both $V_c$ and $H_c$ components of light scattering. The $V_c$ scattering primarily arises from density fluctuations and may largely be attributed to impurities. It may be substantially reduced by careful sample purification. The $H_c$ component is of low intensity, angularly independent and comparable with that found with low-molecular-weight liquids such as toluene. The intensity of the $H_c$ component is given by (Cabannes, 1939)

$$I_{H_c} = \frac{16\pi^2}{15} N [n^2 + (2/9)\delta^2],$$

where $N$ is the number of molecules per cm$^3$, $n$ is the refractive index of the medium and $\delta$ is the anisotropy of the repeat unit within the amorphous phase. The number of monomers in an anisotropic repeat unit is the ratio of this to $\delta_0$, the anisotropy of a single monomer unit. The value of this ratio for polystyrene, for example, proved to be 1.4, which would be orders of magnitude less than would be predicted by the ordered models.

(b) Neutrons: Neutron experiments on bulk amorphous polymers can be conveniently discussed under two categories: molecular dimensions and molecular conformation. The two are, of course, interrelated via the correlation of dimensions with molecular weight, which is governed by the conformation.

(i) Molecular dimensions - the Guinier range: As already mentioned at the previous Conference (Grenoble 1973) neutron results concentrated on the determination of chain dimensions under bulk conditions in the low-$\kappa$ Guinier range. The Flory hypothesis of ideal dimensions was already confirmed for polymethyl methacrylate (Kirste, Kruse & Schelten, 1973; Schelten, Kruse & Kirste, 1973) and polystyrene (Benoit et al., 1973; Ballard, Schelten & Wignall, 1973), both by direct comparison of dimensions in bulk with those $\theta$ conditions and by observation of the linear variation of $\langle R_g \rangle$ with $M_w^{1/2}$, which is a necessary result of the chains' obeying Gaussian statistics. It is not impossible to devise other distributions of chain segments which produce both the $\theta$ dimensions and $M_w$ variation, but these are further discounted by the intermediate-$\kappa$ results described below.

More detailed measurements on these and other polymers followed. Zimm plots confirmed that the second virial coefficient $A_2$ approached zero for long chains, as must be the case if excluded-volume effects are screened out in the bulk (Kirste et al., 1975, Cotton et al., 1974). Measurements on crystallizable polymers such as polyethylene and polyethylene oxide were also made in the molten state and results are discussed in § V C below. Table 2 compares the ratios $\langle R_g^2 \rangle / M_w^{1/2}$ observed by neutron scattering in bulk amorphous samples with the values obtained in $\theta$ solution.

An interesting result of this SANS activity has been to stimulate further attempts to measure dimensions in bulk polymers by SAXS. Hayashi, Hamada & Nakajima (1976) report values of $\langle R_g \rangle$ for polystyrene molecules tagged by iodine addition. Copolymers of styrene and p-iodostyrene were prepared in varying ratios of the two monomers and dissolved in normal polystyrene. The resulting small-angle signal was extrapolated to zero iodine concentration and a value for $\langle R_g \rangle$ extracted which agreed well with the neutron results. $\langle R_g^2 \rangle / M_w^{1/2}$ was found to be $0.27 \times 10^{-1}$ nm.

(ii) Molecular conformation - intermediate-$\kappa$ results: In the low-$\kappa$ region the scattering law for a single chain is an exponential governed by the radius of gyration, irrespective of the shape of the molecule (see equation 19). This is no longer true at higher $\kappa$ values where the distribution of chain segments governs the scattering law. In the range $\langle R_g \rangle^{-1} < \kappa < l$, where $l$ is the length of one segment, the Debye curve (equation 23) for a Gaussian distribution becomes proportional to $\kappa^{-2}$. Thus, a plot of $\kappa^2 S(\kappa)$ should reach a plateau in this $\kappa$ range. Such plateau regions were indeed found for polystyrene (Wignall, Ballard & Schelten, 1974; Cotton et al., 1974) and polyethylene (Fischer et al., 1974) and cited as strong evidence for Gaussian coil statistics. On the other hand $\kappa^2 S(\kappa)$ plots for the atactic polymethyl methacrylate showed a strong downwards slope - similar to effects observed by X-ray scattering for syndiotactic PMMA in dilute solution. Isotactic chains show only the increase expected from solutions with excluded-volume effects (see also results on PS in CS$_2$, Cotton et al., 1974). Such deviations from normal Debye behavior have been attributed to helical sequences in the syndiotactic polymer or to ordered regions in bulk polymers.

The Debye model rests on two assumptions - that the mean square distance between two segments is proportional to the number of segments separating them along the chain and that the probability distribution of chain segments is Gaussian. However, as the $\kappa$ vector increases and increasingly short sections of chains are explored, these assumptions break down and, as pointed out by Yoon & Flory (1975, 1976a, b, 1977), the scattering is governed by local configurations of the chains. Applying the rotational isometric state model, they were able to calculate the local correlations for syndiotactic PMMA. The maxima seen in the experimental results were predicted and shown to arise because of a preference in this molecule for trans-trans conformation and because of the unequal bond angles in the chain. Fig. 3 compares experimental results and theory (Yoon & Flory, 1975). Subsequent refinement taking account of the finite segment size produced even closer agreement with experiment (Yoon & Flory, 1976b).

Similar calculations have been made (Yoon & Flory, 1976a) for polystyrene (PS), polyethylene oxide (PEO) and

<table>
<thead>
<tr>
<th>Polymer</th>
<th>State of bulk</th>
<th>Bulk $\theta$ solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Glass</td>
<td>0.275 0.275</td>
<td>Cottet al. (1974)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Glass</td>
<td>0.28 0.275</td>
<td>Wignall et al. (1974)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Melt</td>
<td>0.46 0.45</td>
<td>Schelten et al. (1976)</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Melt</td>
<td>0.45 0.45</td>
<td>Lieser et al. (1975)</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>Glass</td>
<td>0.31 0.30</td>
<td>Kirste et al. (1975)</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>Melt</td>
<td>0.45</td>
<td>Allen (1976)</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>Glass</td>
<td>0.30 0.37</td>
<td>Herchenroeder &amp; Dettenmaier (1977)</td>
</tr>
</tbody>
</table>

Table 2. Molecular dimensions in bulk polymer samples
polymethylene (PM). Each shows small deviations from simple $\kappa^2 S(\kappa)$ behavior - these deviations being smallest for PEO and largest for PS. The predicted curves are compared to experimental results for PM and for PS. They appear to show more variation than was experimentally observed. However, the signal intensity is low in this $\kappa$ region and agreement may just be within experimental error.

At the risk of reopening the old question about chain folding in amorphous samples, it is worth noting a recent paper (Gennant, Pechold & Grossman, 1977) where the meander model is shown able under certain circumstances to predict behavior similar to Debye curves even in the intermediate-$\kappa$ region.

2. Oriented systems

A basic tenet of many molecular theories of rubber elasticity is that deformation will be affine. The dimensions of the chains deform in direct proportion to the macroscopic dimensions of the samples.

If the macroscopic extension ratio is $\lambda_\perp$ (ratio of stretched to original length) then a possible assumption is that the radius of gyration transforms affinely:

$$\langle R_g^2 \rangle = \langle R_g^2 \rangle_\perp \lambda_\perp^2$$

and $\lambda_\perp \lambda_\parallel = 1$. For uniaxial stretch

$$\langle R_g^2 \rangle_\parallel = \langle R_g^2 \rangle_\perp \lambda_\parallel^2$$

$$\langle R_g^2 \rangle_\perp = \langle R_g^2 \rangle_\perp \lambda_\perp^2$$.

Picot, Duplessix, Decker et al. (1977) tested the affine principle on samples of polystyrene ($M_w = 117000$) with 1% deuterated molecules. The samples were hot-stretched uniaxially and then quenched. Anisotropic scattering patterns were observed both in the low and in the intermediate $\kappa$ ranges.

In the low-$\kappa$ range for extrusion ratios $\lambda < 1.7$ the dimensions were found to vary affinely in the $\perp$ direction but to be slightly non-affine in the $\parallel$ direction (see Fig. 4). This discrepancy was ascribed to entanglements which act as effective crosslinks on the chains. An alternative description to the purely affine for crosslinked networks allows the crosslink points to deform affinely, but between these points the coil deformation is determined by the Brownian statistics of a chain with fixed end points. Such an effect arising from the entanglements acting as crosslinks was invoked to account for the data. Unfortunately it was not possible to extract values for $R_g$ at high extension ratios because of the appearance of a spurious signal associated with cracks or voids in the stretched material.

In the intermediate-$\kappa$ region the scattering law varies as $\kappa^{-2}$ in both $\perp$ and $\parallel$ directions, but for $\kappa > 2$ there are deviations in the $\parallel$ direction. The observed curvature was attributed to rod-like behavior over long distances (small $\kappa$) changing to random-coil behavior over short distances (large $\kappa$).

At low stretch temperatures many entanglements will be effective, so that the deformations would be expected to be closely affine. As the temperature is raised, non-affine effects would become more important as fewer and fewer effective crosslinks are left. These authors observed the effect of stretch temperature at high extension ratios in the intermediate-$\kappa$ range and showed that the crossover from rod-like to coil-like behavior occurs at higher values of $\kappa$ (shorter distances) with increasing $T$ as the end-to-end stretching takes over from affine stretching.

The postulate of affine transformation of the radius of gyration has recently been theoretically examined by Pearson (1977). By allowing for the Brownian motion of all parts of the chain, he concludes that the radius of gyration of a chain in a phantom network changes less rapidly with strain than an affinely deformed chain. He concludes that the data of Benoit et al. (1976) are more consistent with his predictions.

Recent work on SANS from deformed rubbers has also been carried out, at the National Bureau of Standards (Hinkley, Han, Moser & Yu, 1978).

Attention is at present centering on measurement of molecular dimensions during stress-relaxation experiments (Allen & Tanaka, 1978). Initial results have already been obtained in a 'stop-go' experiment, where the samples are uniaxially hot-stretched and then allowed to relax for varying times.

---

**Fig. 3.** (a) Scattering function $F(Q)$ vs. $Q$ for PMMA chains of $Z = 1000$. --- atactic; -- syndiotactic; --- isotactic ($Q$ in the plot corresponds to $\kappa$ in the text). (b) Experimental scattering function $Q^2 S(Q)$ for PMMA. --- neutron scattering from bulk atactic, $M_w = 250000$; --- X-ray scattering from syndiotactic in solution in acetone, $M_w > 100000$; --- X-ray scattering from isotactic in benzene (from Yoon & Flory, 1975).

**Fig. 4.** $R_g$ measured parallel and perpendicular to stretch direction as a function of the degree of elongation. The continuous line corresponds to affine deformation and the broken line to the model described in the text ($\langle S_2 \rangle^{1/2}$ on the figure corresponds to $R_g$ in the text) (from Picot et al., 1977).
times before quenching and SANS measurement. Shortly, however, it is hoped to perform a series of measurements on a continually relaxing sample which avoids the problems which occur because of the inevitable length of time before quenching can be completed.

3. Gels and networks

The question of how binding polymer molecules into a permanent network affects their dimensions and conformation is of fundamental interest to theories of rubber elasticity. A number of attempts have recently been made to investigate this point using SANS. Because the experiment averages over the whole sample area, measurements have been made on model networks where the length of polymer between each crosslink point is always the same. This involves preparing monodisperse polymers and then end-linking them. Two types of networks may then be prepared. In A-type networks a few tagged chains (usually deuterated) are mixed with the (usually protonous) chains before crosslinking. In B-type networks a few deuterated monomers are 'grown onto' each of the protonous chains before crosslinking. This type leads to marked crosslinks whereas the A type has marked chains. In a series of experiments on polystyrene chains end-linked with divinyl benzene Benoit et al. (1976) observed for \( M_n = 26000 \) between crosslinks in a type A network of about 4.4 nm for \( R_g \) with a possible slight decrease in this value as the functionality of the crosslinks increased. This value is, within experimental error, the same as would be observed for the uncrosslinked bulk polymer.

Allen & Maconnachie (1976) on the other hand, observed a reduction of about 40% in the chain dimensions of polyethylene oxide after crosslinking by trifunctional isocyanates. Polybutadiene peroxide crosslinked showed at most a 10% reduction in dimensions (Singleton, 1977).

In their B-type polystyrene networks Benoit et al. (1976) observed a diffraction ring corresponding to a correlation of distances ranging from around 10 nm in the dry network to around 30 nm in highly swollen samples.

The appearance of such a peak is in immediate conflict with the classical theory of rubber elasticity. If the crosslink points are joined by Gaussian elastic chains this implies that distances between crosslink points are also governed by a Gaussian distribution and a maximum in the scattering (except at zero \( \kappa \)) would be impossible. The authors point out that such an effect might arise from the narrow \( M_n \) fraction for the network chains, but only if such chains linked predominantly nearest-neighbor crosslinks.

An alternative explanation is that the very large size of the divinyl benzene crosslinking units imposes an order on the resulting network. In the triisocyanate-linked polyethylene oxide type-B networks (Allen & Maconnachie, 1976) no such peak was observed in the scattering pattern.

As remarked above the diffraction peak moved to larger distances (smaller \( \kappa \) values) for the PS networks as the degree of swelling increased. For affine deformation one would expect this distance to vary as \( Q_s^{1/3} \), where \( Q_s \) is the degree of swelling. For low swelling ratios this was the case, but a marked deviation was observed in good swelling agents. Under uniaxial stretch there was again reasonable agreement with affine predictions for \( \lambda < 1.2 \). Also the peak sharpened in the \( \parallel \) direction and broadened in the \( \perp \) direction, indicating an increase of order along the direction of stretch.

While the crosslink points appear to behave affinely in these PS networks, at least for small deformations, the chains themselves do not. Fig. 5 shows variation of \( R_g \) in type-A networks as the degree of swelling changes. The actual increase falls well below the values predicted either for affine deformation or for an 'end-to-end pulling' mechanism where the ends of the chains 'unravel'.

In the polyethylene oxide type-A networks under uniaxial stretch molecular deformation was also less than predicted for affine systems.

In measurements on polyisobutylene networks (Singleton, 1977) points of equal scattered intensity in the \( \parallel \) and \( \perp \) directions were compared. Since the scattering laws, based upon the affine transformation of the radius of gyration, should be

\[
S(k)_{\parallel} = 1 - \frac{\kappa_{\parallel}^2 R_g^2 k_0}{3 \lambda_{\perp}^2}.
\]

and

\[
S(k)_{\perp} = 1 - \frac{\kappa_{\perp}^2 R_g^2 k_0}{3 \lambda_{\parallel}^2},
\]

then the ratio \( \kappa_{\parallel}/\kappa_{\perp} \) for equal-intensity contours will be

\[
\kappa_{\parallel}^2 = \kappa_{\perp}^2 \lambda_{\parallel}^2/\lambda_{\perp}^2.
\]

The ratio \( \lambda_{\parallel}/\lambda_{\perp} \) can be obtained by plotting \( \kappa_{\parallel}^2 \) vs \( \kappa_{\perp}^2 \) and compared to the macroscopic changes of dimension. The neutron scattering value was 0.8, while the macroscopic value was 0.55, again indicating a molecular deformation much less than affine. This conclusion is in accord with the predictions of Pearson (1977).

These experimental results have recently prompted further attempts to calculate theoretically the scattering function of polymers under external constraints (Benoit et al., 1975). It is shown that the shape of the scattering in the intermediate-\( \kappa \) range is particularly sensitive to the type of restraints imposed, as was observed for the stretched quenched systems described in § III B-2.
1. Solutions

(a) X-rays: The principal advance in the case of SAXS for dilute-solution studies has been in the use of tagged polymer molecules to improve contrast. Durchshlag, Kratky, Olaj & Breitenbach (1970) and Durchshlag, Puchwein, Kratky, Breitenbach & Olaj (1973) have pioneered studies using halogenated polymers and have compared results with those obtained by solution light scattering. They have shown that previous differences in results have arisen from the different sensitivity of the two methods to different size ranges, with light scattering primarily responding to sizes greater than 300 nm while SAXS responds to sizes less than 100 nm. With better contrast and resolving power in the quoted work, they were able to explore intermediate dimensions and have shown that light-scattering results respond more to molecular entanglements and that it was necessary to extend measurements to lower concentrations to obtain data comparable with SAXS results.

More recent results have come from Hayashi, Hamada & Nakajima (1978), who have developed the theory of SAXS from mixtures of randomly tagged molecules mixed with untagged molecules. The principal application of this technique has been in the study of concentrated solutions and bulk polymers as previously discussed (Hayashi et al., 1974, 1977, 1978) and results have been discussed along with corresponding results with SANS. Extensive SAXS investigations of both dilute and concentrated solutions have also come from the laboratory of E. Wada (Hiramatsu, Kurita, Tagawa & Wada, 1976; Okano, Wada, Hiramatsu, Korita & Fukuo, 1977). Preliminary aspects of those studies were reported at the last conference on SANS and SAXS.

(b) Neutrons

(i) Dilute solutions: The study of dilute solutions is a region where neutron SAS overlaps strongly the light and X-ray techniques and in general it has no advantages over the older methods.

In particular cases, the neutron $\kappa$ range, which extends to higher values than in light-scattering experiments, and the differing contrast factors to X-ray scattering may have advantages. Problems of this type so far investigated have included the conformation of low-molecular-weight polymers and the determination of persistence lengths. There have been a number of studies on polyelectrolytes.

Low-molecular-weight polystyrene ($M_w < 400$) in deuterated cyclohexane at the $\theta$ temperature (Ballard, Rayner & Schelten, 1976) has values of $R_g$ which fall below the $M_w^{1/2}$ relationship well established for higher values of $M_w$. Such measurements are extremely difficult with X-ray techniques because of the low contrast factors. Even with neutrons very careful measurement is required. Within the experimental error it was found that the data agreed with a model for 'worm-like' chains, which asymptotically approaches the rod-like behavior expected for very short chains and the Gaussian distribution for long chains at its two limiting values.

Joining together the ends of a polymer chain to form a cyclic compound introduces a restriction on the statistical distribution of chain segments. There have been a number of predictions about the effect this will have on the polymer conformation and dimensions (Cassassa, 1965; Naghizadeh & Sotobayashi, 1974). In general a reduction of the radius of gyration by a factor of order $\sqrt{2}$ is predicted.

Recently it has been possible to separate narrow fractions of cyclic polydimethylsiloxanes with molecular weights up to 20,000. Neutron small-angle scattering data from these ring samples in solution in deuterated benzene were compared with results on corresponding linear fractions (Semlyen, Higgins, Scales & Wright, 1978). Plots of $S^{-1}(\kappa)$ vs $\kappa^2$ were noticeably curved for the ring fractions, as seen in Fig. 6 where they are compared with the normal linear plots obtained for linear fractions. Curvature of this sort was predicted by the calculations of Cassassa (1965). Qualitatively such curvature must arise if $R_g$ (cyclic) $< R_g$ (linear) since in the low-$\kappa$ range the scattering is governed only by molecular
calculated from the observed maxima was independent of concentrations. Investigations of another polyelectrolyte, gives information on molecular dimensions the intermediate-effects arising from oriented polyions. Recent results on rods. The persistence length was shown to increase with the increase of the persistence length to be determined from the value of the ratio falls below theoretical predictions, since these are based on infinitely long chains.

As mentioned several times already, while the low-$\kappa$ range gives information on molecular dimensions the intermediate-$\kappa$ range is sensitive to the details of molecular shape. A study of the polyelectrolyte, polymethacrylic acid, confirmed the increase of $R_g$ with decreasing concentration inferred from viscosity data (Moan, Wolff & Ober, 1975). The intermediate-$\kappa$ results showed a dependence on $\kappa^{-2}$ corresponding to a Gaussian coil at high concentrations, but a dependence on $\kappa^{-1}$ corresponding to a rod-like or expanded zig-zag structure for the very expanded coils at low concentrations. Investigations of another polyelectrolyte, carboxymethylcellulose (Moan & Wolff, 1975) allowed values of the persistence length to be determined from the value of $\kappa$ at the changeover from $\kappa^{-2}$ behavior (statistical distribution of short steps) to $\kappa^{-1}$ behavior (scattering from rods). The persistence length was shown to increase with dilution and with charge density in agreement with viscometric data.

Persistence lengths have also been determined for cellulose tricarboxylate in dioxane and a decrease with increasing temperature was discovered (Gupta et al., 1976). This polymer solvent combination has a lower critical solution temperature, implying a decrease in $R_g$ with temperature, which is in agreement with the decreasing persistence length.

Some interesting effects have been observed in semi-dilute polyelectrolyte solutions which appear to indicate ordering of the polymers. Cotton & Moan (1976) measured a peak in the scattered intensity which they attribute to interference effects arising from oriented polymers. Recent results on polystyrene sulphonate (Williams & Nierlich, 1977) again show peaks in semi-dilute solution. The chain separation calculated from the observed maxima was independent of molecular weight, and proportional to concentration $1/2$.

(ii) Semi-dilute and concentrated solutions: Recent SXS experiments using the same random tagging method described above for bulk polymers (Hayashi et al., 1977) investigated the variation of chain dimensions with concentration in $\theta$ solution. Within experimental error of $8 \%$, there was no variation as the concentration of polystyrene in trans-decalin at $21 ^\circ C$ went from dilute solution through concentrated solution to the bulk.

On the other hand, excluded-volume effects in dilute polymer solutions in good solvents have been investigated by light and X-ray scattering. The 'self-avoiding walk' problem leads to an expansion of the chain and a predicted variation of $R_g^2$ as $N^{6/5}$, which has been confirmed experimentally. On the other hand, as shown above neutron experiments on bulk polymers confirm that at limiting high concentration the excluded volume effects are screened out and the chains return to ideal dimensions. SANS is also eminently suitable for investigating the intermediate concentration ranges and answering the inevitable questions of how dilute-solution behavior goes over to bulk behavior.

Table 1 shows that normal polystyrene has virtually no contrast with CS$_2$ while deuterated PS has a very large contrast. Farnoux et al. (1975) showed that it is possible to observe both single-chain behavior (small PSD in PS in CS$_2$) and collective behavior (PSD in CS$_2$) in these intermediate concentration ranges. Measurements were made in the intermediate scattering range and by consideration of the excluded-volume exponent the authors show that when the single-chain behavior depends on excluded-volume effects, $S(\kappa)^{-1}$ varies as $\kappa^{1/3}$, while the multichain behavior is Lorentzian.

An informative quantity related to the excluded-volume coefficient in these systems is the screening length $\xi$ introduced by Edwards (1965, 1966). This may be loosely defined as the distance beyond which excluded-volume effects are screened out between two segments. It is a length characteristic of chain interactions and is concentration dependent. If observation is made over distances shorter than $\xi$, then the local concentration of any chain will be greater than the average concentration of all the other chains and single-chain behavior is observed. $\xi$ varies from the order of a monomer step length in bulk samples to the length of an entire chain in dilute solution. Thus in untagged samples single-chain behavior is always observed in dilute solution, but in bulk it is only observed in the limit of large $\kappa$. At intermediate concentrations there will be a 'crossover' from single to multiple-chain behavior when $\kappa \approx \xi^{-1}$. $\xi$ may be measured in one of several ways in solutions of intermediate concentration. At high $\kappa$ the scattering law for a sample without tagged molecules is Lorentzian with half width $\xi^{-1}$. $\xi$ also designates the limiting $\kappa$ range for this Lorentzian behavior. Alternatively, for a sample with tagged molecules where the single-chain behavior is observed, $\xi^{-1}$ is the value of $\kappa$ where behavior changes from $\kappa^{2}$ to $\kappa^{5/3}$ dependence (as excluded-volume effects come into play).

As well as $R_g$ and $\xi$, a third quantity characteristic of the force of interaction in a polymer solution is the osmotic pressure $\pi/T$, which is directly related to the derivative with concentration of the free-chain energy. A comparison between theoretical predictions of the temperature and concentration variation of these three parameters and experimental results is an effective test of the validity of a theoretical approach to the problem.

Stimulated to a large extent by the possibilities of checking the predictions by SANS, there has been recently considerable theoretical activity in the field of solutions of intermediate concentrations. Based on an analogy with a ferromagnet subject to an external field des Cloizeaux (1975) used renormalization group theory to derive thermodynamic properties of such solutions. Daoud et al. (1975) show that the same results can be obtained from simpler scaling arguments, and extend the results, using these arguments to discuss local correlations. Some of these results are in contradiction to the mean-field-theory predictions (Edwards 1965, 1966, 1975). Between them, these two theoretical approaches designate four different regions of interest in temperature and concentration. The major predictions for $R_g^2$, $\xi$ and $\pi/T$ in these four regions are summarized in Table 3.

$N$ is the number of segments of length $l$ per chain, $c$ is concentration, $\tau$ is reduced temperature ($[T-\Theta]/\Theta$).

The mean-field $R_g^2$ is calculated for a chain of $n$ bonds of length $l$ and characteristic ratio $\epsilon \tau$, $\kappa$ contains factors de-
Table 3. Theoretical predictions of the temperature and concentration dependence of some parameters for polymer solutions in different concentration ranges

For definition of symbols see § III.B.2.

A gap in the table means that these theories have no particular predictions to make here and not that there are no predictions at all.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>z</th>
<th>π/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>I' θ solution</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>constant</td>
<td>-</td>
</tr>
<tr>
<td>c &lt; C*</td>
<td>N&lt;sup&gt;6/5&lt;/sup&gt;</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>c/N</td>
</tr>
<tr>
<td>I dilute</td>
<td>N&lt;sup&gt;6/5&lt;/sup&gt;</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>c/N</td>
</tr>
<tr>
<td>II semi-dilute</td>
<td>N&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>c&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>III 'semidilute θ' concentrated</td>
<td>c/N&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>c&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Refers to scaling law predictions (Daoud & Jannink, 1976).


Dependent on the number of density of polymer chains, thermodynamic parameters and I.

A number of SANS experiments have been undertaken in order to investigate the predictions for R<sup>2</sup> and ξ in Table 3.

In early experiments on PS in benzene Cotton, Farnoux & Jannink (1972) demonstrated the existence of the semi-dilute region and showed that the screening lengths in this region were consistent with mean-field predictions - ξ varying as c<sup>1/2</sup>. However, subsequent detailed investigation of the concentration dependence of both R<sup>2</sup> and ξ (Daoud et al., 1975) on solutions of polystyrene in CS<sub>2</sub> showed very good agreement with scaling-law predictions of c<sup>-1/4</sup> and c<sup>-3/4</sup> dependence respectively for these two parameters. Predictions for π/T were successfully tested.

It was at this point that a remark by de Gennes about the correspondence between the tricritical temperature of a magnetic system and the θ temperature of a polymer solution led to the construction of temperature concentration 'phase' diagram for such solutions by Daoud & Jannink (1976).

For temperatures below θ the chain is collapsed, while above θ the chain statistics form the so-called 'self-avoiding walk' problem which is equivalent to a second-order phase-transition problem. The phase diagram is shown in Fig. 7. The numbering of the various regions corresponds to Table 3, but for a detailed discussion the reader is referred to the original authors. Q is the polymer volume fraction (as opposed to c, the mass concentration) and N is the number of statistical segments in a chain, each of length l.

Q<sup>**</sup> separates semi-dilute and concentrated solutions, c/N<sup>1/4</sup> defines the tricritical region (or θ solution), while Q separates dilute and semi-dilute solutions. Region IV is the normal phase-separation region, since by symmetry arguments the authors associate the reflection of Q<sup>**</sup> in the Q axis with the asymptote of the phase-separation curve.

In a recent paper (Cotton et al., 1976) a number of points on this diagram were experimentally determined for polystyrene in cyclohexane. In particular, the variation of R<sup>2</sup> with t<sup>1/4</sup> in the semi-dilute region was confirmed. Fig. 8<sup>a</sup> shows data for a similar experiment (Richards, Macnachnie & Allen, 1977). At low temperatures the data is constant with temperature (region III) but as temperature increases the line Q<sup>**</sup> is crossed at the predicted t<sup>1/4</sup> variation is observed.

At this point one of the discrepancies between mean-field results and scaling-law results appears in Table 3. For concentrated solution the mean-field theory predicts a temperature variation for R<sup>2</sup> not predicted by scaling laws. Richards et al. (1977) were able to observe such a variation in a 50% solution, in excellent agreement with the predicted equation. Some of these results are shown in Fig. 8<sup>b</sup>. Furthermore, the value of c<sub>ε</sub> obtained from the data is 9.4, in very good agreement with the value of 100 obtained in θ solution.

Clearly, if experimental results agree with both theories in different temperature-concentration ranges, further discussion is both inevitable and necessary.

2. Polymer blends
(a) X-rays: There has been recent revival of interest in the nature of blends or 'alloys' of polymers with each other.
(Manson & Sperling, 1976; Paul & Newman, 1978). While the majority of polymer pairs are incompatible, there are several important cases of compatibility. Notable is the blend of polydimethyl phenylene oxide with polystyrene, commercially marketed as 'Noryl'. Compatibility is commonly judged from the existence of a single glass transition, as determined calorimetrically or from dynamic mechanical or dielectric-constant studies, as well as from the absence of optical turbidity and from crystallization behavior. Interaction coefficients between components have been deduced approximately from those studies or from the thermodynamic determinations calorimetrically or from dynamic mechanical measurements of ternary systems in which both components are dissolved in a mutual low-molecular-weight solvent. The SANS approach offers a possibility for measuring directly the properties of such compatible blends.

From a scattering point of view, a compatible polymer blend is like a solution of a tagged polymer in an untagged one. The electron-density contrast arises from the difference in composition of the components. SAXS studies from such systems were suggested by Price (1978) and continued by Stein, Khambatta et al. (1978), in their studies of the PCL/PVC blend system previously discussed. Measurements of dilute solutions of PCL in PVC were carried out. Radii of gyration were estimated from the slope of Guinier plots by using equation (20). The intercepts were interpreted by using equation (29) to give molecular weights and virial coefficients. Values of \( M_w \) and \( R_g \) obtained from such solid-state measurements agreed well with values obtained from dilute-solution studies on PCL in a low-molecular-weight solvent. The value of \( A_2 \) was very small, indicating approximate theta-solvent conditions in the blend.

(b) Neutrons: SANS offers the unique opportunity of observing directly molecular behavior in mixed samples. A first series of results was obtained on mixtures where the two components have the same chemical composition, but widely differing molecular weights (Kirste & Lehnen, 1976). High-molecular-weight polydimethylsiloxane \( (M_w = 200000) \) was dissolved in concentrations from 0 to 1.2% in deuterated PDMS samples with molecular weights between 180 (dimer) and 250,000. From the Zimm plots values of the second virial coefficient \( A_2 \) and of the radius of gyration were obtained. The values of \( A_2 \) varied from around zero (in agreement with unperturbed behavior found for bulk systems generally), when the two molecular weights matched, to large positive values in low-molecular-weight solvents. Similarly the value of the radius of gyration increases as the chains expand in the low-molecular-weight solvent from the unperturbed dimensions of 11.4 nm to a value of 19.0 nm in the dimer. The variation of \( A_2 \) and of the expansion coefficients determined from the radius of gyration were shown to be in good agreement with Flory–Huggins lattice theory for athermal solutions at 20 and 120°C. The dimer produced anomalous values and this was attributed to non-athermal behavior.

Investigation of mixtures continued with polystyrene acrylonitrile copolymer and poly-\( \alpha \)-methyl styrene, both in deuterated polymethyl methacrylate (Kruse et al., 1976).

Both of these mixtures form clear glasses showing none of the cloudiness associated with incompatible mixtures. For some copolymer compositions normal Zimm plots were found at temperatures between 25 and 130°C. The \( A_2 \) values were positive and the molecules expanded compared to the unperturbed dimensions. In other copolymer compositions, negative \( A_2 \) values and partially collapsed dimensions are found, sometimes only over part of the temperature range. Work by Kirste and co-workers on incompatible mixtures is discussed in § IV C.2.

Experiments were recently extended to the observation of another apparently compatible mixture – polystyrene in poly-\( \alpha \)-methyl styrene (P\( \alpha \)S). The tagged molecules were normal polystyrene (5% by weight of total sample) in mixtures of deuterated PS and P\( \alpha \)S. Two mixtures, 5% PS + 5% PSD in P\( \alpha \)SD were studied. The \( M_w \) values obtained from the extrapolated forward scattering agreed well with GPC data, indicating a statistical distribution of tagged molecules. The molecular dimensions of 5.4 nm for radius of gyration of 54,000 \( M_w \) was somewhat less than the value of 6.3 nm calculated for an unperturbed system, but unfortunately the concentration was not varied so that \( A_2 \) values were not obtained. The reduced dimensions may indicate some incompatibility which will be clarified by further investigation of \( A_2 \).

The question of molecular compatibility in mixtures clearly offers wide scope for investigation by SANS and the next few years may see an increase of applications in this domain. Some work on incompatible systems is described below (§ IV C.2).
IV. Heterophase amorphous polymers

A. Polymeric dispersions

As previously indicated, most polymer mixtures are incompatible. When phase separation occurs, particle sizes usually rapidly grow to values in excess of 0.1–1 μm so that the SALS technique has proved of greater utility than SAXS. In many cases, the refractive index between components is sufficiently great so that modification of the field of the electromagnetic wave in crossing the interface must be considered. (This situation rarely, if ever, arises with SANS and SAXS). This effect has been neglected in the previous theoretical discussions in this review where the Rayleigh–Gans–Debye approximation has been adopted. The more general Mie scattering theory has been derived for spheres and other particles of simple geometry. Applications have been made to the study of particle-size distribution which have been reviewed elsewhere (Kerker, 1969). Such considerations are of practical importance in considering the turbidity of commercially interesting systems such as high-impact polymers, which are often dispersions of rubbers in glassy polymers. Semi-empirical analysis has been made of the effect of particle-size and refractive-index difference on the scattering (Conaghan & Rosen, 1972, 1974).

In cases where the size and refractive-index differences are such that Rayleigh–Gans approximation may be used, Guinier and Debye–Bueche plots have been used for analysis. These have been tested by Caulfield, Yao & Ullman (1968), who have compared particle diameters obtained with a dilute suspension of glass spheres (n = 1.515) in a styrene–butadiene block copolymer (n = 1.534) and determined in this way with those measured microscopically. Yuen & Kinsinger (1974) have fitted SALS data from blends of polymethyl methacrylate and polystyrene to a correlation function of the form

\[ \gamma(r) = f \exp (-r/a_1) + (1-f) \exp (-r^2/a_2^2), \]  

where the correlation distances \( a_1 \) and \( a_2 \) are associated with intra- and interparticle correlations. Visconti & Marchessault (1974) have carried out similar analyses for elastomer-reinforced epoxy resins.

The correlation-function approach was also used by Blundell, Longman, Wignall & Bowden (1974) for examining interstitial copolymers where a vinyl polymer (polymethyl methacrylate) was polymerized in a matrix of a crosslinked epoxy resin. These have been tested by Caulfield, Yao & Ullman (1968), who have compared particle diameters obtained with a dilute suspension of glass spheres (n = 1.515) in a styrene–butadiene block copolymer (n = 1.534) and determined in this way with those measured microscopically. Yuen & Kinsinger (1974) have fitted SALS data from blends of polymethyl methacrylate and polystyrene to a correlation function of the form

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B. Block copolymers

1. General comments

Block copolymers consist of molecules composed of two or more different types of monomer units. In random copolymers these monomers occur in a random sequence along the polymer chain; whereas in block copolymers there are sequences of successive units of one monomer (a block) followed by sequences of successive units of the other(s). There may exist diblock, possessing just two blocks, triblock or multiblock copolymers.

Since, as previously indicated, different polymers are generally incompatible, blocks tend to phase-segregate. Corresponding regions of different monomers clump together to form domains. These differ from those in blends in that their size and arrangement are constrained by block molecular weight. Theories for phase separation in block copolymers have been proposed by Meier (1969), Helfand (1974, 1975), Kraus (1973) and Inoue, Soen, Hashimoto & Kawai (1969, 1970). These theories predict the formation of domains that may be in the form of spheres, cylinders, or lamellae depending upon the relative molecular weights of the blocks. These may be seen with an electron microscope, especially if contrast may be enhanced by staining one of the blocks with a reagent such as OsO₄. If molecular weights are uniform, then domains tend to be arranged in the form of a surprisingly regular lattice, which gives rise to diffraction phenomena that may be readily studied using SANS or SAXS.

The characterization of block copolymers can be carried out by dilute-solution scattering techniques. Earlier work by Benoit & Froelich (1972) with light scattering involved adjusting the refractive index of the solvent so that the relative contrast of the two blocks could be changed. More recent work, to be discussed presently, involves deuterium substitution in one of the blocks and then carrying out SANS in a protonated or deuterated solvent.

2. SALS from block copolymers

Extensive SALS studies of solid block copolymers have come from the laboratory of H. Kawai in Kyoto. Moritani, Inoue, Motegi & Kawai (1970) applied correlation-function analysis to blends of styrene/isoprene diblock copolymers with polysoprene and polystyrene, where results were interpreted by the correlation-function technique using equation (36), and comparisons were made with electron-microscope results.

The above scattering arose principally from density differences between the components of the copolymers and was polarized so as to have a very strong \( V_0 \) component and a negligible \( H_0 \) component. Wilkes & Stein (1969) have observed a fairly appreciable \( H_1 \) component from styrene–butadiene triblock copolymers. The individual styrene cylinders or lamellae in these copolymers have dimensions of a few tens of nanometers, too small to scatter light, and are individually isotropic. It has been observed by Lewis & Price (1971) that these domains have a grain structure of the order of several hundred nanometers in size, within which the domains are locally parallel. The lamellae in different grains are arranged randomly with respect to each other so that the sample is macroscopically isotropic. This parallel ordering of the domains leads to local form birefringence (Folkes & Keller, 1971) with an optic-axis direction corresponding to the direction of local orientation of the domains. This leads to \( H_1 \) scattering (Stein, 1971) described by equation (17) with a correlation function characterizing the orientation correlation of the domains.

A recent application of SALS to the study of copolymers has been published by Boissiere & Marchessault (1977), when the correlation-function approach has been used to characterize the heterogeneity of epoxy–elastomer resins.

3. SAXS from block copolymers

Earlier work on the SAXS from block copolymers was carried out by Skoullos (1973), McIntyre (McIntyre & Campos-Lopez, 1970; Campos-Lopez, McIntyre & Fetters, 1973) and Lewis & Price (1971), who were able to characterize the superlattices of domain arrangement in block copolymers having narrow block molecular weight distributions. More recent work has come from the laboratory of Wada (Kurita, Tagawa, Hiramatsu, Sano & Wada, 1976) with a typical result shown in Fig. 9 for two styrene–butadiene–styrene block copolymers. These results are interpret-
able on the basis of a model of spherical styrene domains with dimensions in good agreement with those calculated assuming that the domains have the composition of the pure components.

It was shown by Keller and co-workers (Folkes & Keller, 1971, 1973, 1976; Folkes & Arridge, 1975; Folkes, Keller & Odell, 1976; Keller, Pedemonte & Willmouth, 1970) that it was possible to prepare, by means of extrusion and shearing processes, highly oriented samples of such triblock copolymers having single-crystal-like texture, in which cylindrical domains were oriented parallel to each other in a hexagonal lattice. Such samples are highly anisotropic in their mechanical properties, having a much higher modulus parallel to the cylinder axis than perpendicular to it in a manner which may be calculated using composite theory. Also they exhibit theoretically predictable form birefringence.

Recent studies have been concerned with the characterization of such structures by SAXS (Mathis, Hadziionnou & Skoulios, 1977, 1978), where the high degree of orientation was quantitatively assessed. Fig. 10 shows the variation of X-ray intensity with rotation angle about the cylinder axes in which the sharp peaks occurring at angles which are multiples of $\phi = 30^\circ$ are characteristic of a high degree of hexagonal order.

The changes in unit-cell dimensions with deformation parallel and perpendicular to the hexagonal cylinder axis were observed. With perpendicular stress, the deformation is close to affine, while with stress parallel to the styrene cylinders the structure is destroyed rapidly with deformation.

Studies of highly oriented lamellar-morphology styrene–isoprene diblock copolymers prepared by solution casting have been described by Hashimoto et al. (1974, 1977). These samples have lamellar planes parallel to the sample surface. The ordering of the lamellae is sufficiently great to give scattering patterns showing as many as ten orders of interference, as shown in Fig. 11. This indicated that the fluctuation in repeat distance must be less than 4% of its average value. The thickness of the domain boundary was estimated from analysis of the deviation of the scattering of the large-angle tail from Porod’s law. For a one-dimensionally oriented array of lamellae with sharp boundaries, Porod’s law should assume the form for large $s$:

$$I(s) = C_1 s^{-2}.$$  \hspace{1cm} (41)

For a system with a Gaussian shaped electron-density profile at the boundary, Porod’s law must be modified to give

$$I(s) = C_2 s^{-2} \left[1 - (4\pi\sigma^2)s^2 + O(s^4)\right].$$  \hspace{1cm} (42)

If $\sigma$ is small compared with the size of the lamellar domain, higher-order terms are negligible, and a plot of $I(s) \times s^{-2}$ should give a straight line, the slope/intercept of which characterizes $\sigma$. Plots of this sort are shown in Fig. 12 corresponding to thicknesses of the order of 2 nm, which are comparable with those that are theoretically predicted.

Studies of SAXS from segmented polyurethanes have been reported. These are essentially multiblock copolymers consisting of ‘soft’ or low-$T_c$ blocks, often composed of a polyl,
alternated with 'hard' or high-$T_g$ blocks formed by the reaction of a diisocyanate and a chain extender such as 1,4-butanediol. These domains often phase-separate, leading to SAXS. In work reported by Fulcher & Corbett (1975) SAXS curves showing broad maxima were obtained indicating a lower degree of ordering of the domains than commonly found for styrene-butadiene triblock copolymers. When rod-like morphology was assumed for the domains, diameters in the range of 4–10 nm and separations of the order of 10–17 nm were obtained. Volume fractions of domains 0.15–0.50 were calculated from the invariant, using equation (9) with complete phase segregation assumed. Values were correlated with chemical composition and physical properties.

Studies of the morphology of segmented polyurethanes by SAXS have also come from the laboratories of Bonart (Bonart, Morbitizer & Hentze, 1969; Bonart, Morbitizer & Müller, 1976; Bonart & Müller, 1974), Samuels & G. L. Wilkes (1973), C. E. Wilkes & Yusek (1973) and Schneider et al. (1975). G. L. Wilkes and coworkers have utilized SALS to study the organization of polyurethanes into spherulitic structures.

G. L. Wilkes & Emerson (1976) have correlated variations of SAXS intensity with changes in $T_g$ following quenching and aging a segmented polyurethane. A polymer which is homogeneous at high temperature may be quenched into a pseudo-compatible state, following which phase separation gradually occurs.

For purposes of study of multiblock copolymers such as those of polycarbonate with polysiloxanes, Vitale & LeGrand (1976) have carried out calculations involving an extension of the Debye theory of scattering from homopolymer coils and rods. These indicated, as might be expected, that the SAXS angular variation from solutions of such polymers varies with changes in the relative electron density of solvents and the blocks.

### 4. SANS from block copolymers

Small-angle scattering from block copolymers in solution is more complex than for normal polymers since the components will probably have different contrast factors with the solvent.

$$R_{\text{g app}} = \sum_\alpha Y_\alpha (R_\alpha + G_\alpha)^2 - \left( \sum_\alpha Y_\alpha G_\alpha \right)^2,$$

$G_\alpha$ is the position vector of the geometric centre of species $\alpha$, $Y_\alpha$ is the partial contrast factor of species $\alpha$, and $R_\alpha$ is the radius of gyration of species $\alpha$, where the block copolymer is assumed to consist of blocks of different species, $\alpha$.

The partial contrast factor, $Y_\alpha$, is defined as $Z_\alpha K_\alpha / Z K_\alpha$. $Z$ is the total number of monomers in a chain and $Z_\alpha$ the number of species $\alpha$. $K_\alpha$, the contrast factor of species $\alpha$, is defined as in equation (2):

$$K_\alpha Z_\alpha = \left| B_\alpha - \frac{V_\alpha}{V_s} B_s \right|.$$
\[
\frac{V_1(B_1 - B_3)}{V_1(B_1 - B_3) + V_2(B_2 - B_3)} \quad (47)
\]

\(R_1\) and \(R_2\) are the radii of gyration of the two species and \(G_{12}^2\) is the mean square distance between their centers of mass.

The apparent radius of gyration is a parabolic function of \(Y\) and in neutron scattering it is possible to vary \(Y\) almost continuously simply by varying the deuterium–hydrogen content of solvent and sample. The actual composition of the particular sample may forbid certain ranges of \(Y\). If the values of \(Y=1\) and \(Y=0\) are accessible, these will immediately give the values of \(R_1^2\) and \(R_2^2\) separately and a third measurement will give \(G_{12}^2\).

First-published neutron results (Duval et al., 1976) investigated this parabola for a diblock copolymer of polystyrene and deuterated polystyrene. The polystyrene sections had \(M_w\) of 59000 while the total \(M_w\) was 106000. The solvent was a mixture of deuterated and normal cyclohexane at 40°C, which is slightly higher than the \(\theta\) temperatures of all the possible combinations, PSH in \(C_6D_{12}\), PSD in \(C_6H_{12}\) etc.

For this particular polymer–solvent combination it is impossible to attain values of \(Y\) between 0 and 0.75 and, since large \(Y\) values correspond to a small denominator in the contrast expression (equation 47) corresponding to small overall polymer–solvent contrast, values of \(Y\) greater than one are difficult to use. Within these limitations an overall parabolic variation of \((R_g)_{app}\) with \(Y\) was found, as seen in Fig. 13.

The values of the radii of gyration of the PSH and PSD sequences found from \(Y=0\) and 1 respectively were 10 and 8.5 nm. These should be compared with corresponding values for homopolymers of the same molecular weight of 7 and 6 nm. The authors suggest that such a discrepancy might be attributed to polydispersity.

A much more detailed study of the effects of polydispersity and of excluded volume on the variation of \((R_g)_{app}\) with \(Y\) is contained in a recent doctoral thesis (Ionescu, 1977). In this case the samples were diblock copolymers of deuterated polystyrene and polyisoprene (PSD–PI). Calculations predicted a very large effect on the shape of the parabola for polydispersities of the two sequences of order \(M_w/M_m=1.3\). The calculations show good agreement with experimental results.

The value of \(R_g\) found for the PSD sequences in PSD–PI copolymers in cyclohexane at 40°C was in very good agreement with the value for the homopolymer under the same conditions. At 20°C the PSD sequence was markedly collapsed, while the PI sequence was unchanged with temperature.

In toluene, a good solvent for both sequences, it is not possible for \(Y\) to be zero or unity. Thus \(R_1\) and \(R_2\) must be calculated by fitting the theoretical curve to the data points. Again, when polydispersity was taken into account, a good fit to the data was found, together with a value of \(R_g\) for the PSD sequence very close to that of a homopolymer of the same \(M_w\) under the same conditions. The excluded-volume effects of a ‘good solvent’ on the shape of the \((R_g)_{app}\) curve are masked by the effects of polydispersity.

Application of these techniques to copolymers where the two species are incompatible should lead to information on the structure. Some measurements have been made by the group at CRM Strasbourg (Picot, Duplessix, Decker et al., 1977) on the diblock copolymer, polymethyl methacrylate (PMMA)–deuterated polystyrene (PSD) in dimethyl formamide solution. More recent results in toluene are presented at this meeting (Picot, Duplessix, Benoit, Rempp & Cotton, 1977). The authors found that the radius of gyration of the PSD sequence markedly decreased at high values of \(M_w\) for the PMMA sequence. In the case for a high \(M_w\), PMMA sequence a straight-line variation of \((R_g)_{app}\) with \(Y\) was found. One possible explanation is that \(G_{12}^2\) is zero. This could mean a micellar structure with one or other species coiled concentrically round the other. Measurements on the PSD sequence in a solvent with zero contrast for PMMA did indeed show a collapsed conformation, indicating that such a micellar structure might exist – with PSD inside.

However, recent investigation of the same copolymer, but with lower \(M_w\) PMMA, this time in toluene (Han & Mozer, 1977) indicates a similar structure, but inverted! These authors use SANS to determine \(R_g\) for the PMMA by dissolving the copolymer in deuterated toluene, in which the PSD sequence has no contrast. In a light-scattering experiment there is no contrast between the PMMA sequence and toluene so that \(R_g\) could be determined for the PSD. The PSD was found to be slightly expanded from values for a homopolymer, while the PMMA was very collapsed compared to its theta dimensions.

The authors therefore propose a micellar structure with the PMMA inside. While it is possible that such large differences are caused by subtle differences in the different solvent–polymer interactions and the different molecular weights of the PMMA sequence, clearly further investigation would be desirable.

C. Incompatibility

1. SALS studies

A phenomenon common to many polymers is the existence of a lower critical solution temperature. That is, two poly-
mers may be compatible at a low temperature but may phase-separate at higher temperature. Phase separation may occur by two different mechanisms. One of these is through nucleation and subsequent growth by means of expanding spheres of the new phase within the matrix. The second is the process of spinodal transformation, in which a periodic concentration fluctuation develops and grows in amplitude leading to a morphology characterized by interpenetrating phases. A characteristic observation accompanying phase separation is the occurrence of a cloud point, a temperature at which turbidity develops. This turbidity is obviously associated with light scattering, which can yield information about the morphology of the process. Preliminary observations have been made by Goldstein & Stein (unpublished) of SALS occurring when a blend of poly(o-chlorostyrene) and polystyrene is heated above its lower critical solution temperature. A typical result is shown in Fig. 14. A scattering maximum is seen which moves toward smaller angles with time at the phase-separating temperature. It appears that this may be interpreted in terms of a spinodal decomposition process. It is proposed to extend these studies using SAXS so that earlier stages of the process may be observed.

2. SANS studies

Work on compatible mixtures was described in § III C. 3(b). Kruse et al. (1976) gave an example of results from an incompatible system. This was poly(a-methyl styrene) in PMMA and the resulting Zimm plot is shown in Fig. 15. Extreme negative $A_2$ values are found together with molecular dimensions corresponding to a collapsed coil. In these systems evidence was found for micellar aggregates of about 16 molecules.

Very recent experiments by the group at Imperial College (unpublished) indicate that phase separation effects are observable as a low-molecular-weight blend is cooled through the cloud point at an upper critical solution temperature. Such measurements, involving the short neutron wavelengths, are sensitive to much shorter-range effects than the usual light-scattering techniques and may be able to refine these phase-separation curves.

V. Crystalline polymers

A. General discussion

Crystalline polymers scatter light, X-rays and neutrons because of the density differences between crystalline and amorphous regions. In addition depolarized light scattering occurs because of the aggregation of crystals into optically anisotropic structures. Crystal sizes are such as to scatter X-rays and neutrons in the small-angle region. Such measurements may be used to characterize thicknesses of solution-grown single crystals and thicknesses and intercrystal distances in crystalline mattes and bulk-crystallized samples. Aggregates of crystals such as spherulites achieve dimensions comparable with the wavelength of visible light and consequently may be studied by SALS.

B. SAXS studies

1. Theoretical considerations

Most theories of SAXS from crystalline polymers are based upon one-dimensional models consisting of arrays of alternating crystalline and amorphous regions. For such a perfect array, the scattering is described by Bragg's law. In reality there is a distribution of both crystal thickness and crystal separation leading to deviations from ideal behavior; some are nicely reviewed by Crist (1973) and Burmester & Geil (1972). A commonly used procedure is that proposed by Tsvankin (1964; Zubov & Tsvankin, 1964) and extended...
by Buchanan (1971), in which a trapezoidal electron-density profile along the lattice is assumed to represent a linear density change from the crystalline region to the amorphous region. An exponential amorphous-thickness distribution and a symmetrical rectangular crystal-thickness distribution are adopted. As a result of the types of distribution chosen, the crystallinity is uniquely related to the position and width of the scattering maximum for a given dispersion of thicknesses and boundary-layer widths. Calibration curves were proposed which permit the determination of the average crystal and amorphous-layer thicknesses. While the theory is convenient, it does not do a very good job of fitting the entire scattering curve. For example, Fig. 16 compares the measured scattering (Warner, MacKnight & Stein, 1977) with the best Tsvankin-Buchanan fit for crystalline isotactic polystyrene and appreciable deviations are seen.

Improvements in fit may be obtained by generalizing the model. One approach is that of Hosemann & Bagchi (1962), extended by Brämer (1972, 1973, 1974) and Wenig (1974), where a finite number of lamellae are considered and para-crystalline statistics are used to arrange the crystalline and amorphous regions. Gaussian distributions of crystalline and amorphous thicknesses are commonly adopted and a transition zone between lamellae is introduced. As can be seen in Fig. 17, the isotactic polystyrene data (Warner et al., 1977) may be adequately fitted by this model. However, it is often necessary, as in this case, to assume an unrealistically low number of lamellae in the stack in order to fit the data. An explanation may be that the apparent small size of the crystalline stack is a consequence of misalignment of the crystals (Baczek, 1977). Similar effects arising from lamellar distortion of curvature will be discussed by Vonk (1978) at this meeting. Alternative explanations may be in terms of inhomogeneous statistics (Ruland, private discussion) or in terms of other than Gaussian statistics (e.g. Poisson distribution) for interlamellar separation (Vonk, private discussion).

An alternative approach to this description of the scattering has been proposed by Vonk & Kortleve (1967, 1968; Vonk, 1973), in which a one-dimensional correlation function is calculated from the scattering data by Fourier transformation with

\[
\gamma(x) = \frac{\int_0^\infty s^2 I(s) \cos(2\pi xs) ds}{\int_0^\infty s^2 I(s) ds}.
\]

Such correlation functions calculated for isotactic polystyrene and for a blend with atactic polystyrene are shown in Fig. 18 (Warner et al., 1977). This experimental correlation function may then be compared with those calculated on the basis of models of layered structures. Procedures for fitting the correlation function to the model have been proposed by Vonk. For example, the depth of the first minimum is equal to \((1 - \phi)/\phi\) where \(\phi\) is the volume fraction crystallinity.

A significant extension of the correlation-function approach using interface distribution functions is described at this meeting by Ruland (Stribeck & Ruland, 1978).

A method for analysis of SAXS from lamellar polymers has been proposed by Strobl (1973) in which the scattering curve is considered to be determined by the position and structure of the amorphous boundary layers about the lamellar interfaces. Assumption of a model is not necessary. The method yields the mean lamellar thickness, its range of fluctuation, the electron-density defect per unit area of the lamellar interface and the second moment of the electron density profile of the boundary layer.

Fig. 16. A comparison of the measured SAXS intensity variation of isotactic polystyrene with the best Tsvankin–Buchanan fit (from Warner et al., 1977).

Fig. 17. A comparison of the measured SAXS intensity variation of isotactic polystyrene with the best Hosemann fit using Gaussian statistics (from Warner et al., 1977).
2. SAXS of polymer single-crystal mats

An interesting application of SAXS by Fischer & Kloos (1970) has been in the estimation of the glass transition temperature of the surface layer from observations of the variation of intensity of scattering at the maximum of the long-period spacing with temperature. This intensity depends upon the square of the electron-density difference between crystalline and amorphous layers and hence reflects the break in the variation of amorphous density with temperature occurring at \( T_g \).

Keller and co-workers (Keller & Udagawa, 1972; D'Ilario Keller & Martuscelli, 1972) have examined the folding behavior of short iodine-terminated aliphatic chains and demonstrated the transition from crystals with a single fold of the chain to completely chain-extended crystals.

In a series of papers by Keller's group (Dreyfuss, Keller & Willmouth, 1972; Dreyfuss, 1973; Dreyfuss & Keller, 1973; Jones, Latham, Keller & Girolamo, 1973; Atkins, Keller & Sadler, 1972) the folding behavior of solution-grown nylon crystals is examined. The combined examination of wide-angle X-ray scattering (WAXS) and SAXS reveal that for these polymers having long monomer repeat distances WAXS and SAXS cannot be considered in isolation. The effect of a rather small number of monomer units per fold is evident and results can only be interpreted on the basis of sharp folds.

The thickening of single crystals of polyethylene oxide upon heating was studied by combined use of SAXS with NMR by Fitzsche & Fischer (1973). Different thickening mechanisms are observed at low and high temperatures. The melting and recrystallization processes accompanying thickening are deduced from the development and disappearance of a narrow line component of the NMR spectrum. Theories and observations of crystal thickening have been published by Sanchez, Colson & Eby (1973) and Sanchez, Peterlin, Eby & McCrackin (1974) which are successful in accounting for the SAXS observed linear variation of long period with the logarithm of annealing time.

The surface melting of single crystals of linear polyethylene was studied by Suehiro, Kanizaki & Takayanagi (1976). It was shown that while the long period remained constant with melting, the intensity of SAXS varied reversibly with temperature. Results were correlated with changes in crystal thicknesses estimated from changes in widths of wide-angle reflections.

Keller and coworkers have been active in comparing crystal thicknesses measured by SAXS with those calculated from linear acoustic mode (LAM) Raman frequencies (Folkes et al., 1975; Dlugosz et al., 1976). It is found that if the chains are tilted with respect to the lamellar normal, the Raman frequencies are associated with the tilted chain length, while the SAXS measurement yields the crystal thickness. Differences between the results of the two methods may be related to coupling between crystal layers through amorphous regions, as has been shown by Krimm and co-workers.

Studies on solution-grown isotactic polystyrene crystals have been recently reported by Overbergh, Sadler & Keller (1977), who compared fold length as measured by SAXS with the crystal core thickness estimated from wide-angle line width. The 'linear crystallinity' obtained from the ratio was unaffected by fold-length changes produced by heat annealing. The kinetics of changes caused by annealing were also investigated.

3. SAXS studies of bulk polymers

The emphasis in the use of SAXS for the study of bulk polymers during the past few years has been in the analysis of crystallization and melting processes. Earlier studies have involved the interpretation of data by the Tsvenkin or Vonk techniques. For example, Overbergh, Berghmans & Reynaers (1976) have applied Tsvenkin analysis to the study of the crystallization of isotactic polystyrene and have concluded that the linear crystallinity from SAXS is significantly higher than the macroscopic crystallinity obtained from DSC and WAXS. They interpret the discrepancy as being due to amorphous material not incorporated in interlamellar regions. This result differs from the conclusions of Wenig, Karasz & MacKnight (1975) and Warner, MacKnight & Stein, 1977), who have used Hosemann analysis for this polymer and have concluded that the linear crystallinity measured by SAXS agrees with the macroscopic crystallinity. The fit of data to the theory required, however, the assumption, as previously discussed, of an unreasonably low number of lamellae contributing to the scattering.

The use of various types of distribution functions for thicknesses of the crystalline and amorphous phases with the Vonk approach has been discussed by Brown, Fulcher & Wetton (1973) in their studies of polyethylene, poly(trimethylene oxide) and poly(tetramethylene oxide). They point out that for highly crystalline polymers, the choice of distribution functions was not important, but for the lower crystallinities it was significant. Better fits were obtained using Gaussian functions for both phases rather than log normal distributions. Somewhat higher crystallinities were obtained with SAXS than with WAXS.

This study was continued by Warner (1975) with further studies on poly(tetramethylene oxide) (PTMO) and poly(ethylene oxide), who followed secondary crystallization and concluded that during this process, lamellae become more nearly perfect and thicken slightly and that the amorphous phase densities. On isothermally crystallizing PTMO additional lamellae grow in the amorphous regions between existing lamellae. Crystallization under pressure yielded thicker and more nearly perfect lamellae.
The structure of partially crystalline polymer systems was reviewed by Fischer & Fakirov (1976), who discussed variations in SAXS occurring during melting and annealing. These authors believe that the decrease in crystallinity during melting is due to an increase in thickness of the disordered surface layer. Thickening during annealing is due in part to melting and recrystallization and in part to refolding in the solid state, depending upon crystallization conditions, heating rate and molecular weight.

The temperature dependence of the SAXS from polyethylene has been discussed by Raman, Deopura, Varma & Gupta (1977), who consider the continuing problem of non-integral ratios of long periods obtained from the two scattering maxima. This has been previously reviewed by Geil (1966), Kaves & Schultz (1971) and Burmester (1970). They agree with previous conclusions that the two maxima are not two orders of the same spacing but are the result of two morphological structures in the sample. It is found that the two spacings remain quite constant up to the crystallization temperature of 123°C. Beyond this temperature, both spacings increase as a result of the growth of larger crystals at the expense of smaller ones and at around 127°C they merge into a single spacing. Crystallinity is found to decrease sharply with increasing temperature above 123°C.

Morphological changes during the melting of bulk-crystallized polymers have also been studied by Fulcher, Brown & Wetton (1972) using the correlation-function technique. Changes in thicknesses and widths of distributions of crystalline and amorphous layers of PTMO and PE were studied as a function of temperature. Crystal thicknesses were found to decrease and amorphous thicknesses increase with temperature in a manner favoring a 'surface melting' mechanism involving a progressive transfer of chain segments from the 'fold surfaces' of the single-crystal lamellae to the amorphous or melt-like phase.

An interesting study of observations of rapid SAXS (using a position-sensitive detector) and WAXS during polymer crystallization has been published by Schultz (1976). He concludes that during primary crystallization amorphous groups within the primary lamellae stacking become filled in. During secondary crystallization lamellae behind the spherulitic growth front are found and existing lamellae thicken.

A study of crystallization of PET was reported by Müller (1974). An analysis of the changes in the SAXS invariant during crystallization was interpreted in terms of density changes of the amorphous phase. The density is found to decrease in a manner dependent upon the crystalline volume fraction but not upon the temperature of crystallization. Crystallization ends when the sizes of the non-crystalline regions drop below a certain limit. Since the number of crystals depends upon the crystallization temperature, this determines the maximum crystallinity achieved at long times.

4. SAXS of crystalline copolymers

Studies of the SAXS from ethylene–vinyl acetate and ethylene–acrylic acid copolymers were reported by Kortleve, Tuijman & Vonk (1972) and Vonk (1972). Comparisons were made between the SAXS invariant, the overall density and the crystallinity and were interpreted in terms of the densities of the phases of an assumed two-phase structure. In both cases it is found that increasing the concentration of the comonomer leads to a deviation in crystalline density from that determined by the lattice constants, suggesting an appreciable inclusion of comonomeric side groups within the crystalline phase. The crystallinity decreases with increasing comonomer content and an increase in amorphous phase density occurs. Vonk compares these results with similar studies on linear and alkyl-branched polyethylenes (Kortleve & Vonk, 1960) where good agreement is obtained from the SAXS calculated crystal density and that calculated from lattice constants. In view of this it seems surprising that the bulky acid and acetate side groups are accommodated within the crystal. The results are rationalized by assuming that the side groups are 'encapsulated' by the crystal lattice, which forms 'kinks' to circumvent the substituent, so that deviations from the normal lattice parameters are minimized and the decrease in free energy arising from the increased crystallinity balances the increase due to the kink.

This observation may help explain the observation by Kajiyama, Oda, Stein & MacKnight (1971) that the inclusion of methacrylic acid groups in branched polyethylene in their unionized or ionized form (ionomers) did not lead to an appreciable decrease in crystallinity of annealed samples. Spherulitic structure was found to form (Prud'Honne & Stein, 1971) but having more disorder than for unsubstituted polyethylene.

SAXS from metal salts of such ionomers has been observed to lead to a scattering maximum (Wilson, Longworth & Vaughan, 1968) associated with some sort of ordering of the metal cations. A radial-distribution-function analysis of the combined excess SAXS and wide-angle scattering from such salts (from which the scattering of the unionized acid is subtracted) supports the existence of clusters of cations in these structures (Kao, Stein, MacKnight & Cargill, 1974). The existence of the maximum has been interpreted (MacKnight, Taggart & Stein, 1974) as being due to the distance of closest approach of other cations to this cluster, which is surrounded by a sheath of unionized polymer. Recent unpublished studies by Roche of the SAXS invariant for such scattering have indicated that a relatively small concentration of such structures is adequate for accounting for the scattering maximum.

The effect of chlorination of polyethylene on the SAXS of polyethylene has been described by Roe & Gieniewski (1973), where the partitioning of chlorine between the crystalline and amorphous phases was studied through observation of the invariant. It was concluded that typically 15% of the chlorine may be incorporated into the crystal, leading to an increase in the lattice dimensions and a decrease in the degree of crystallinity.

A study of the SAXS from 1,3,5-trioxane-1,3-dioxolane copolymers was reported by Holdsworth & Fischer (1974). In this system unit-cell parameters also depend upon composition, suggesting the incorporation of comonomer units in the crystal lattice. The value of the SAXS invariant also requires such inclusion. The two-phase model was justified for interpretation of the scattering. Melting of this copolymer suggests a more complex process, involving both increasing thickness of amorphous regions and the melting of whole crystallites.

5. SAXS of crystalline polymer blends

The location of the non-crystalline component in a blend with a crystalline polymer may be studied by SAXS by observing the effect of composition upon the lamellar structure of the crystalline polymer and upon the scattering invariant. The SAXS from a blend of i-PS with atactic poly-2,6-dimethylphenylene oxide (PPO) (Wenig et al., 1975) indicated that the lamellar spacing of the i-PS increased with PPO content in such a way as to accommodate the PPO between
the lamellae. Similar results were found by Khambatta et al. (1976) for PCL/PVC blends, in which the PVC was accommodated between the PCL lamellae. In both cases the SAXS-determined linear crystallinity agreed with the macroscopic crystallinity.

Different results have been obtained with i-PS/a-PS blends in which the i-PS lamellar spacing was found to be independent of a-PS content, leading to a crystallinity determined by SAXS greater than the macroscopic crystallinity. In such blends of more than 70% i-PS, the structure was found to be volume-filled with spherulites, suggesting that the a-PS resides within the spherulites but in volumes larger than inter-lamellar regions.

The differences between this latter system and the former were rationalized in terms of the $\delta$ parameter of Keith & Padden (1964), defined as $\delta = D/G$, where $D$ is the diffusion coefficient of the non-crystalline compound and $G$ the linear growth rate of the crystals. This parameter is of the order of the distance that the non-crystallizing component may diffuse during the time of crystallization and must be of the order of the resulting morphological size. The differences between the two types of system may be understood on the basis of the variation of $\delta$ with $T_s$ and molecular weight.

6. SAXS from oriented crystalline polymers

The SAXS from unoriented polymers is isotropic. That is, the scattered intensity is cylindrically symmetrical about the incident beam direction. For oriented crystalline polymers this spherical symmetry gives way to an azimuthally dependent pattern with an angular distribution characteristic of the distribution of lamellar orientation. Commonly observed types of patterns are 'two-point patterns', characteristic of structures in which lamellae are oriented in parallel arrays perpendicular to the draw direction, and 'four-point patterns', which may be interpreted in terms of lamellae tilted at positive and negative angles with respect to the draw direction. A recently acquired set of patterns obtained during the stretching of a low-density polyethylene and with the two-dimensional position-sensitive detector technique is shown in Fig. 19 (Baczek, 1977). The circularly symmetrical intensity contours for the unstretched sample change, at small strains, to ellipsoidal patterns, in which the scattering maxima shift in a manner characteristic of increasing separation of those lamellae oriented perpendicular to stretching and decreasing separation of lamellae oriented parallel to stretching. Such patterns have been observed by Peterlin & Sakaoku (1966, 1967; Sakaoku & Peterlin, 1967, 1971) and have more recently been discussed by Gerasimov, Genin & Tsankin (1974) in terms of spherulite deformation models. At small strains spherulitic aggregates of crystals can be considered to deform in an affine manner (Hay & Keller, 1965), in which changes in lamellar separation mirror changes in macroscopic dimensions. Approximate conformity to this behavior has been quantitatively demonstrated (Baczek, 1977) but deviations are seen at higher strains. Gerasimov et al. show how these changes in patterns at higher stress can be obtained by summing patterns from extruded films drawn parallel and perpendicular to the extrusion direction. While at small strains branched polyethylene shows that there is no appreciable increase in the SAXS invariant with stretching, indicating no density depletion, intensity increases signifying void formation are seen at higher strains, especially with more crystalline samples. A quantitative study of such density changes has recently been published by Hara (1976).

The complex structure of spherulitic polymers renders the unambiguous characterization of changes occurring with stretching difficult. The problem has been simplified by Keller & Pope (1971: Pope & Keller, 1975, 1976, 1977a) who studied films having simpler 'single-crystal' type texture prepared by successively stretching, rolling and annealing at various temperatures. Such films contain arrays of parallel lamellae either perpendicular to or tilted with respect to the machine direction, depending upon the annealing temperature. Stretching such films results in changing separation of lamellae, changing tilt angle of lamellae with respect to the stretch direction and changing tilt angle of molecular chains with respect to the lamellar plane in a manner that may be readily resolved from analysis of the SAXS pattern, so that morphology, macroscopic and microscopic strain can be interrelated.

Hosemann and co-workers have championed the use of paracrystalline concepts to explain both WAXS and SAXS from polymer films and fibers (Hosemann & Bagchi, 1962). They have explained deformation and yielding phenomena in terms of changes in arrangements of the presumed building blocks of the structure called 'microparacrystals'. These concepts have been used, for example, to account for the four-point patterns obtained with branched cold-stretched polyethylene (Loboda-Cackovic, Cackovic & Hosemann, 1973). This approach has recently been extended to account for the SAXS from quenched and cold-drawn sheets of isotactic polypropylene (Loboda-Cackovic et al., 1976), where it is concluded that microparacrystals, 5 nm wide and 4 nm long build up a monoclinic macrolattice. The equatorial SAXS is explained by broadened lateral grain boundaries between the microparacrystals of one layer in the direction of the sheet surface.

Highly oriented fibrous systems are simplified in that they
The perfection of such regions and an increase in size of the crystalline and amorphous phases through combined measurement from an ~ helical phase to a 13 planar zigzag phase upon crystallization and by Stein and coworkers (1973), and consists of a four-leaf-clover-type crossed-polaroid (13) pattern and a parallel-polarization pattern having twofold symmetry. The 13 pattern exhibits an interesting maximum occurring at an angle inversely related to the spherulite size. Recent studies have been concerned with the utilization of this maximum for following changes in spherulite size accompanying crystallization (Misra, 1974; Picot et al. 1968; Van Antwerpen & Van Krevelan, 1972; Baba, 1972; Baranov, Zhu-Chan, Volkov & Frenkel, 1967).

Recent theoretical efforts have been concerned with deviations from ideal scattering patterns occurring because of truncation of spherulites by each other (Prud’homme & Stein, 1973), internal disorder (Yoon & Stein, 1974) and distribution of spherulite size (Ishikawa & Stein, 1976; Prud’homme & Stein, 1977).

Experimental efforts have been concerned with the quantitative comparison of theory with observed scattering patterns. Such studies have been reported by Kambatta et al. (1976) for PCL/PVC blends, by Baba (1972) for PET crystallization and by Stein et al. (1977) for the melting of polyethylene and for i-PS/a-PS blends. It is found that scattering intensities depend upon the number, size, degree of crystallinity and perfection of spherulites in a manner useful for sample characterization. Studies are greatly facilitated through use of the optical multichannel analyser.

Some polymers exhibit rod-like morphology. Following earlier theory by Rhodes & Stein (1969) theories for rod scattering have been extended, notably by Kawai, Hashimoto and coworkers (Moritani, Hayashi, Utsuo & Kawai, 1971). Because of the difficulty of treating inter-rod interference effects (Prud’homme & Stein, 1974), the quantitative description of the scattering by rods is less successful than that for spherulites.

C. SALS studies

1. Unoriented bulk polymers

The most commonly observed SALS pattern for unoriented polymers is that due to spherulites, which may be interpreted in terms of the scattering by anisotropic spheres (Stein & Rhodes, 1960; Stein, 1973), and consists of a four-leaf-clover-type crossed-polaroid (13) pattern and a parallel-polarization pattern having twofold symmetry. The 13 pattern exhibits an interesting maximum occurring at an angle inversely related to the spherulite size. Recent studies have been concerned with the utilization of this maximum for following changes in spherulite size accompanying crystallization (Misra, 1974; Picot et al. 1968; Van Antwerpen & Van Krevelan, 1972; Baba, 1972; Baranov, Zhu-Chan, Volkov & Frenkel, 1967).

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2. Oriented bulk polymers

The change in spherulitic SALS patterns with deformation was first observed by Stein & Rhodes (1960) and theoretically described by Stein, Clough & Van Aartsen (1962), Van Aartsen & Stein (1971) and Samuels (1966). The theory is based upon the model of a sphere deforming to an ellipsoid, the axial ratio of which may be determined from measurements on the pattern. This technique has been used to study spherulitic deformation and to characterize its time dependence (Erhardt & Stein, 1967, 1968; Hashimoto & Stein, 1973).

The SALS patterns accompanying formation of crystals in an oriented amorphous polymer have been described for cis-1,4-polyisoprene by Yau & Stein (1968) and by Hashiyama (1976), for trans-1,4-polybutadiene by Akana & Stein (1975), for poly-N-vinyl carbazole by Su (1975) for PET by Misra (1974) and Baranov, Kenarov & Volkov (1970) and for nylon-66 by Baranov, Bychkovsky, Gokhman & Nosov (1972). While quantitative theories for the SALS by such structures have not been developed, qualitative conclusions consistent with microscopic observations may be drawn. At low strains, spherulitic-like structures develop with their principal axes oriented perpendicular to the sample orientation direction. These increase in number and eccentricity with increasing strain and ultimately evolve toward rod-like ‘shish-kebob’ structures with their long axes oriented parallel to the sample-stretching direction. Recrystallization of such structures accompanying annealing may be observed.

D. SANS studies

SANS measurements have been made on partially crystalline bulk polymers and on single-crystal lamellar structures. In these experiments the first aim was a determination of the chain conformation, usually via radius-of-gyration measurement in the Guinier range. An important area of attack has been the question of adjacent re-entry in lamellar structures. In this case the more fruitful source of information may be the intermediate and wide-angle range, which is more sensitive to local structure.

1. Measurements of radius of gyration

Until recently the only crystallizable polymer studied in any detail by SANS has been polyethylene. Measurements of the conformation in the melt yielded values for \( R_g^2/M_w \) of 0.063 ± 0.015 nm (Wignall, Ballard & Schelten, 1976), subsequently revised 0.046 ± 0.005 nm (Schelten et al., 1976) and 0.045 (Lieser, Fischer & Ibel, 1975) in good agreement with values obtained in theta solution (0.045).

Even in these melt experiments it became apparent that there may be problems of sample preparation. Schelten, Wignall, Ballard & Schmatz (1974; Schelten, Wignall & Ballard, 1976) noted that the values of the molecular weight obtained from the neutron scattering extrapolated to forward angle were in some cases anomalously large and that in these cases larger values of the radius of gyration were obtained. The authors attribute this effect to some clustering of the tagged molecules due to small thermodynamic differences between polyethylene-\( h \) and polyethylene-\( d \). Much more important effects were observed in the solid state. Some authors (Schelten et al., 1976) later showed that samples precipitated from xylene and compression-molded were particularly subject to anomalous effects in the forward scattering. They were able more or less to eliminate the problem by changing their solvent to o-dichlorobenzene and rapid quenching from the melt after compression molding. X-ray measurements indicated the presence of lamellar regions in these samples but the values of \( R_g^2/M_w \) of 0.045 nm were found to be the same as for measurement in the melt. However, for solution-grown crystals, \( R_g \) has been found to be very much less than expected for the melt (Sadler & Keller, 1977). In this case crystallization was at relatively high supercooling (70 °C in xylene) and the crystals were sedimented to give oriented mattes in the conventional manner.

The so-called ‘clustering’ effect has been the subject of much discussion. It appears to be a particularly troublesome problem in polyethylene. There is a 6% difference in the crystallization temperature for the deuterated and undeuterated species which is thought to be relevant. However, Schelten et al. (1976) etched some of their samples to remove preferentially the amorphous regions. Analyses for deuterium content showed no differences before and after etching, even though there was a 6% increase in crystallinity in the etched samples. Nevertheless since the effect is removed by fast quenching it appears to be associated with crystallinity in the samples.

In a recent publication Schelten, Wignall, Ballard & Longman (1977) have compared model calculations based on aggregates of tagged molecules with the experimental results. In particular, these authors have used the calculations of the effects of clustering to explain the anomalous features of their neutron data. It is perhaps easier to envisage regions of higher density of tagged molecules, arising from a different rate of crystallization, than actual clusters of molecules. It should be noted that the presence of voids, or of density fluctuations in samples, produces a small-angle signal which will affect the extrapolated forward scattering (see § II B) and certainly varying concentration of H and D across the sample would be equally disastrous. Measurements have been made (Sadler & Keller, 1977) which identify a particular signal, attributable to zones of different density of tagged molecules, the density difference increasing with decreasing supercooling for both melt and solution growth. A simplified analysis is given of these signals in terms of that expected for a two-phase model (the ‘Porod’ law), and reasonable values for surface-to-volume ratios are obtained. A particularly decisive observation was that mild crosslinking prior to slow crystallization much reduces the excess forward scattering, as would be expected if diffusion in the melt during crystallization is inhibited in this way. Another model, similar in concept, which attempts to take proper account of this type of concentration fluctuation has recently been proposed by Summerfield, King & Ullman (1978). Corrections based on this model were applied to SANS data from solutions and bulk crystallized PE. In two cases it was found (Ullman et al., 1977) that solution-grown PE shows smaller molecular dimensions than bulk-formed PE. This effect is associated by the authors with greater adjacent reentry in the solution-grown crystals.

2. Chain folding and adjacent re-entry

In pressure-crystallized samples the lamellae may be up to several thousand angstroms thick. Recent neutron scattering experiments in the very-small-angle range investigated the conformation of molecules of about one lamella thickness in length and of molecules twice as long. Problems of isotopic density fluctuations were as usual encountered, but Ballard et al. (1977) measured radii of gyration of molecules, which they relate to rod-like configurations of lengths in good
agreement with the lamellar stem lengths determined by nitric-acid etching. Since doubling the chain length produced no change in the radius of gyration it was concluded that the chains were folded within the same lamella.

The earlier work by the same group on rapidly quenched polyethylene (Schelten et al., 1976) in the low-$\kappa$ range was extended into the intermediate range. They found Kratky plots $[K^2S(K) \propto \kappa]$ which were very similar to those for molten samples. Since a random-coil model, which would fit both this and the low-$\kappa$ data, is in conflict with the known crystallinity of the samples, the authors attempted to fit their data to a model based on folding within one crystal plane in a lamella and random wandering between lamellae. They were, however, unable to fit such a model satisfactorily to the data, and conclude that it is difficult to explain the SANS data for rapidly quenched samples on the basis of adjacent re-entry.

Investigation of oriented mates of solution-grown crystals (crystallized from xylene) mounted with the crystal planes parallel to the plane of the holder (i.e. perpendicular to the incident neutrons) first encountered anomalous scattering in the forward direction (Sadler & Keller, 1976). In samples oriented with the crystal planes parallel to the incident neutrons this scattering was even more intense. Pressing the sample at 60°C reduced the forward scattering and for this reason it was tentatively assigned to multiple internal scattering between voids and stacks of crystals. Results were found to be consistent with sheet structures and with a model where stems of folded molecules are confined to the same (110) plane. This conclusion was based on observed decrease of values of $K^2S(K)$ with increasing $\kappa$. Furthermore, the density of tagged molecules obtained when the model was fitted to the data was consistent with predominantly adjacent re-entry along a crystallographic plane, which is presumed to be (110). Further measurements (Sadler & Keller, 1977) have been made for both solution- and melt-growth for $\kappa$ large enough (up to $0.3 \text{Å}^{-1}$) for the alternative models of adjacent or randomly re-entrant folding to give particularly simple predictions. For solution-grown crystals, predominantly adjacent re-entry was found to explain the data, but a difference according to molecular weight suggests that as molecular weight increases, adjacent folded sheets approach one another and yield higher intensities. Measurements were made on the forward scattering which confirmed that these effects cannot in this case be attributed to lack of complete randomness of the tagged molecules (‘clustering’). Results for melt growth were quite different, agreement being obtained for effectively random re-entry, each chain traverse of the lamella acting as an independent rod-like scatterer. For this range of $\kappa$ the finite size of the polyethylene chain has to be accounted for.

High intensities which give rise to a peak in a $K^2S(K)$ plot have been found by Ullman et al. (1977) to be concentration dependent and associated with anomalous values of radii of gyration. These authors also attribute the effect to isotopic separation and find that, when their data are corrected for concentration fluctuations, crystals obtained by precipitation show evidence of adjacent re-entry, while bulk crystallized samples do not.

These data have been qualitatively compared to calculations of Yoon & Flory (1977), who calculated the effects of adjacent stems on the scattering in the intermediate-$\kappa$ region. The solution-grown crystals would require about seven adjacent stems, while the bulk data can be explained with less than one adjacent stem on average.

The above discussion serves to emphasize the problems of investigating crystalline polymers and the very large number of questions which have still to be elucidated. Until recently published work existed only for polyethylene. It remains to be seen whether the problems are specific to this polymer or more general to the crystalline state. Indications are that such problems are not so important for polyethylene oxide (Allen & Maconnachie, 1976) in the melt where the ratio $R_g^2/M_w$ was found to be 0.047 nm.

In PEO spherulite crystal structures on the other hand Allen & Tanaka (1977) have recently found evidence not only for clusters of up to 10 rod-like tagged molecules in the constituent lamellae but also for large (20 nm) domains of varying overall density of these tagged molecules.

Data shortly to be published for both natural and regenerated cellulose (Fischer, Herchenroeder & Manley, 1978) shows a peak corresponding to a long period of 16.5 nm in Fortisan (regenerated) and 19.5 nm in rayon, when these are deuterium exchanged, but no such period for natural cellulose. However, an intense scattering in the meridional direction in natural cellulose, tentatively associated by the authors with spindle-shaped defects, may be enough to mask the appearance of diffraction peaks in the natural fibres.

Results presented recently, and at the Gatlinburg conference (Ballard, Cunningham & Schelten, 1977; Ballard, Schelten & Longman, 1977; Ballard, Cheshire, Longman & Schelten, 1978) indicate that isotopic separation problems are not important for polypropylene. They found the somewhat surprising result that molecular dimensions are identical above and below the crystallization temperature and in good agreement with $\theta$ dimensions.

References


Baba, K. (1972). MS Thesis, Univ. of Massachusetts, Amherst, MA.


