The structure of amorphous polymers

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Over the past ten years the structure of amorphous polymers has been extensively investigated. Publications on this topic were concerned with various aspects of the amorphous structure and were often based on specific molecular models. This review article attempts to discuss the interrelations between the different structural properties which were studied. The topics covered are the short range positional order, the orientational order, the chain conformation, the supermolecular structure and the relation between molecular and macroscopical properties both of the fluid and the glassy state. The basic theory of the fluid state is introduced at the beginning as well as the experimental techniques currently used to characterize the amorphous structure. Experimental results on different amorphous polymers and oligomers are then discussed and the information is pointed out which can be derived from these data. Finally models on the structure of amorphous polymers are considered briefly.

Keywords Amorphous polymers; structure; fluid state; orientation; conformation

INTRODUCTION

The study of the amorphous state in general is divided historically into two parts, the static and the dynamic properties. The early work on the amorphous state was predominantly concerned with macroscopic aspects; such as thermodynamic and transport properties. Sometime later the molecular aspects of the amorphous state were also taken into account, as it became clear that a basic understanding could only be developed if the relation between molecular and macroscopic properties were known. It soon became obvious that the quantities which determine macroscopic static and dynamic phenomena were the interaction potentials, the spatial arrangement and the motions of the particles in the amorphous state[1,2].

In the past twenty years a fairly satisfactory understanding of atomic fluids and, in a more restricted way, also of low molecular weight fluids, has been developed. Considerable advances have also been achieved in the area of the static and dynamic properties in concentrated polymer solutions and in the bulk amorphous phase both in the molten and in the glassy state[3]. Detailed investigations of the chain conformation, that is of the rotational isomeric state, by small angle neutron scattering have contributed greatly to our present knowledge on the structure of amorphous polymers[3–5].

It seems, however, that less progress has been made in determining the local molecular structure, namely the short range positional and orientational order of the chain segments[70]. These quantities are, of course, highly important, since macroscopic properties such as pressure and compressibility or the surface free energy may be expressed in terms of molecular properties[1,2].

It is the main aim of this review article to demonstrate what has been learned up to now about the short range order in amorphous polymers and its relation to macroscopical properties. While writing up the paper it became clear, that it is necessary to give a brief introduction into theoretical concepts which have been used to characterize the amorphous state in general. Furthermore, experimental techniques which allow the determination of those properties, which are characteristic of the amorphous state, will be discussed. Molecular models of the structure of amorphous polymers will be considered only briefly since they are in most cases not sufficiently well defined for adequate testing with respect to the short range order. Finally the chain conformation in the glassy state as well as in the molten state will be treated again in a short chapter, since excellent review articles have recently been published on this subject[4,5].

GENERAL DESCRIPTION OF THE LOCAL STRUCTURE OF MOLECULAR FLUIDS

Molecular interactions and the local structure

The structure and the properties of the fluid state are known to depend on the interactions between all particles of the fluid[1,2]. The many-body interaction potential $u(\vec{r}_1 \ldots \vec{r}_N)$ may in principle be written in terms of the pair-potential, the three-body potential and higher-order potentials[6]. The pair theory of the liquid state represents an attempt to derive equations for all liquid properties solely on the basis of pair functions. Higher order functions are neglected, since many-body effects cannot be adequately taken into account as yet. It is not known, however, how important the higher order terms are. The pair potential can be calculated, in principle, from the basic properties of the atoms which comprise the amorphous material. Usually a Lennard–Jones potential or a modified version of it is taken[7].

The structure of the amorphous state is represented by probability functions $n_N^n\ (\vec{r}_1 \ldots \vec{r}_n)$, which give the probability of observing a particular configuration of n particles out of a total number of N particles in the system. This is shown schematically in *Figure 1*. The term 'configuration' denotes the spatial arrangements of atoms or molecules.

Again it is assumed, in the pair approximation, that the structure and those properties, which are governed by it, can be described solely by the probability for the

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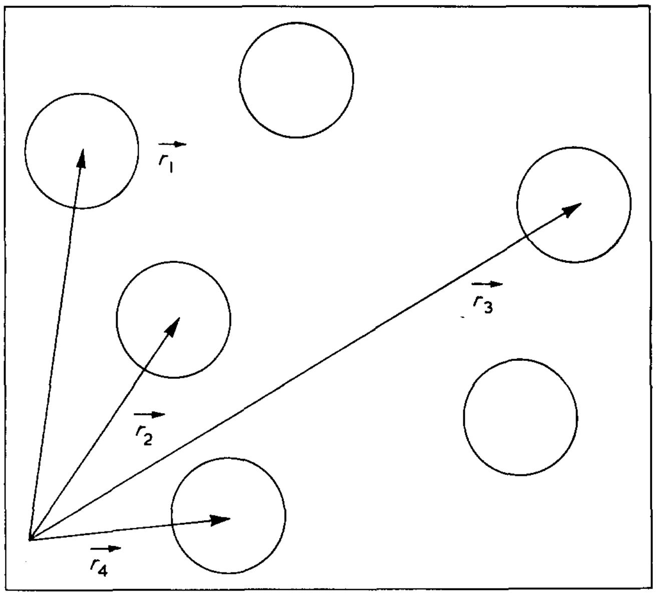

Figure 1 Configuration of spherical particles

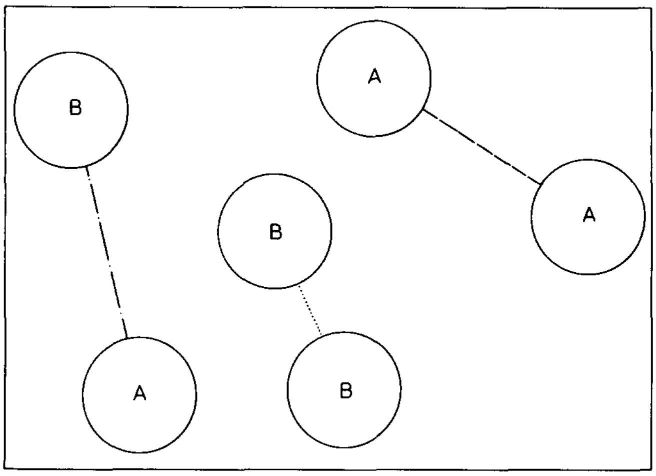

Figure 2 Configuration of spherical particles in a binary mixture (— — —)$g_{AA}(r_{12})$; (· · ·)$g_{BB}(r_{12})$; (—·—·)$g_{AB}(r_{12})$

configuration of pairs of particles of the system. This function, known as the density correlation function, is equal to the square of the particle density ρ_N, if no correlations exist, as in the case of a gas.

$$n_N^2(\vec{r}_1\vec{r}_2)=\langle n_N^1(\vec{1})n_N^1(\vec{2})\rangle=\rho_N^2 \qquad (1)$$

where the particle density is given by

$$\rho_N=N/V \qquad (2)$$

N is the number of particles and V the volume.

The correlations, which do exist in the amorphous state, are represented by the pair correlation function $g(r_{12})$, which for homogeneous fluids is defined as:

$$n_N^2(\vec{r}_1\vec{r}_2)=\rho_N^2 g(\vec{r}_{12}) \qquad (3)$$

$$\vec{r}_{12}=\vec{r}_2-\vec{r}_1 \qquad (4)$$

The quantity $\rho_N g(\vec{r}_{12})$ gives the probability of observing the particle 2 at $\vec{r}_{12}$ relative to a reference particle at 1. This is a sufficient (one dimensional) representation of the three dimensional structure of a homogeneous isotropic liquid.

The pair correlation function introduced so far gives an adequate description of the amorphous structure only for one component atomic systems. For multi-component mixtures it becomes necessary to know partial correlation functions such as for instance $g_{AA}(\vec{r}_{12})$, $g_{BB}(\vec{r}_{12})$ and $g_{AB}(\vec{r}_{12})$ for the particular case of a binary fluid composed of particles A and B (*Figure 2*).

The structure of molecular fluids as well as the interaction energy can be expressed in terms of partial correlation functions containing intra- and intermolecular correlations of the atoms as well as in terms of the interactions between all atoms belonging to the same molecule and to the neighbouring molecules[7,8]. This situation is depicted schematically in *Figure 3*.

A different approach for molecular fluids consists of specifying the distribution of the centres of the molecules and, in addition, of the orientations of the molecular axes relative to some arbitrary frame of reference ω_i. *Figure 4* demonstrates this schematically for particles having an ellipsoidal shape. The interaction energy u_N will, of course, also depend on the relative orientation of the molecular axes in addition to the dependence on the separation of the molecular centres:

$$n_N^2=\rho_N^2 g(\vec{r}_{12},\omega_1,\omega_2) \qquad (5)$$

$$u_N^2=u(\vec{r}_{12},\omega_1,\omega_2) \qquad (6)$$

It is often convenient to expand these quantities in terms of spherical harmonics $Y_{lm}(\omega_i)$, since the spherical harmonic coefficients $gl_1l_2m(r_{12})$ will depend only on the position of the molecules:

$$g(r_{12},\omega_1,\omega_2)=4\pi\sum_{l_1l_{2m}} g_{l_1l_{2m}}(r_{12}Y_{l_{1m}}(\omega_1)Y_{l2-m}(\omega_2) \qquad (7)$$

and since particular coefficients $g_{l_1l_{2m}}(r_{12})$ are directly obtainable from experiment, as will be described below[7,8].

The structure and consequently the pair correlation

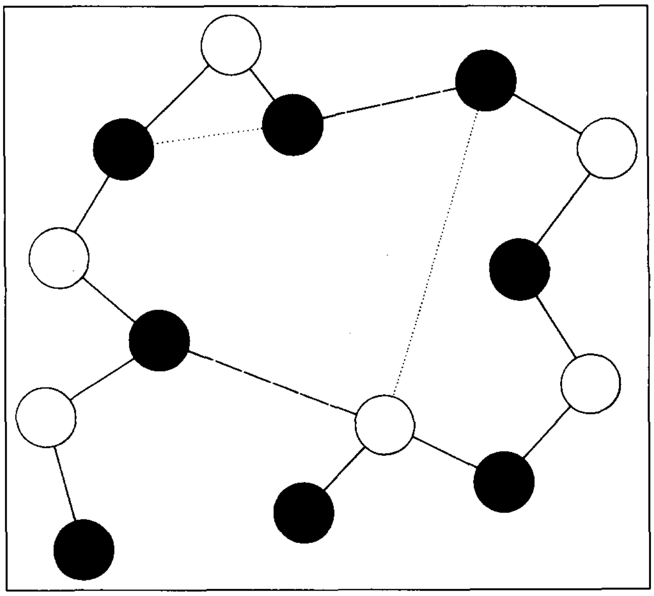

Figure 3 Correlations in molecular fluids (— — — intermolecular and · · · intramolecular correlations)

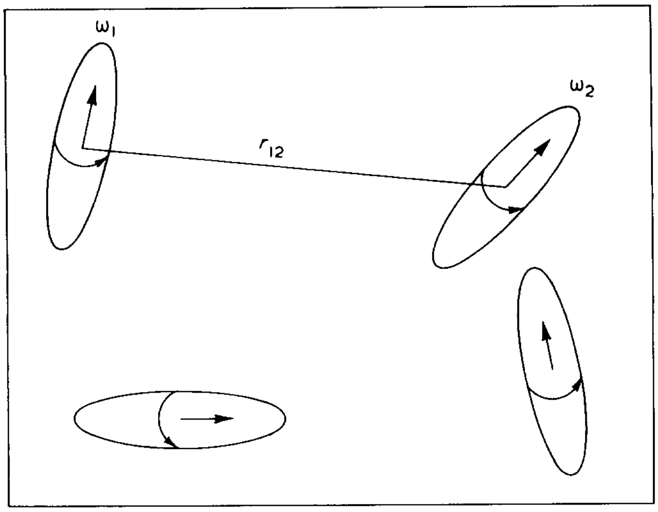

Figure 4 Configuration of elliptic particles

function is determined directly by the interaction potential. The two quantities have been related to one another by a number of approximate theories[1,2]. None of them has proved to be satisfactory for molecular fluids (Percus–Yevick equation, Yvon–Born–Green equation).

For this reason computer simulation calculations have been used to gain new insight into the relation between interaction potential and the local structure[7]. One way of determining the properties of classical many particle systems (the Monte Carlo method) consists in applying statistical mechanics to a limited number of particles, for which a large number of states are created by the computer simulations. The averaging procedure is usually done numerically. In the most direct approach (the Molecular Dynamics method) the properties are determined by setting up the Newtonian equations of motion, assuming approximate interaction potentials. This set of equations is then solved numerically to give the structure and motions as well as static and dynamic properties. The static properties are obtained by time averaging. Both methods have been used to obtain non-experimental data on the positional as well as orientational order for low molecular weight fluids such as water[9], ammonia[9] and n-alkanes[10]. They have so far, however, not been applied to fluids composed of long chain molecules.

A general conclusion to be drawn about the relation between interaction potentials and the local structure of liquids is that the structure is primarily determined by the sizes and the shapes of the molecules, that is by the short range repulsive forces, and that the intermolecular attractive forces are of minor importance in most cases[8,11].

Relation between molecular and macroscopical properties

Macroscopical properties such as thermodynamic properties or mechanical properties can be expressed as volume integrals over certain molecular correlation functions and pair interaction functions. Two examples are given for the pressure p and the isothermal compressibility $\kappa(T)$[1,2,7]:

$$P=\rho_N kT-\frac{1}{6}\rho_N^2\int \mathrm{d}\vec{r}_{12}\left\langle \vec{r}_{12}\frac{\partial u(\vec{r}_{12}\omega_1\omega_2)}{\partial\vec{r}_{12}}g(\vec{r}_{12},\omega_1,\omega_2)\right\rangle_{\omega_1,\omega_2} \tag{8}$$

$$\rho_N kT\kappa(T)=1+\rho_N\int \mathrm{d}\vec{r}_{12}\langle g(\vec{r}_{12},\omega_1,\omega_2)-1\rangle_{\omega_1,\omega_2} \tag{9}$$

The macroscopical properties are in most cases strongly determined by the short range part of the pair potential and the pair correlation function. The orientation dependent properties of both molecular functions—interaction potential and pair correlation function—enter into the expressions which relate molecular and macroscopical properties. The compressibility is an exception insofar as it is determined only by the distribution of the centres of the molecules (see below), averaged over all orientations, and because it depends strongly on the asymptotic behaviour of the pair correlation function for large distances $|\vec{r}_{12}|$[12,13]. It is known for instance that the short range part of the pair correlation function does not change significantly if a critical point is approached whereas the compressibility diverges at this point[12,13]. The asymptotic behaviour of the pair correlation function is governed by long range forces which originate from the interaction of the particles, which compose the fluid, with long-range waves of the fluctuating electromagnetic field[14].

It is clear that the pair correlation function and the pair potential must be known accurately over a sufficiently large range of distances and orientations if one wants to calculate macroscopic properties from molecular pair functions. Consequently only few examples are known where this approach has been used to calculate macroscopic properties. These examples are restricted to simple atomic and low molecular fluids such as water[15]. Some information on the relation between molecular and macroscopic properties can nevertheless be obtained even for complex amorphous systems such as amorphous polymers, as will be discussed below.

Structure determinations in amorphous systems

The scattering of radiation by condensed matter gives information about the distribution of atoms or molecules. Almost any kind of radiation may be used for such experiments, provided that the wavelength of the radiation is of the order of magnitude of the interatomic spacings. Differences arise due to the differences in the scattering properties of single atoms for each kind of radiation as expressed by different values of the scattering amplitude[1,16]. The distribution of the scattered intensity is determined by the Fourier transform of the appropriate pair correlation function for amorphous materials.

For molecular fluids two different approaches have been used to relate the local structure to the scattering diagram. If the internal structure of molecular groups or of the total molecule is known one is able to express the scattered intensity in terms of the configuration of the molecules[17]:

$$I(\vec{s})=\langle F_m^2\rangle+\rho_N\left[\int \mathrm{d}\vec{r}_{12}\exp(\vec{i}\vec{s}\vec{r})\langle F(\vec{s}_1\omega_1)F(\vec{s},\omega_2)(g(\vec{r}_{12},\omega_1,\omega_2)-1)\rangle\right] \tag{10}$$

where $F(\vec{s},\omega)$ is the scattering amplitude of molecules having a certain orientation with respect to the scattering plane, $\langle F_m^2\rangle$ is the scattering of the independent molecules and $\vec{s}$ is the scattering vector:

$$s=|\vec{s}|=(4\pi/\lambda)\sin\theta \tag{11}$$

(λ = wave length of radiation, 2θ: scattering angle).

In the case of molecules having a spherical symmetric distribution of the electrons and for fluids without orientational correlations, this equation may be considerably simplified[17,114] for an isotropic fluid:

$$I(s)=\langle F_m\rangle^2\left[1+\rho_N\int 4\pi r_{12}^2\mathrm{d}r_{12}(g_{000}(r_{12})-1)\exp(isr_{12})\right] \tag{12}$$

where $g_{000}(r_{12})$ represents the spatial distribution of the molecular centres.

This approach has been used exclusively for simple molecular fluids such as water[17]; since in general the internal structure of molecules is not known accurately enough. In that case one is forced to express the scattered intensity in terms of the scattering of independent atoms $[f_i^2]$ which compose the system and the correlation functions $g_a(r_{12})$ of the atoms. These functions are composed of intra- and intermolecular partial correlation function, weighted by the atomic concentration of the atomic species[18]:

$$I(s)=\left[\sum_i f_i^2\right]+\left\{\left[\sum_i f_i\right]^2\rho_N\int 4\pi r_{12}^2\mathrm{d}r_{12}\exp(isr_{12})\right.$$
$$\left.(g_a(r_{12})-1)\right\} \tag{13}$$

Since the scattering amplitudes are different for different radiations and since (in the case of neutron scattering) they also depend on the isotopes involved, it is possible to gain some insight into the local structure by comparing scattering diagrams obtained by using different types of radiations or different isotopes. This approach has been used for metal alloys and solutions[6,19,20].

The analysis of the experimentally obtained scattering curves is not straightforward, however, since Fourier integral transforms are employed to derive data on the correlation function. They require scattering values over an infinite range of scattering variables s, which cannot be achieved for finite wavelength. In addition, the scattered intensity at large values of s becomes difficult to measure. Nevertheless these data are significant for the Fourier transform method. The intensity data must be terminated at some value of s, this gives rise to termination errors which can be serious.

One way of handling this problem is to multiply the scattering curve with a damping function in such a way that the intensity at large s values no longer makes significant contributions to the Fourier transform. This procedure may of course result in changes of the pair correlation function obtained experimentally. It certainly broadens the peaks considerably and may mask significant effects. Furthermore, the scattering arising from the coherent and incoherent atomic scattering, from multiple scattering and the scattering caused by the specific experimental set up has to be subtracted from the total scattering in order to obtain the coherent interatomic interference scattering, which contains the structural information[21]. These corrections, if not done properly, may falsify the information, causing the discrepancies between the pair correlation functions reported in the literature. It is obvious that certain properties of the positional order can be revealed by the scattering techniques described so far, but that they are not able to yield accurate data on the orientational order on a local scale. Certain aspects of the orientational order can, however, be investigated by employing other experimental methods to be described below. It was demonstrated by Steele[22] that the orientational order may be represented either in terms of the spherical harmonics coefficients $g_{l_1l_{2m}}(r_{12})$ or in terms of angular correlation parameters G_K which are closely related to the $g_{l_1l_{2m}}(r_{12})$[7,8]. The angular correlation parameters are defined as:

$$G_k=1+\rho_N\int 4\pi r_{12}^2\mathrm{d}r_{12}\langle P_k(\cos\theta_{12})g(r_{12},\omega_1,\omega_2)\rangle_{\omega_1\omega_2} \tag{14}$$

where θ_{12} is the angle between appropriate axes of the molecules 1 and 2 separated by a distance r_{12} and P_K the k-th Legendre polynom. Each parameter describes a particular moment of the distribution. G_1 is given by:

$$G_1=1+\rho_N\int 4\pi r_{12}^2\mathrm{d}r_{12}\langle\cos\theta_{12}g(r_{12},\omega_1,\omega_2)\rangle_{\omega_1\omega_2} \tag{15}$$

and is obtainable experimentally from dielectric constant measurements

$$\varepsilon_0-\varepsilon_\infty=2\pi N[(n^2+2)/3]^2(\mu_0^2/kT)G_1 \tag{16}$$

(n = refractive index, μ_0 = dipole moment).

The parameter G_2 is given by:

$$G_2=1+\rho_N\int 4\pi r_{12}^2\mathrm{d}r_{12}\langle(3\cos^2\theta_{12}-1)$$
$$g(r_{12},\omega_1,\omega_2\rangle_{\omega_1\omega_2} \tag{17}$$

and can be determined experimentally by means of depolarized light scattering, electric and magnetic birefringence. The depolarized Rayleigh ratio H_v for instance can be expressed as[8,23,24]:

$$H_v=(16\pi^4/135\lambda^4)N(n^2+2)^2\delta_0{}^2G_2 \tag{18}$$

where δ_0 is the optical anisotropy. The accuracy of this method is limited by local field effects[25] which have not been treated rigorously as yet, as well as by a depolarized component due to collision induced scattering[26]. It is apparent that the total orientation dependent pair correlation function is not available from experiments. Computer simulations have been the major source of non-experimental information on the positional and orientational structure of liquids composed of simple molecules, as already discussed earlier. Unfortunately this method has not been extended to chain molecules up to now[7].

One of the most important structural parameters of chain molecules is the conformation of the individual chain in the bulk amorphous material. It can be defined by the spatial distribution of all segments or monomer units belonging to the same chain, that is, by the probability $w_{ij}(\vec{r}_{ij})$ that a chain element j is located at $\vec{r}_{ij}$ within a volume element $d\vec{r}_{ij}$ with respect to a chain element i. The average is taken over an ensemble of many identical chains[27]. A quantity, which is widely used to characterize the long range correlation of segments, is the second moment $\langle r^2 \rangle$ of the end-to-end distance of the chains or the mean square radius of gyration $\langle s'^2 \rangle$ defined as[27]:

$$s'^2 = \frac{1}{n+1}\sum_0^n s_i'^2 \qquad (19)$$

(where s_i' is the distance of atom i from the centre of gravity). It can be determined by means of X-ray and light scattering for dilute solutions[27]. The scattered intensity depends on the difference between the scattering amplitudes of the solvent and the polymer. Consequently no information on the long range chain conformation in the bulk amorphous material is available from X-ray and light scattering, since the contrast is zero. If, however, a dilute solution of deuterated chains in a protonated matrix or *vice versa* is investigated using neutron scattering, it becomes possible to determine the chain conformation because of the large difference between the scattering amplitudes of hydrogen and deuterium[3-5]. The scattering curves can be analysed along the same lines as in the case of dilute solutions. According to Debye the scattered intensity for a monodisperse coil in the limit of infinite chain length is expressable as[3-5,27]:

$$I(s)/I(0) = (2/v^2)(v - 1 + \exp(v)) \qquad (20$$

where $v = s^2\langle s'^2 \rangle$ and $\langle s'^2 \rangle$ is the mean-square-radius of gyration. For small values of v ($v < 3$) this equation can be represented by:

$$I(s)/I(0) \approx 1 + v/3 \qquad (21)$$

so that the radius of gyration is obtainable from the slope of the straight line in a plot of $I(s)^{-1}$ *versus* s^2.

In the intermediate range of v-values the prediction is that the scattering can be approximated by $I(s) \sim 2/v$ so that a plot of $I(s)s^2$ *versus* s should thus give a horizontal line. The scattering at still larger s values is determined by the persistence length, that is by the local conformation of the chain.

EXPERIMENTAL RESULTS ON THE STRUCTURE OF AMORPHOUS POLYMERS

The pair correlation function

This review on the results of structural analysis on amorphous polymers is restricted to single phase systems. The structures in the amorphous regions of partially crystalline substances, which are known to differ from those in the pure amorphous state, and the structure of liquid crystalline polymers[28], will not be considered in this paper.

The short range order in amorphous polymers has been investigated by wide angle X-ray and by electron diffraction. The latter method has the advantage that a larger range of s-values can be covered than with X-ray diffraction. The technique is, however, limited to thin films, having a thickness of about 1000 Å.

Experiments were carried out on glassy isotropic and oriented samples, on the molten state of crystallizable polymers and on so-called amorphized samples, where the crystalline structure is reported to be destroyed by radiation[47-49].

The diffraction pattern of amorphous polymers contains typically several scattering maxima, the so-called amorphous halos, the first halo being usually the most prominent one. One example is given in *Figure 5*. The first halo is predominantly determined by intermolecular distances[32,35], although it may also contain contributions from intramolecular distances. Stretching causes the first halo to arc about the equator whereas the halos at larger s-values tend to arc about the meridian, indicative of intramolecular contributions to the total scattering[35]. Similar conclusions can be drawn from the temperature dependence of the position of the halos. The first halo is shifted to smaller s-values, which corresponds to larger distances, with increasing temperature above the glass transition temperature[32]. The positions of the other halos are nearly independent of the temperature. The position of the first halo depends furthermore on the concentration of the individual components in compatible blends, as shown in *Figure 6* for blends of poly(methyl methacrylate) and poly(vinylidene fluoride) in the molten state[29]. The first amorphous halo is consequently strongly determined by intermolecular distances. Data on the packing density

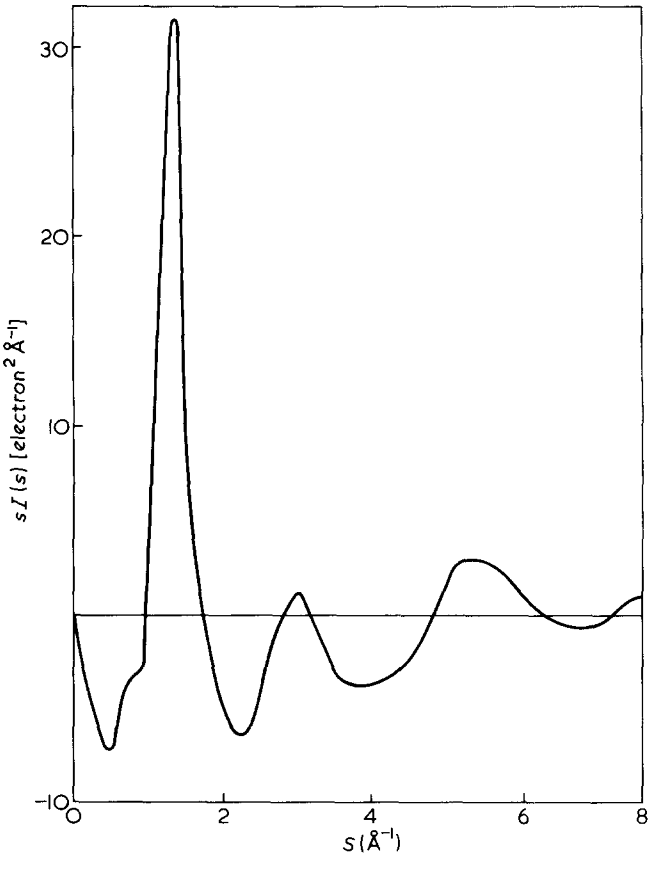

Figure 5 Reduced intensity function for glassy atactic polystyrene (Data from S. M. Wecker, T. Davidson, J. B. Cohen, *J. Mater. Sci.* 1972, **7**, 1249, reproduced from Adams, R., Balyuzi, H. H. M. and Burge, R. E., *J. Mater. Sci.* 1978, **13**, 391 by permission of Chapman and Hall Ltd.)

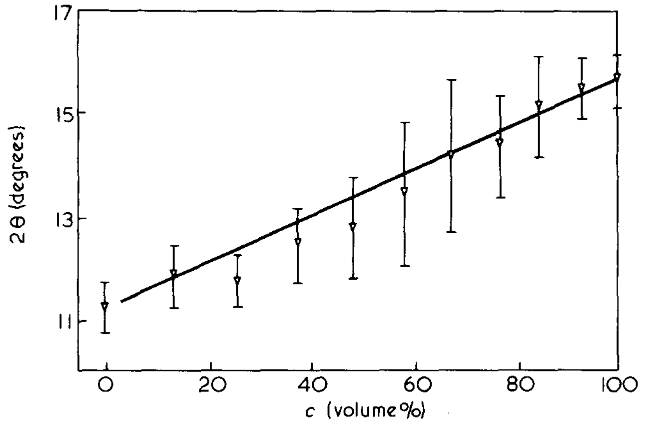

Figure 6 Dependence of the position of the amorphous halo 2 θ on the concentration of poly(vinylidene fluoride) c in blends with poly(methyl methacrylate) (Wave length: 0.154 nm)

and intermolecular distances, derived from the position of the halo, should nevertheless be considered with extreme care, since intramolecular distances will certainly contribute to the first halo.

The analysis of the scattering data has followed two different routes:

(a) The scattering diagrams of isotropic or oriented samples are compared with those diagrams which are obtained from structural models of the local chain conformation and of the packing of segments.

(b) The scattering data, after having been corrected, as described earlier, are expressed in terms of the reduced interference function $i(s)$

$$i(s)=\left[\frac{I(s)^{\text{coherent}}}{N}-\sum_{i=1}^{n}x_i f_i^2(s)\right]\Bigg/\left[\sum_{i=1}^{n}x_i f_i(s)\right]^2 \tag{22}$$

where x_i = atomic function of species i, N total number of atoms, which in turn is transformed into the pair correlation function. It is determined by the superposition of intra- and intermolecular partial atomic correlations. The pair correlation function is compared with theoretical functions derived from suitable models of the local chain conformation and of the intermolecular packing.

Sufficiently accurate data on the local chain conformation can be obtained from the experimental results for simple chain molecules such as polyethylene of polytetrafluoroethylene[35,21,51]. Results on the local conformation derived from scattering experiments on polymers with a more complex chemical structure such as polycarbonate of poly(ethylene terephthalate) are less accurate because many different intramolecular distances have similar atomic distances so that the pair correlation function consists of overlapping maxima and minima which are difficult to resolve.

Different views are expressed in the literature concerning the possibility of determining the local orientational and positional order of segments from wide angle X-ray and electron diffraction diagrams[9,42,45–49,39,40,21,51]. Several authors have reported that the pair correlation function of amorphous polymers exhibits several broad intermolecular maxima which extend to about 20 or 30 Å having a periodicity which corresponds approximately to the intermolecular separation[41,42,45–49]. It was concluded that a parallel arrangement of segments within regions having diameters between 15 and 40 Å exist in the amorphous phase.

This conclusion has been criticised by several authors, particularly by Voigt-Martin and Mijlhoff[21,51], who demonstrated how spurious oscillations can be created in the pair correlation function of molten polyethylene, both by termination effects, which lead to short range oscillations, but also by incorrect background corrections. The disappointing lack of features in the intermediate and long distance range was attributed to overlapping contributions from the increasing number of almost equivalent atomic distances with increasing distance from the atom at the origin.

Indirect information on the local orientational order is obtainable from an analysis of the chain conformation, this has been particularly stressed by Lovell *et al.*[35]. The assumption is that a parallel arrangement of segments can only be achieved if a significant number of extended chain segments is present in the amorphous phase.

Several studies were concerned with the influence of the thermal history of the amorphous polymers on the local structure[33,39–41]. It is known that thermodynamic and mechanical properties can be strongly influenced by annealing the glasses below the glass transition temperature[30]. The general conclusion is that these changes of macroscopical properties are not directly related to observable changes of the local structure as long as crystallization is not induced.

Polystyrene

Quenched isotactic and atactic polystyrene was investigated by several groups using wide angle X-ray diffraction. Krimm[31] attributed the halos mostly to intermolecular correlations of atomic positions, whereas Kilian and Boeke pointed out that intramolecular correlations dominate the diffraction pattern[32]. They interpreted the intramolecular correlations on the basis of the 3_1 helix of isotactic polystyrene. Wecker *et al.*[33] conclude that the chain conformation and the intermolecular packing is strongly influenced by steric interactions of the phenyl groups. Atactic polystyrene is reported to have a planar zig-zag conformation resulting in large separations of the phenyl groups whereas the isotactic chain is characterized by a disturbed helical structure.

Adams *et al.*[34] based their interpretations of the diffraction data on conformational energy calculations. They concluded that the three fold helix is an unsuitable model for the local chain conformation and that *gg* and gg^- conformations causing large phenyl group separations lead to a reasonable agreement between calculated and experimental values. Lovell *et al.*[35,36] investigated non-oriented as well as oriented samples of polystyrene, taking into account results on conformational energies. The finding is that *ttgg* sequences are preferred over *tttt* sequences, although the latter conformation corresponds to the state of lowest energy. The closest agreement between calculations and experiment is achieved for regular sequences containing about 12 monomer units.

Wecker *et al.*[33] considered the influence of the thermal history on the local structure of polystyrene. They found no difference between the diffraction data of samples slowly cooled down or quenched from above the glass transition temperature.

Poly(methyl methacrylate)

Atatic poly(methyl methacrylate) was studied by Bjørnhaugh *et al.*[37] They attributed the diffraction diagram to a nonplanar zig-zag conformation[37]. Lovell *et al.*[35,38] pointed out, however, that conformational energy calculations and small angle neutron scattering results are at variance with this model. They observed that the scattering pattern of non-oriented samples and oriented samples were very similar for atactic and syndiotactic poly(methyl methacrylate) and could be explained on the basis of all *trans* sequences. Regular conformations were found to persist over 16 bonds for the syndiotactic polymer, in agreement with data on the conformational energy and the total conformation of the chain. Differences between the alternate backbone bonds (110° and 128°) are believed to be responsible for curved segments.

Polycarbonate

Poly(bisphenol-A carbonate) was studied by means of X-ray diffraction, using isotropic samples only[39]. The intermolecular correlations were calculated by Wignall and Longman solely on the basis of correlations within the monomer units. The state was identical to that of the crystalline state. The authors were able to resolve successfully most of the intramolecular distances. Two broad maxima of the pair correlation function at 5.5 Å and at 11 Å were attributed to intermolecular distances. The authors concluded from their data that the intermolecular ordering must be very weak. No changes were observed if the samples were annealed below the glass transition temperature for prolonged times, whereas annealing above T_g resulted in the occurrence of several additional maxima, which repeated every 5.5 Å for many orders before decaying. These maxima were assigned to an enhanced intermolecular ordering caused by the onset of crystallization.

Poly(ethylene terephthalate)

Samples of poly(ethylene terephthalate) with different thermal histories were analysed by X-ray diffraction by Longman *et al.*[40] as well as by Gupta and Yeh[41]. Gupta and Yeh assigned most of the maxima of the pair correlation function which extended to about 18 Å for distances larger than about 5 Å to intermolecular correlations, originating from the existence of ordered regions within the amorphous state. These regions were believed to have a nematic-like lateral ordering, extending over 20 to 40 Å. The structure was looked upon as a very distorted paracrystalline lattice. Annealing of the samples caused an increase of the intensity of several maxima of the pair correlation function as well as the formation of additional maxima. The conclusion based on these results was that an improved packing of the segments leads to an increase of the correlation length of intermolecular correlations. Longman *et al.*[40] found, however, no indications of ordering beyond distances corresponding to the separation between neighbouring segments for samples, which were unannealed or annealed below the glass transition temperature. In particular no long range oscillations of the pair correlation function were detected for these samples. Samples having a crystallinity of about 20%, however, exhibited peaks at 4.5, 11, 17 and 21 Å, indicative of increased intermolecular correlations due to the presence of crystals.

Natural rubber

Natural rubber was investigated by Simard *et al.*[43], Bokhyan *et al.*[44] as well as Wang and Yeh[42], using X-ray diffraction. Simard[43] interpreted their results mainly in terms of intramolecular correlations whereas Bokhyan *et al.* and Wang and Yeh were mainly concerned with intermolecular correlations. Bokhyan *et al.* proposed an orthorhombic arrangement of chain segments, based on maxima in the pair correlation functions which they assigned to intermolecular distances. Wang *et al.*[42] attributed these intermolecular correlations to a chain conformation which is characteristic of the crystalline state. The remaining maxima in the pair correlation function were interpreted in terms of local ordering which was assumed to persist over distances of about 30 Å.

Polyethylene and polypropylene

Ovchinnikov *et al.*[45,46] were the first to perform structural analysis on polyethylene in the molten state in the temperature range between 136° and 211°C. They observed several maxima in the pair correlation function and attributed those at 4.8 Å and 5.8 Å to intermolecular distances. They proposed a model according to which chain segments are parallel within regions with diameters of about 50 Å. Very similar conclusions were drawn by Odajima and coworkers[47–49]. They found that the pair correlation function of polyethylene amorphized by irradiation exhibits broad maxima with a periodicity of about 5 Å which persist to about 20 Å. They were attributed to a local ordering with a hexagonal packing of chain segments. In addition, maxima in the pair correlation function at small values of s in amorphized samples of polyethylene and polypropylene were attributed to intramolecular distances and the ratio of *trans* to *gauche* conformations was determined. It was found that the ratio agrees well with that expected for chains in θ-solvents. Broad oscillations of the pair correlation function were also reported by Longman *et al.*[52,60] and attributed to local order, which does not persist beyond about 30 Å[52].

These conclusions were criticized by Voigt-Martin and Mijlhoff[21,51] who did not observe long range oscillations in the pair correlation function of molten polyethylene. Using electron diffraction, which makes a very wide range in reciprocal space experimentally accessible, and analysing their data very carefully, they were able to attribute all of the short range maxima to well known intramolecular distances. A broad maximum ranging from 4 Å to 7 Å in the intermediate range was attributed to intermolecular correlations. Similar results were reported by Lovell and coworkers[35]. They pointed out that the diffraction pattern is predominantly determined by intramolecular correlations, that is by the local chain conformation. They performed model calculations assuming bundles of extended chain segments and found that the scattering disagreed with this bundle structure but agrees very well with a random chain structure, in which no effective correlation of segmental orientation exists. They proposed a three state chain with an average *trans* sequence length of 3.4 backbone bonds.

Some of the discrepancies between the results on the pair correlation functions obtained by different groups may be caused by crystallinity. A comparison between molten polyethylene and amorphized samples showed that the first maximum in the intensity distribution of the

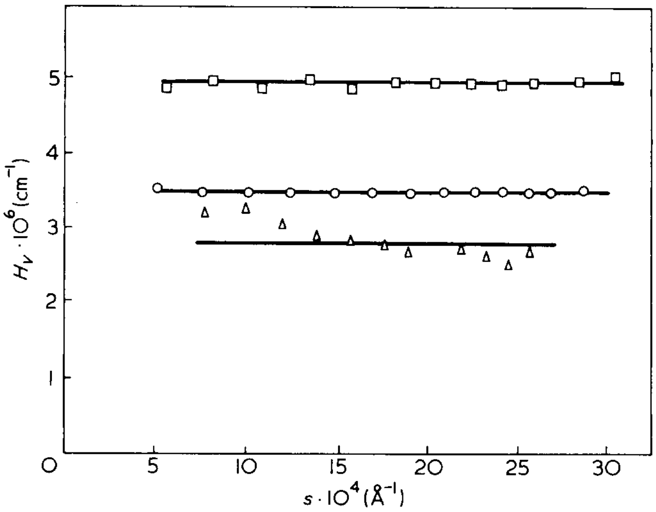

Figure 7 Depolarized light scattering of polystyrene (□), Poly (methyl methacrylate) x 10 (△) and toluene (○). (Reproduced from Dettenmaier, M., *Progr. Colloid Polym. Sci.* 1979, **66**, 169 by permission of Dr. Dietrich Steinkopff Verlag GmbH & Co. KG, Darmstadt)

latter was narrower and occurred at lower *s*-value than in molten polyethylene[35]. In addition selected area diffraction experiments on the amorphized samples of Odajima[47-49] gave sharp spots arising from small areas in the sample, indicating that the crystallinity had not been totally destroyed by irradiation[53].

Poly(tetrafluoroethylene)

The short range order of poly(tetrafluoroethylene) in the molten state was investigated by Lovell *et al.*, using X-ray diffraction[35]. They found that a model of parallel straight chain segments packed in a disordered fashion was able to account for the observed scattering curves. They state that the molecules are probably disordered between the two most likely rotational states t^+ and t^-. This structure is attributed to the rigidity of the chain which is also manifested in the high viscosity of the melt. Stiff chains are known to have a tendency for the formation of orientationally ordered regions or even nematic phases. This has been treated extensively by Flory[11] and coworkers. It seems that poly(tetrafluoroethylene) is at the borderline between flexible and rigid chains.

The orientational order in amorphous polymers

It has repeatedly been pointed out that the structure of the amorphous state is not sufficiently defined if only the distribution of the centres of the molecules is known[62,70,112]. Well known examples are liquid crystals. Their optical and electro-optical properties are mainly determined by the orientational order rather than by their positional order[55,56]. Liquid crystalline orientational order is also exhibited by main chain and side chain polymers[28].

Methods which are able to yield data on certain aspects of the orientational order are depolarized light scattering as well as magnetic and electric birefringence and in addition X-ray and neutron scattering[114-116].

These methods have been applied to a surprisingly small number of amorphous polymers such as poly(methyl methacrylate), polystyrene, polycarbonate and poly(dimethylsiloxane)[58-60]. X-ray and neutron scattering studies on orientation correlations have so far been limited to low molecular weight fluids including liquid crystals[115,116].

For poly(methylmethacrylate), polystyrene and polycarbonate it was found that the depolarized light scattering is independent of the temperature as well as of the scattering angle (*Figure 7*). This result can be taken as an indication that no long range orientation correlations exist in these polymers and that the orientational order is approximately independent of the temperature. The absolute value of the depolarized Rayleigh ratio indicates that very small angular correlations of chain segments exist.

The experimentally obtained Rayleigh ratio has often been expressed in terms of the effective-mean-square optical anisotropy

$$\delta^2_{\text{effective}} = \delta_0^2 G_2 \qquad (23)$$

$G_2 = 1$ indicates the absence of any angular correlation, $G > 1$ represents a tendency for parallel and $G < 1$ for perpendicular alignment of neighbouring segments. A specific value of G_2 can be obtained for a large variety of different orientational correlations. One simple example is the case in which p segments within a structural unit are strictly parallel to each other and the orientation of these structural units is random. G_2 then has a value of p. A model of the amorphous state of polymers assuming regions with parallel chain segments requires large values of G_2 whereas models based on random chain conformation without specific intersegmental orientational correlations predict low values of G_2 which are determined by intramolecular orientation correlations.

The value usually obtained for amorphous polymers is below 10, strongly suggesting that no bundles of parallel chain segments are present[62].

In the case of polystyrene it was found that the value of the effective anisotropy in the bulk amorphous state agreed surprisingly well with the value in solution and also with the value derived by Tonelli *et al.*[23] from the rotational isomeric state model. Similar results were obtained from magnetic birefringence studies on polystyrene[61,62]. *Figure 8* shows some results on polystyrene as well as on oligomers and on ethyl benzene as a model system. The orientational order could be attributed solely to intramolecular correlations of the chain units. The results on poly(methyl methacrylate) are somewhat inconclusive[58]. The effective anisotropy is quite large compared to values obtained from the stress optical coefficients. It seems, however, that inner field effects and contributions to the depolarized light scattering from collision induced scattering are very important in the case of poly(methyl methacrylate) and influence the experimentally obtained value in an unknown way. Thus conclusions about the orientational order in amorphous PMMA from depolarized scattering are not straightforward.

Some surprising results are represented in the literature for n-alkanes, which have been investigated extensively[65-67]. It was found that the value of the effective anisotropy δ_{eff} was considerably larger in the molten state compared with dilute solutions. The ratio of the anisotropy from the bulk to the dilute solution increases with chain length and levels off at large numbers

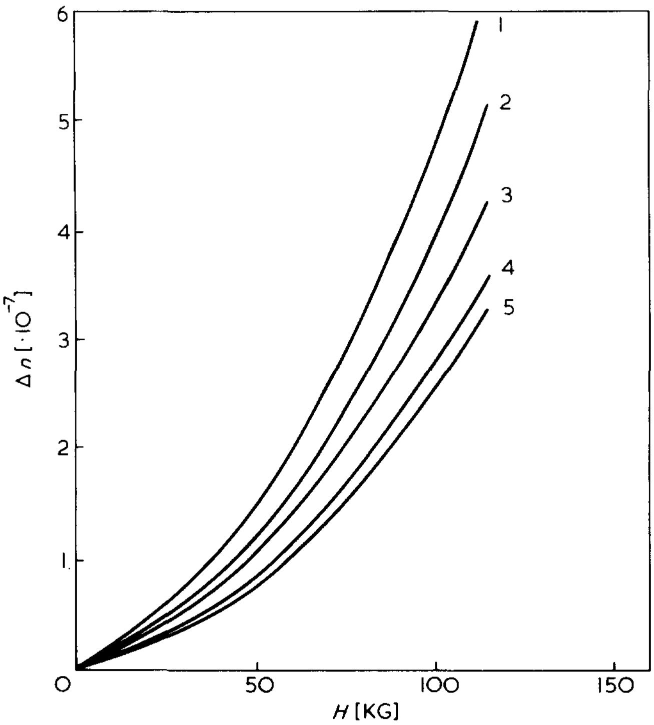

Figure 8 Magnetic birefringence in amorphous materials above their glass transition temperatures (1: styrene, 2: polystyrene, 3: oligomer of polystyrene, 4: solution of polystyrene in benzene, 5: styrene-dimer)

of chain elements. The orientational orders differs, however, strongly from that of a nematic like state. It is characterized by a correlation which extends to about 10 Å. The orientational order displays a temperature dependence as predicted by the de Gennes theory of pretransitional short range orientational correlations^{55}. The critical temperature, to be considered as a fictive quantity, is located far below the melting temperature of the alkanes. The temperature dependence could alternatively be interpreted in terms of heterophase fluctuations proposed by Frenkel^{68}, with about 10 units in the ordered phase. The conformation of the chains turned out to be independent of these ordering effects. The orientational order was attributed to weak orientation correlations of *trans* sequences present in the molten state^{66}. Similar effects were observed for oligomers of polyoxyethylene^{69,70}.

The chain conformation in the amorphous state

Excellent textbooks and reviews dealing with the chain conformation in bulk amorphous polymers have recently been published$^{3-5}$. The experimental technique which has been employed in order to elucidate the chain conformation is neutron small angle scattering on partially deuterated polymers.

Flory^{97} pointed out some time ago that polymers in the bulk amorphous state should have unperturbed dimensions and an interpenetrable Gaussian coil structure^{27}. The results obtained over the last few years seem to support his point of view. Experiments were performed on polystyrene^{71,72,78,86}, poly(methyl methacrylate)^{73,74}, polyethylene$^{75-77,86}$, polyethylene oxide^{4} and polydimethylsiloxane^{71}. *Figure 9* gives some results of neutron small angle scattering on poly(methyl methacrylate). Except for polyethylene oxide a good agreement was obtained for the magnitude of the radius of gyration in the bulk and in dilute solution, as predicted by Flory (*Figure 10*).

This value of the radius of gyration can be accounted for, however, also on the basis of structural models which will be discussed later and which are characterized by local orientational order^{87}. It has been observed, for instance, that the radius of gyration is not much affected by crystallization in many cases^{80,81}. The obvious conclusion is that data on the internal structure of the

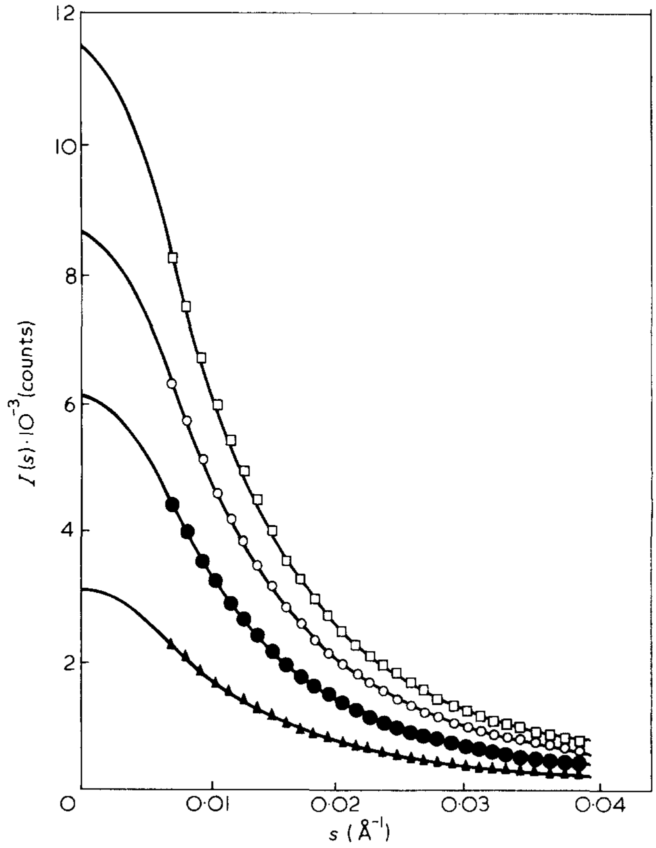

Figure 9 Neutron scattering of poly(methyl methacrylate) dispersed in *D*-poly(methyl methacrylate). (1.19% (□), 0.93% (○), 0.63% (●), and 0.31% (▲)). (Reproduced from Kirste, R. G., Kruse, W. A. and Ibel, K. *Polymer* 1975, **16**, 120)

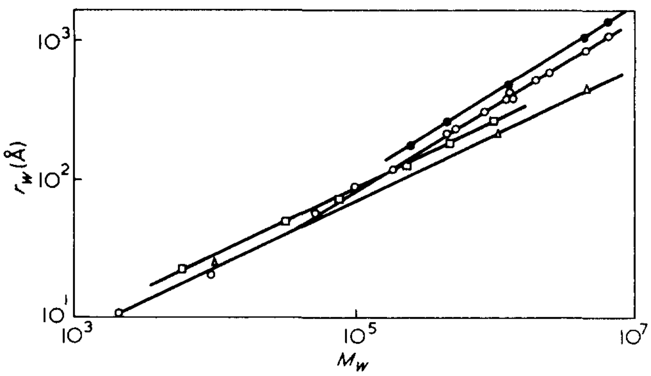

Figure 10 Comparison between the radius of gyration of poly (methyl methacrylate) in the vitreous state and in dilute solutions in low molecular weight compounds. (Vitreous sample, neutron scattering (□), dioxane, light scattering (●), acetone, light and X-ray scattering (○), butyl chloride, θ-solvent, light and X-ray scattering (△), reproduced from Kirste, R. G., Kruse, W. A. and Ibel, K. *Polymer* 1975, **16**, 210)

chain, that is on the local chain conformation, are needed in order to characterize the chain conformation more detailed. These data are obtainable from neutron scattering at larger values of s. The Debye equation predicts that the scattering function in this region should be given by $I(s) \sim s^{-2}$ so that a plot of $I(s)\, s^2$ *versus* s should yield a horizontal line.

This behaviour has been observed for polystyrene, polyethylene and polyethylene oxide. Deviations from this behaviour were found, however, for poly(methyl methacrylate)[74]. This is not surprising, as Flory has pointed out, because the Debye equation is no longer correct in the range of s-values considered here. Flory and Yoon were able to predict scattering curves for polystyrene, polyethylene and polyethylene oxide[82,83] on the basis of realistic rotational isomeric state models which have properties similar to those given by the Debye equation. The maxima in the $I(s)\, s^2$ *versus* s plot, which occur in the case of poly(methyl methacrylate), could also be accounted for on the basis of the rotational isomeric state theory[83]. Similar scattering curves are known from small angle X-ray diffraction on solutions of poly(methyl methacrylate) at θ-conditions[74].

The chain conformation was also investigated in binary mixtures of compatible polymers by Kirste and coworkers[84] and by Ballard *et al.*[85] and by Allen and coworkers[4]. Some of the mixtures studied are polystyrene–polybutadiene[4], poly(methyl methacrylate)–poly(styrene acrylonitrile), poly(methyl methacrylate)–poly(vinyl chloride), polystyrene–poly(phenylene-oxide)[84]. The results were interpreted in terms of the coil expansion relative to the unperturbed state and in terms of the interaction energy parameter, which turned out to be negative in most mixtures.

MOLECULAR CORRELATION FUNCTIONS AND MACROSCOPICAL PROPERTIES

It has already been pointed out that macroscopic properties of fluids such as the pressure, the compressibility, etc., can be calculated provided that the pair correlation function and the pair potential is known. The compressibility, for instance, is determined by the correlation of the molecular centres, averaged over all orientations. It depends strongly on the long range tail of the correlation function. The disadvantage is that this part of the correlation function cannot accurately be derived from scattering data discussed so far. Some aspects of the long range properties of the pair correlation function are obtainable from small angle X-ray diffraction and in particular cases also from light scattering. This can be demonstrated by looking at the structure of an amorphous system from a slightly different point of view[1,2,88,89].

The number N of particles, molecules, atoms or parts of chain-molecules within a small subunit V of the macroscopical system, is not constant throughout the system but fluctuates about the mean value as a function of the position of the sampling volume V and also as a function of the time. This situation is depicted in *Figure 11*. Particle fluctuations originate from the thermal motions of the molecules. The distribution of the actual particle number about the mean value can, to a good approximation, be represented by a Gaussian distribution, the width of which is given by the mean-square fluctuation $\overline{\delta N^2}$ (refs 88 and 89):

$$\overline{\delta N^2} = \overline{(N - \bar{N})^2} \qquad (24)$$

The correlation of the particle fluctuations within two different volumes can be expressed in terms of the density–density correlation function already introduced at the beginning of this article:

$$\mathrm{C}(r) = \langle (n_N^1(0) - \bar{n})(n_N^1(r) - \bar{n}) \rangle \qquad (25)$$

This function is related to the pair correlation function. The scattering caused by particle fluctuations is given by:

$$I(s)/\langle F_m^2 \rangle = \frac{1}{N} \int \mathrm{C}(r) \exp(isr) 4\pi r^2 \mathrm{d}r \qquad (26)$$

The long range tail of the pair correlation function, which we intend to investigate, determines the scattering curve at small values of s. This corresponds to the small angle region of X-ray diffraction and to light scattering in the total accessible range. A scattering curve, decaying with increasing s, is indicative of long range correlations. They exist, for instance, in fluids close to their critical points. The forward scattering is known to diverge in this case and the scattering curve can be represented by:

$$I(s) = I(0)/(s^2 + \xi^2) \qquad (27)$$

according to the Ornstein Zernike approximation[1,2]. The asymptotic behaviour of the pair correlation function responsible for this scattering curve is given by:

$$g(r) = r^{-1} \exp(-r/\xi) \qquad (28)$$

where ξ is the correlation length. It increases strongly when the critical point is approached.

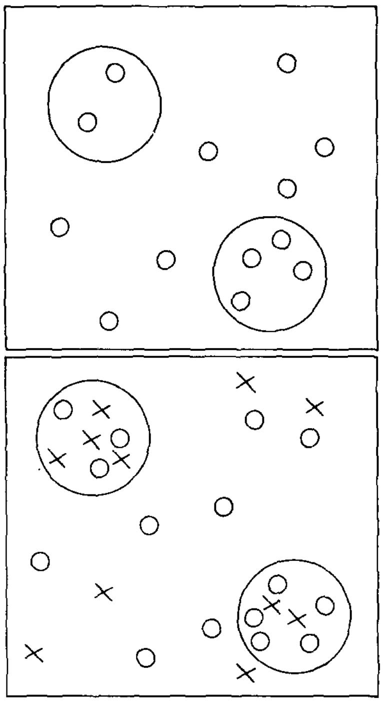

Figure 11 Schematic representation of particle and concentration fluctuations (X and ○ molecules with different chemical structure)

Scattering curves which are independent of s in the small angle range on the other hand originate from particle fluctuations which decay very quickly with increasing s.

The scattered intensity at $s=0$ is obtained from the scattering data by means of extrapolation from larger s-values. It is related to the mean square fluctuations which in turn are determined by the isothermal compressibility.

$$\begin{aligned} I(0)/\langle F_m^2\rangle &= 1+\rho_N\int 4\pi r^2 dr(g_{000}(r)-1) \\ &= \overline{\delta N^2}/\bar{N} \\ &= \rho_N kT\kappa(T) \qquad (29) \end{aligned}$$

Scattering experiments can consequently be used to test the relation between molecular correlation functions and macroscopical properties, given by the pair theory.

Fluctuations in mixtures, including mixtures of compatible polymers, can be decomposed in two statistically independent components: fluctuations of the particle number at constant composition and fluctuations of the composition at constant particle number[88,89]. The first component is determined by the isothermal compressibility of the mixture whereas the second component is determined by the derivative of the chemical potential μ with respect to the composition c:

$$\overline{\delta c^2} = \overline{(l_c - l_c)^2} \sim [\partial\mu/\partial c]^{-1} \qquad (30)$$

Theoretical aspects of concentration fluctuations and their relation to the scattering of electromagnetic radiation have been treated by Kirkwood *et al.*[117] and by des Cloizeaux *et al.*[118]. Light scattering or X-ray scattering, originating from concentration fluctuations, can thus be used to obtain information on correlations of compositional fluctuations as well as on thermodynamic properties of the mixtures. Compositional fluctuations cause scattering of electromagnetic radiation, however, only if the scattering amplitudes of the components of the blend are different. Contrast is needed to see compositional fluctuations.

Particle fluctuations

Thermal particle fluctuations have been investigated in a variety of amorphous polymers and model systems by means of X-ray diffraction as well as light scattering[60,62,90,92]. The substances studied so far include polyethylene, poly(methyl methacrylate), polystyrene, polycarbonate, poly(ethylene terephthalate), polysiloxand, oligomers of polystyrene and polycarbonate and also phenolphthaleine.

It is generally found that the scattering curve is independent of s over a considerable range with the exception of very small values of s. An excess scattering is usually observed in this range which has been attributed to the scattering at impurities, voids or monomer droplets[62,90,94]. Examples of scattering curves are given in *Figure 13* for poly(methyl methacrylate) and poly(vinylidene fluoride) in the melt. The conclusion is that the scattering arising from particle fluctuations is independent of s. This shows that the pair correlation function in these substances is short ranged despite the connectivity of the polymer chains.

The temperature dependence of the mean square fluctuations of the particle number is very similar for all amorphous polymers studied so far but also for oligomers and low molecular weight glass-forming substances. Three characteristic temperature ranges are apparent, as can be seen in *Figure 12* for the case of PMMA; the temperature range above T_g, the temperature range between a temperature T' and T_g and finally the temperature range below T'. The temperature dependence of the particle fluctuations can be represented by the equation:

$$\overline{\delta N^2}/\bar{N} = \rho_N kT\kappa(T) \qquad (31)$$

given by statistical mechanics. Data on the compressibility were taken from the literature in order to test this equation[95]. The pair approximation obviously is able to describe the relation between the short range order and the compressibility; the compressibility equation is an equation of state for polymer melts.

This is no longer the case below the glass transition temperature, due to the nonequilibrium thermodynamic state of the glass. The compressibility is known to change stepwise at T_g whereas the particle fluctuation changes continuously at this transition. The derivative of the fluctuations with respect to the temperature changes discontinuously at T_g, as can be seen in *Figure 12*. This behaviour can be accounted for on the basis of fluctuation theory if fluctuations of internal parameters of the glassy state are considered in addition to fluctuations of thermodynamic parameters such as the entropy and the pressure. Wendorff and Fischer derived the following equation[62,90]:

$$\overline{\delta N^2}/\bar{N} = \rho_N kT\kappa(T_g) \qquad (32)$$

which represents the data within a large temperature range in the glassy state. It is a surprising observation that the extrapolation towards $T=0K$ predicts the existence of a glassy state having an ideally homogeneous distribution of the particles or, in other terms, of the free volume.

It turned out that the modified compressibility equation was no equation of state for the glass. It was observed that thermodynamic quantities such as the enthalpy and the volume relax towards their equilibrium

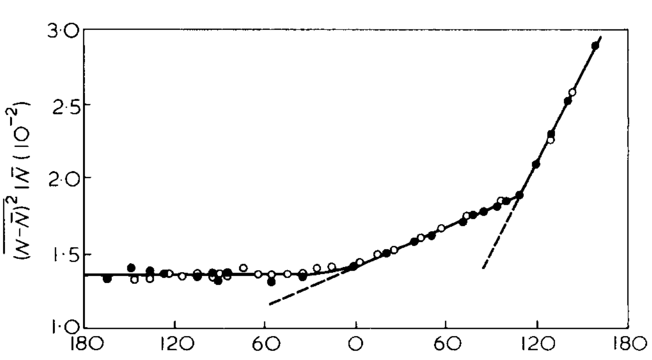

Figure 12 Dependence of the mean-square of the particle fluctuations in poly(methyl methacrylate) on the temperature T. (Heating cycle (○), cooling cycle (●))

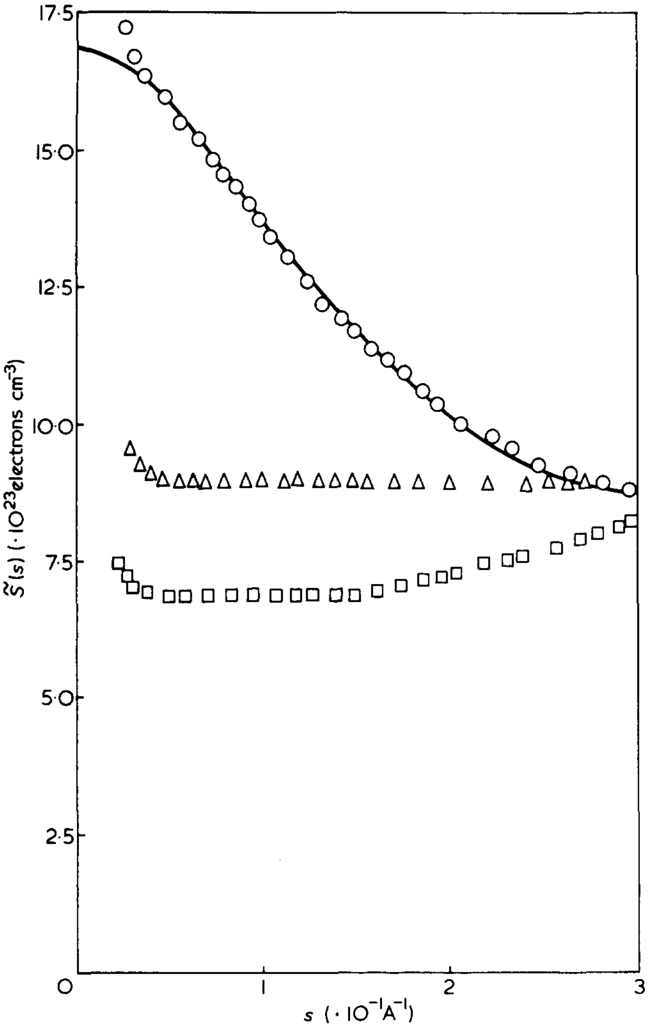

Figure 13 Structure factors $\tilde{S}(s)$ of poly(methyl methacrylate) (□), poly(vinylidene fluoride) (△) and a 50 weight % mixture of them (○)

values if the glass is annealed for long times below T_g whereas the mean square fluctuations stay constant[96]. The fluctuations have thus to be considered as an independent parameter.

Only a very slight dependence of the particle fluctuations on the temperature is displayed by all glasses below a characteristic temperature T'. The fluctuations are believed to be either frozen in this temperature range[62] or to depend on the temperature because of phonon contributions to the fluctuations[54,92]. The temperature T' is apparently related to the temperature at which secondary relaxations are known to freeze in.

Steele *et al.* have shown equation (29) to be correct even if orientation correlations exist in molecular fluids[114]. At $s > 0$, however, additional scattering arises from these fluctuations leading to deviations between the experimentally determined scattering intensity and the scattering intensity calculated on the basis of the compressibility equations. These deviations were observed for liquid crystals even in their isotropic fluid state[116], they were, however, not observed for amorphous polymers studied so far. The conclusion is that orientation fluctuations must be negligible in these systems, in agreement with the data on orientational order presented above.

Concentration fluctuations

Concentration fluctuations have been analysed by means of light scattering or small angle X-ray scattering mainly in dilute solutions of polymers to obtain data on the molecular weight or in more concentrated solutions in order to study phase transitions[97,98]. Small angle X-ray diffraction has recently been employed for elucidating structural and thermodynamic properties of a compatible blend of polymers, namely poly(methyl methacrylate) and poly(vinylidene fluoride) in the molten state[99]. It was shown that the total scattering of these blends can be decomposed into contributions independent of s and those which decay continuously with increasing s (*Figure 13*). The first component can be attributed to particle fluctuations at constant composition, whereas the s-dependent component was due to compositional fluctuations at constant particle number. An example is given in *Figure 13* for a particular blend of PMMA and PVDF. The scattering function given above was used to perform the extrapolation to $s = 0$. The value thus obtained is determined according to statistical mechanics by the derivative of the chemical potential with respect to the composition. This quantity was obtained independently using melting point depression data for PVDF-crystals in PVDF/PMMA blends[29]. The result was that the compositional fluctuations obey the equation known from fluctuation theory.

The shape of the scattering curve indicates that correlations of compositional fluctuations exist in the blends which extend over distances of about 10 Å at about 470K. Slightly larger values are obtained for low concentrations of any of the components whereas smaller values are characteristic for blends of equal composition.

The local deviations from a random distribution of the components have been interpreted for low molecular weight mixtures in two different ways: by local clustering due to specific interactions or in a more general way in terms of critical phenomena. Specific interactions between unlike components of blends, as characterized by negative interaction energy parameters, may result in deviations from a random distribution. Local clustering as a short range structural phenomenon is known to occur also in metal alloys[101], the correlation length being of the order of 10 Å.

Correlations of concentration fluctuations in polymeric systems have been treated extensively by de Gennes, particularly for the case of mixtures of deuterated and protonated polymers[3,119]. The connection of the segments belonging to the same chain was found to be responsible for correlated concentration fluctuations. The correlation function was reported to be of the Ornstein–Zernike form, leading to the following scattering function

$$I(s) = I(0)[1 + s^2\xi_s^2]^{-1} \qquad (33)$$

where $I(0)$ is related to the derivative of the chemical potential with respect to the concentration and where the correlation length ξ_s depends on the chain conformation as well as on the energetic interactions of the compounds[3]. The scattering data obtained for mixtures of PVDF and PMMA are in good agreement with the theoretical predictions[120]. It was furthermore observed that the correlation length and the scattering intensity increase strongly with increasing temperature.

A plot of $I(0)^{-1}$ *versus* T yields a straight line, which

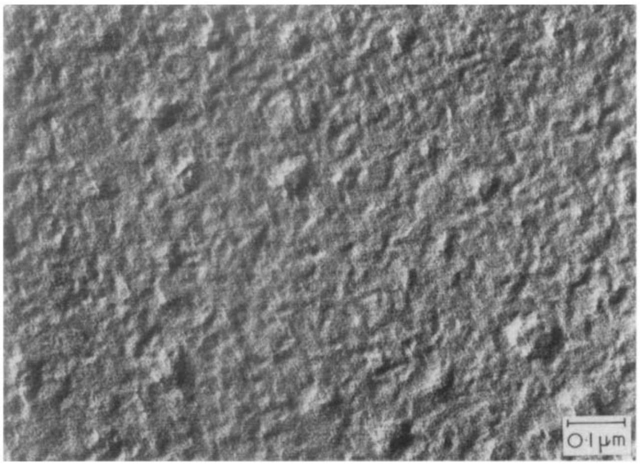

Figure 14 The granular texture in amorphous systems (polycarbonate)

intercepts the ordinate at high values of the temperature. The scattering is predicted to be infinite at this temperature and $[\partial\mu/\partial c]$ should therefore approach zero. This defines the spinodale[102]. The correlation of the compositional fluctuations may thus be attributed to phenomena associated with the spinodale decomposition, in agreement with the predictions of de Gennes[3].

The general conclusions drawn from the results presented above are that the correlation of the molecular centres is short-ranged whereas the distribution of the individual components around a reference particle is characterized by long range correlation. Furthermore it is obvious that macroscopical properties may be expressed in terms of molecular correlation function, as predicted by the pair theory.

THE GRANULAR TEXTURE

When thin amorphous polymer films (cast from solutions) or the surfaces of thicker films (obtained from the molten state or fracture surfaces) are examined with an electron microscope a grainy texture is usually seen as shown in *Figure 14*. The sizes of the grains, to be considered at first, vary between 15 and 100 Å[103,104]. The sizes of the grains and their arrangement are reported to depend on the annealing conditions as well as on deformation. Non-crystallizable polymers such as atactic polystyrene as well as crystallizable polymers such as poly(ethylene terephthalate) are known to display the granular texture. The texture has been attributed to a specific local structure characterized by an improved orientational order of chain segments (nodules). Evidence in favour of this interpretation was produced mainly from dark field electron microscopical investigations which appeared to suggest that in amorphous polymers tiny regions of the order of several nm exist within which chain segments are parallel. It is further concluded that this order is improved, if the samples are annealed or elongated.

Results of small angle X-ray diffraction as well as depolarized light scattering discussed above contradict this interpretation[62,121]. These investigations showed that the orientational order is only determined by the local chain conformation and due to intramolecular correlations. In addition, amorphous polymers were found to be homogeneous with respect to the density[62]. The interpretation of similar contrast variations in the field of semiconductors has been the subject of considerable debate[105,106]. The bright areas in the dark field image formed from the first diffuse diffraction halo were originally interpreted as arising from areas sufficiently ordered to diffract coherently[105]. However, theoretical studies have shown that coherently scattering regions are not incompatible with a random network model[106]. Calculations of the contrast transfer function have shown that only if the 'speckle' size observed in the dark field image of a suitably thin film is considerably larger than the Airy disc size, are the bright spots indicative of local ordering[112]. For small grain sizes, only carefully controlled experiments on extremely thin samples involving beam tilt, defocus, aperture size and location series will enable a distinction to be made between real structure and statistical noise effects. The grainy texture is in any case not a specific property of chain molecules. It has been observed in inorganic glasses such as SiO_2 and GeO_2[107] as well as in low molecular weight organic glass forming substances[62].

In addition to the grainy texture discussed so far much larger grains can also be detected by electron microscopy. These structures have diameters of the order of 1000 to 10000 Å and were called supernodules by Yeh[50,93,103,104,108–110]. Inhomogeneities having about the same sizes have been detected also by light scattering[59,60]. It was found, however, that it is possible to prepare glasses which did not display these inhomogeneities. Purification of the material as well as careful annealing may result in polymers free of these inhomogeneities[59,60].

A puzzling observation is the fact that the shape and the arrangement of the gains depend stongly on the deformation of the samples. A uniaxial deformation results in a layer structure, the separation of the layers decreases with increasing strain. A biaxial deformation, on the other hand, results in a structure which resembles a regular arrangement of bricks. The brick dimensions depend again directly on the deformation. The exact nature of the grains described here is unknown. They cannot be related directly to specific chain conformations because of their large size. They have been attributed to regions of different density, possibly resulting from inhomogeneous deformation processes. They may be associated with yield.

MODELS OF THE STRUCTURE OF AMORPHOUS POLYMERS

In order to understand the physical properties of a material it is most helpful to devise a molecular model, which is in quantitative agreement with all experimental evidence known so far but which is hopefully also able to predict certain physical properties which are yet unknown. The structural models proposed for bulk amorphous polymers can in general be divided into two groups:

(a) those which assume that chains of sufficient chain flexibility should have a random conformation, uneffected by neighbouring chains[27] and

(b) those which assume that regions of local order, characterized by vaious degrees of orientational order, exist in the bulk amorphous material. These models may be called 'bundle models'[57,87,100,104,111,122].

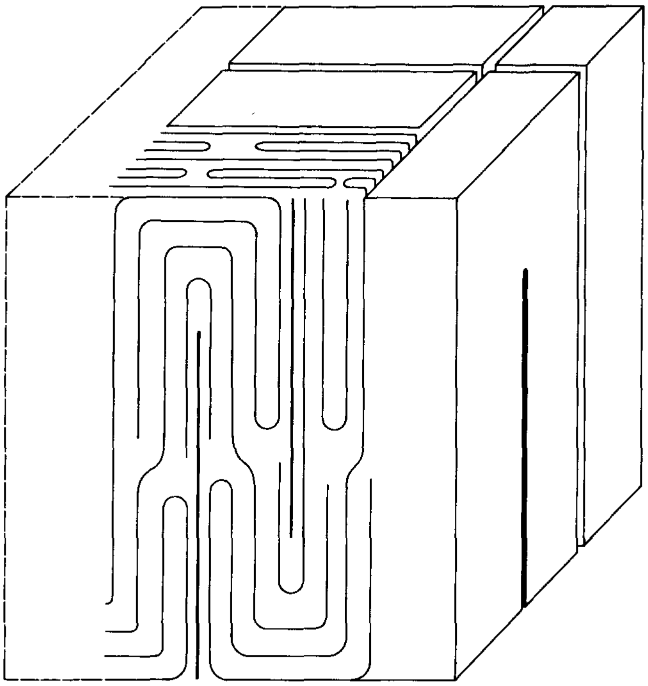

Figure 15 Schematic representation of the meander model, proposed by Pechhold *et al.*[122]

Several qualitative bundle models have been proposed in the literature, notably by Kargin and coworkers, who assume that bundles of parallel segments with lateral dimensions of about 100 Å exist[111], by Yeh[104], who proposed a folded chain fringed-micellar model, by Schoon and coworkers[57], who suggested a string model of structural units as well as by Vollmert[100], who reported experimental results in favour of a cell structure in polymer gels. The evidence for a local orientational order within small units of the bulk amorphous polymers comes mainly from dark field electron microscopic investigations of the granular texture described above. The models discussed so far cannot be accurately tested since they are insufficiently defined with respect to the exact nature of the overall chain conformation, of the local orientational order and of the local positional order and the homogeneity of the density. Furthermore no attempt has been made to calculate macroscopical properties on the basis of the structural models proposed. The meander model proposed by Pechhold and coworkers[87,129] is much better defined. According to this model the short range order of amorphous polymers is characterized by bundles of nearly parallel chain segments as shown schematically in *Figure 15.* Chain bundles are supposed to be energetically favoured despite the restricted number of possible chain conformations since a mutual disorientation of neighbouring chain segments may give rise to the formation of energetically unfavourable regions of low packing density.

Within the bundles the molecules are assumed to fold back. The bundles may contain additional defects such as jogs. The diameter of the bundles ranges between 50 and 300 Å depending on the chemical structure and the molecular weight of the polymers. The direction of the bundles is assumed to change in a meander-like fashion. This allows for a macroscopical isotropy.

Properties such as the chain conformation or the stress–strain behaviour of high molecular weight melts have been calculated from this model. One of the drawbacks of the theoretical concept of the model is that it is based on the so-called cluster-entropy hypothesis[122] which still has to be proved.

At the present stage it also seems, that the model is not able to predict the local orientational order and the local chain conformation accurately. The meander model has not been exploited so far to predict molecular correlation functions which are needed in order to calculate macroscopical properties on the basis of the pair theory of fluids.

The 'coil model', developed by Flory[27] is able to predict the overall chain conformation as well as the local chain conformation accurately. In addition it was possible to calculate the local orientational order for flexible chains solely on the basis of intramolecular correlations. The conclusion is that presently the 'coil model' is the most promising model, if we are concerned with the chain conformation in bulk amorphous polymers and its relation to the local structure. Obviously the 'coil model' cannot be employed to derive intermolecular pair correlation functions.

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