

Lectures during the labour conference of the Fachausschuß Physik der Hochpolymeren in the course of the spring meeting of the Arbeitskreis Festkörperphysik bei der Deutschen Physikalischen Gesellschaft from March 21 to 23, 1973 at Münster/Westf.

From the Institut für Physikalische Chemie der Universität Mainz, 2. Ordinariat

## Small angle X-ray scattering from amorphous polymers arising from heterogeneities

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With 6 figures and 1 table

(Received June 12, 1973)

### 1. Introduction

For many years the glassy state and the melt of polymers have been considered to be homogeneous and random in structure. However, in recent years, experimental results have been obtained, which seem to indicate that the amorphous phases of polymers are not homogeneous on the microscopic level, but that a low level of order may exist. A nodular structure has been observed by electron microscopy on several glassy polymers (1–4). *Kargin* (5) and coworkers performed electron diffraction experiments on polymer melts and interpreted their data in terms of bundles of parallel polymer chains. In addition calorimetric measurements (6), mechanical properties (7), crystallisation properties (8), rheological properties (9) and the density values of the amorphous phases suggest the existence of some order in the amorphous phase.

These results have stimulated the proposal of many structural models, which assume various degrees of order in the amorphous phase. Among these models are the chain packet model of *Kargin* (5), the Määnder-model of *Pechold* (11) and the folded chain fringed micellar grain model of *Yeh* (12). Although the models mentioned are in agreement with a variety of experimental facts, there are also results which seem to contradict these models. For instance neutron scattering experiments on atactic PMMA (13) showed that the radius of gyration of a single chain in the glassy phase has approximately the same value as in a  $\theta$  solvent. This result indicates that in contrast to the models mentioned above the conformation of the chain is similar to that in a dilute solution, namely a statistical coil. *Flory* (14) strongly supports this idea. Light scattering experiments have been performed by *E. W. Fischer* and *M. Dettenmaier* (15) on atactic PMMA. From the value of the

depolarisation they calculated the upper limit of the number of monomer units in a bundle of parallel chains, which would just give the experimental value of the depolarisation. The number turned out to be 160, which corresponds to a diameter of the bundle of about 30 Å. This value is much smaller than the value assumed in most of the models.

It is obvious that more information is needed about the structure before we can decide which of the models is closest to reality. Our present work is concerned with this general area.

A convenient and direct method of determining the structure of a substance is the diffraction of electromagnetic waves. We decided to perform small angle X-ray scattering experiments on polymers in the glassy state and in the melt, as we wanted to know specifically whether the amorphous phase is homogeneous or consists of small regions with different average densities. As discussed in a previous paper small angle X-ray diffraction experiments yield this information. Up to now only a few papers have been published which were concerned with the small angle X-ray scattering by amorphous polymers. *Vonk* (16) reported small angle scattering in a linear polyethylene melt, but he did not interpret the results. *Kirste* and *Steinbach* studied the small angle X-ray scattering of a variety of amorphous PMMA-samples and of polydimethyl siloxane (25, 26). They detected an increase of the scattered intensity at small angles.

*Harget* and *Siegmann* (17) detected small angle scattering in amorphous polyethylene terephthalate. From the curves they estimated that the diameter of the scattering particles was in the range between 30 and 40 Å. They interpreted their data on the basis of the two phase structural model suggested by *Yeh* (12) which is based mainly on electron microscopic studies of the nodular structure. The two major ele-

ments of his model are the grain, which consists of a high density ordered domain with parallel chains and a grain boundary and the low density intergranular region, which consists of chain ends and molecules that are in a random conformation. *Harget* and *Siegmann* assumed that the small angle X-ray scattering arises from these different structural units.

We performed experiments similar to those of *Harget* and *Siegmann* on a variety of glassy polymers (PET, PMMA, PVC, PC) and on the melts of different polyethylenes. The nodular structure has been observed for PMMA, PS, PC and PET but never for amorphous polyethylene. The scattering theory and results concerning thermal density fluctuations have been presented in a previous paper. In this paper we will report the results of continuous X-ray scattering at small angles.

## 2. Experimental

Thin films with a thickness ranging from 0.3 mm to 1.45 mm were used for the experiments. The samples studied in more detail were

a) Polycarbonate-PC (Makrolon, Bayer AG Dormagen)  $M_w = 35\,000$  (Poly 4,4'-dihydroxydiphenyl-2,2-propanecarbonate).

b) Polyethylene terephthalate-PET (Kalle Company Wiesbaden).

c) Polyvinylchloride-PVC, commercial sample.

d) Stanyl 8800, linear polyethylene-PE 1 (DSM)  $3\text{ CH}_3/1000\text{ C}$   $M_w = 130\,000$   $M_w/M_n = 10$

e) Lupolen 6011 L, linear polyethylene-PE 2 (BASF)  $1\text{ CH}_3/1000\text{ C}$   $M_w = 345\,000$   $M_w/M_n = 19$

f) Lupolen 1800 D, branched polyethylene-PE 3 (BASF)

$36\text{ CH}_3/1000\text{ C}$   $M_w = 400\,000$   $M_w/M_n = 17.2$

g) Linear polyethylene (Allied chemical) -PE 4  $M_w = 2.5 \cdot 10^6$

h) Fractionated linear polyethylene

PE 5  $M_w = 10\,460$   $M_n = 6\,210$   $M_w/M_n = 1.7$

PE 6  $M_w = 41\,600$   $M_n = 20\,900$   $M_w/M_n = 2.0$

PE 7  $M_w = 155\,000$   $M_n = 42\,300$   $M_w/M_n = 3.7$

First the scattering behaviour was measured for the untreated samples (T 0) at room-temperature; in the case of the polyethylene melts at 140 °C. Then the samples were subjected to a variety of treatments  $T_i$ . These treatments are:

(T1) *Stepwise increase in temperature*: The temperatures ranged from 25 °C to temperatures above the glass transition temperature  $T_g$  for the amorphous samples and from 140 °C to 200 °C for the polyethylene melts. The scattering experiments were performed at constant temperatures.

(T2) *Annealing*: The samples were held at constant temperatures above and below  $T_g$  (at 140 °C, 170 °C and 200 °C in the case of the polyethylene melts) for up to 48 hours.

(T3) *Crystallisation*: The samples were crystallized at different temperatures and slowly cooled down to room-temperature.

(T4) *Stretching*: The PET samples were drawn at 60 °C and subsequently annealed at different temperatures in the range between 60 °C and 255 °C.

(T5) *Crystallisation from dilute solution*: The PE-samples were dissolved in tetrachloroethylene at 95 °C. After filtering the dilute solution (0.2%), it was cooled down to 80 °C and to 20 °C. The solution grown crystals were molten to a film.

(T6) *Removal of additives*: 2n HCl was added to a dilute solution of PE in tetrachloroethylene at 95 °C, the mixture was stirred for several hours at that temperature. This method is used to remove insoluble substances from a solution by chemical conversion into a substance which is solvable in a second phase (in our case water and HCl) and removing it together with the second phase. After separation of the acid from the organic solution the solution was cooled down to 80 °C. The polyethylene crystals were molten to a film.

(T7) *Increase of the additive content*: To a dilute solution of PE in tetrachloroethylene we added small amounts of MgO, which was known to be contained in the sample. The solution grown crystals were molten to a film.

(T8) *Swelling*: Polyethylene samples were swollen in tetralin for 4 weeks. Subsequently the weight of the samples remained constant. The total increase of the sample weight was between 6.4% and 16%, depending on the degree of crystallinity of the sample. The measurements at high temperatures were performed in the presence of tetralin in the sample cell.

A survey of the treatments and of the treated samples is given in table 1.

Experiments were also performed on samples with different molecular weights and on samples with different kinds of additives.

(A1) *Different molecular weights*: We studied samples of PE (PE 1–PE 4) with different molecular weights, ranging from 130 000 to  $2.5 \cdot 10^6$ . The samples came from different sources, the molecular weight distribution was fairly broad. We also studied fractionated PE-samples (PE 5–PE 7), which came from the same mother substance. The width of the distribution is given above.

(A2) *Samples with different additives*: Scattering experiments were performed on PET-samples with different amounts and kinds of additives.

The scattering experiments were performed with a Rigaku Denki small angle X-ray camera, which has been described in a previous paper (24).

## Results and discussion

The amorphous polymers and the polyethylene melts exhibited strong small angle X-ray scattering. This is indicated in fig. 1. The intensities and the shape of the scattering curves depend on the nature of the polymer. Polymers of the same kind but from different sources show differing scattering behaviour. The origin of the scattering is not clear. Three possibilities can be imagined:

1) The amorphous phase may be assumed to consist of regions of different densities. This interpretation is in agreement with the model of *Yeh* (12) and the work of *Harget* and *Siegmann* (17).

2) Microholes may be present in the polymer samples. The density difference between the holes and the polymer matrix determines the value of the scattered intensity. Microholes have been identified as the origin of the small angle X-ray scattering in a variety of fibres (18, 19). *Statton* (18) arrived at this conclusion by studying the influence of different treatments of the fibres on the scattering behaviour of the fibres.

3) Foreign particles may be present in the polymer phase. The scattering curve and the intensity are determined by the shape, amount and density of these particles. Foreign particles are catalyzers, stabilizers etc. Small angle X-ray scattering studies have successfully been used as a means of characterizing the specific surface of fillers in amorphous polymers (20).

Considering these three possibilities we devised two series of experiments:

In the first series of experiments, we treated the same sample in different ways (*T1–T8*) and measured the influence of the particular treatment on the scattering behaviour.

In the second series of experiments we studied polymers of the same chemical nature but with different molecular weights, molecular weight distribution or different kinds of additives (*A1, A2*).

We will now discuss the response of the scattering behaviour to the different treatments, the results are also given in Table 2 in comparison to the scattering of the untreated samples.

(*T1*) The scattered intensity of the samples *PMMA/T*, *PC/T*, *PET/T* and *PE1, 2, 3/T* increased only very slightly with increasing temperature. The shape of the curve did not change, it remained constant even at the glass transition temperature of the amorphous polymers.

(*T2*) The shape and intensity of the scattering curves of the samples *PMMA/a*, *PC/a*, *PET/a* and *PE1, 2, 3/a* were not influenced by the annealing process.

(*T3*) The scattering curves of the crystallized samples *PET/c* and *PE1, 2/c*, after correction for the absorption, were the same as those of the untreated samples. This was indicated by two facts. At very small angles the scattering behaviour from a semi crystalline sample gives rise to a continuously decreasing scattering curve; the contribution of the two phase system crystalline-amorphous to the scattering is small.

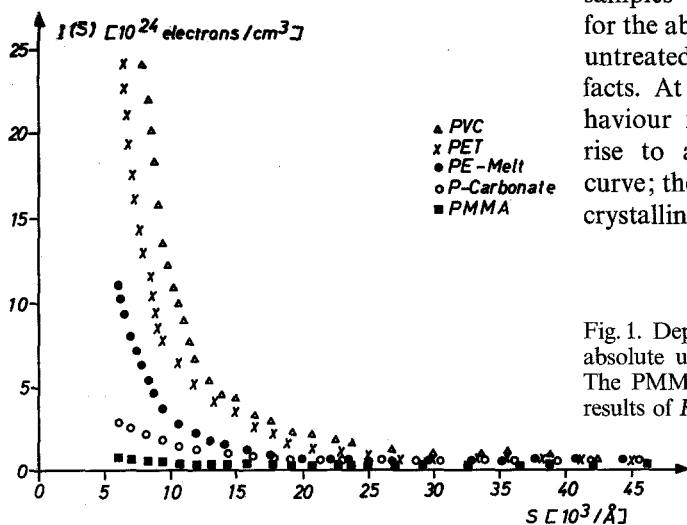


Fig. 1. Dependence of the scattered intensity  $I(s)$  in absolute units on  $s$  for various amorphous polymers. The PMMA scattering curve is in agreement with the results of *Kirste* and *Steinbach* (25, 26)

Table 1. Survey of the treated samples

Sample treatment	PC	PET	PVC	PE 1	PE 2	PE 3
T0) No treatment	PC/u	PET/u	PVC/u	PE1/u	PE2/u	PE3/u
T1) Temperature increase	PC/T	PET/T	—	PE1/T	PE2/T	PE3/T
T2) Annealing	PC/a	PET/a	—	PE1/a	PE2/a	PE3/a
T3) Crystallisation	—	PET/c	—	PE1/c	PE2/c	—
T4) Stretching	—	PET/d	—	—	—	—
T5) Crystallisation from solution	—	—	—	PE1/s	PE2/s	PE3/s
T6) Removing of additives	—	—	—	PE1/r	—	—
T7) Increase of the additive content	—	—	—	PE1/in	—	—
T8) Swelling	—	—	—	PE1/sw	PE2/sw	PE3/sw

It is in this region that the scattering curve agrees with the scattering curve of the amorphous sample. The second indication comes from the fact, that after the subtraction of the amorphous scattering curve from the scattering curve obtained from the semi-crystalline material we get a corrected curve, which has exactly the shape which we would expect from the *Kiessig* pattern.

(T4) The small angle scattering obtained from the drawn PET-samples PET/d was isotropic, as in the case of the untreated sample. The shape and the intensity of the scattering curve did not change.

(T5) The scattering behaviour of the samples which were crystallized from dilute solution (PE 1, 2, 3/s) was the same as that of the untreated samples. This is shown in fig. 2.

(T6) The samples from which foreign particles were removed (PE 1/r) scattered much less than the untreated samples. This is shown in fig. 2.

(T7) Samples to which foreign particles had been added (PE 1/in) scattered more strongly than the original sample.

(T8) The scattered intensity of swollen samples PE 1, 2, 3/sw was slightly decreased compared with the untreated samples. The decrease occurred mainly at very small angles.

(A1) The scattering behaviour of samples with different molecular weight and different molecular weight distribution (PE 1–PE 7) did not show a systematic dependence on these parameters.

(A2) The scattered intensity and the shape of the scattering curves depend strongly on the amount and kind of additives in the polymer samples. This is shown in fig. 3 for the case of different PET-samples. When the polymerisation was performed such as to prevent the formation of heterogeneous particles in the polymer matrix, the scattering intensity was low. In that case we observed an increase of the intensity only at very small angles, the increase was just above the limit of error of our experiments.

Without going into detail, we will now discuss possible reasons for the small angle scattering from amorphous polymers with respect to the results given above. From these results we can obviously conclude that, in the case of the polymers studied, the small angle X-ray scattering cannot be attributed to the inherent structure of the pure amorphous phase. This is shown by

the response of the scattering behaviour to the treatments  $T_i$ . For instance, if the small angle scattering arises from the structure of the pure polymer phase, it should not depend on the amount and nature of the additive (T6, T7, A2). We will discuss the consequence of this result later in more detail.

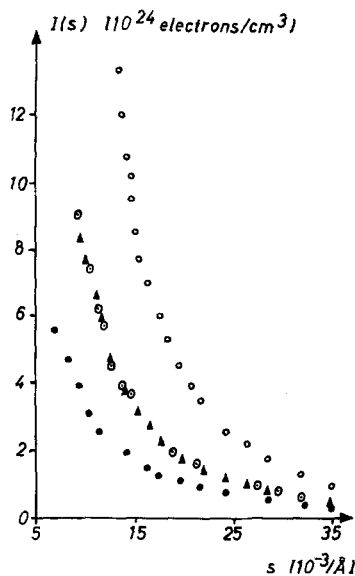


Fig. 2. Dependence of the scattered intensity  $I(s)$  in absolute units on  $s$  for polyethylene melts at  $140^\circ\text{C}$ . ( $\odot$ ) untreated sample,  $\blacktriangle$  sample crystallized from dilute solution,  $\odot$  sample with additional additives,  $\bullet$  sample after the removal of some additives)

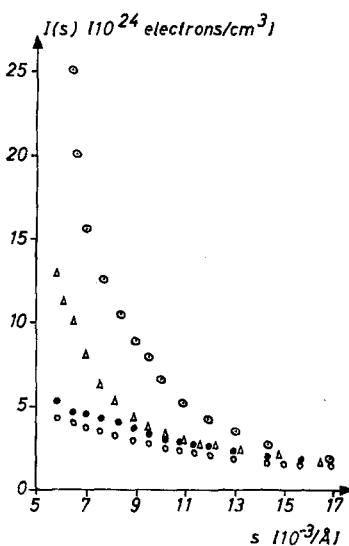


Fig. 3. Dependence of the scattered intensity  $I(s)$  in absolute units on  $s$  for PET-samples with different kinds of additives

From our experiments we also can conclude that in general the small angle X-ray scattering of the samples studied cannot be attributed to microholes in the sample. Comparing our results with *Statton's* results on fibres (18), we can conclude that the response of the scattering behaviour to the treatments *T2, T4, T6, T7, T8* and *A2* contradicts the hole theory. During the drawing process, for instance, the holes should be elongated in the drawing direction, consequently the scattering pattern should become anisotropic; annealing of the sample should decrease the scattered intensity. Swelling a sample should lead to a decrease in intensity, if holes were producing the scattering.

We thus conclude that the scattering is caused by foreign particles in the polymer such as additives, which are heterogeneously distributed in the polymer matrix. Foreign particles can also arise from the processing of the polymer in extruders etc. In commercial polymers a variety of additives can be found. They are stabilizers against heat, UV-light, oxygen, they are catalyzers, pigments of fillers. With the possible exception of fillers and pigments, the amount of additives in the polymer is small. However in many cases the density difference between the additive and the polymer is large as for instance in the case of metal oxides, consequently the scattered intensity is high even for small amounts of additives. This interpretation of the small angle scattering of amorphous polymers is in agreement with all experimental results. Especially the response of the scattering behaviour to the treatments *T1, T4, T6, T7, A2* favor this explanation. We will discuss the consequences of this result in a later part of this paper.

First we will discuss this result with respect to the nodular structure in the amorphous phase. Our conclusion is, that the small angle X-ray scattering does not originate from the inherent structure of the pure polymer phase, but arises from foreign particles. This result, however, does not necessarily imply that small regions of different density do not exist in the pure polymer phase. If they exist their density must be so small that we do not detect the intensity scattered by them. At small angles the total scattering curve can be assumed to be composed of the constant intensity, which is caused by thermal density fluctuations, of the additive-scattering and possibly of the scattering, which

arises from the inhomogeneous pure polymer phase. From the total scattering curve we can subtract the additive scattering if it can be represented in some analytical form. This was possible for most of the samples studied. In the case of a particular PMMA-sample the additive scattering was negligible. We can also subtract the scattering which is caused by thermal fluctuations. We attributed the remaining scattering totally to the scattering of the pure polymer phase. Then we can calculate the upper limit of the density difference between different regions in the amorphous phase, since for a two phase structure the scattered intensity is given by the expression

$$I(s) = (\rho - \rho_0)^2 \left| \sum(s) \right|^2$$

where  $\sum(s)$  is the *Fourier* transform of the shape of the particles (21). The calculations were done in several ways by assuming various distributions and sizes of the regions of different densities in accordance with the suggested structural models. The result was that in all cases the density difference between different parts of the amorphous phase must be smaller than 0.3%. For a judgement of the homogeneity of the amorphous phase we have to compare this value with the actual value of the density in regions of the order of 20 Å to 100 Å in diameter, as the models assume regions of this size. For this purpose we consider the following experiment.

In a homogeneous structure we measure the density at different points averaged over large volumes, in which case the density will be nearly constant in all volumes. However if we decrease the size of the volume, over which we average, the density will not be the same in all volumes. Due to thermal fluctuations we get a distribution of the density, the width of the distribution increases with decreasing volume. We can represent the probability of any deviation of the density from the mean by a *Gaussian* distribution with the standard relative deviation  $\sigma$  where

$$\sigma^2 = \overline{(\rho - \rho^-)^2} = kT\kappa/V$$

$\kappa$  is the isothermal compressibility,  $V$  the volume considered. This equations has been discussed in a previous paper. Fig. 4 represents the density distribution in volumes which contain about 30 PMMA-monomeric units (diameter 20 Å) and 480 monomeric units (diameter 50 Å) for the case of PMMA at 25 °C. It also shows the upper limit of the density difference between

regions of different average density (0.3%). The result is that for these small dimensions it is unreasonable to differentiate between two phases, if the density difference between the phases is smaller than 0.3% since the fluctuation within one phase is much larger than the fluctuation between the phases.

One immediate conclusion is, that the observed nodules cannot be related to regions of different density. Due to the thermal fluctuations small density differences between different regions of the amorphous phase are smeared out, consequently they cannot be observed as nodules.

We now return to the result that the small angle X-ray scattering in amorphous polymers is caused in general by foreign particles. We will discuss two consequences of this result.

1. As the small angle scattering results from foreign particles, it must be independent of treatments of the sample involving crystallisation and stretching. Thus we can measure the scattered intensity in the amorphous phase and subtract it after appropriate corrections from the total scattering of the partially crystalline sample. By this correction – which has already been used by Vonk (16) – we get more reliable data from the scattering curve. We applied this correction with good results for the case of the slit smeared intensity curves of drawn and annealed PET-samples.

2. In many cases the small angle X-ray scattering method can be used to characterize the microscopic and macroscopic distribution of the additives in a polymer sample. Chemical analysis, fluorescence measurements, UV and IR measurements have been used for this purpose. The small angle X-ray scattering method has the advantage, that the experiments can be performed on undestroyed, relatively thick samples. The method can be used to determine the amount of the additive in a particular part of the sample, the size, and in some cases, even the shape of the additives. The limit of the method is related to the density difference between the polymer matrix and the additive, the amount and the kind of distribution of the additive in the sample. If for instance the distribution is homogeneous (solid solution) no continuous scattering curve can be observed. The curves can be analysed to get values such as the radius of gyration, intersects or the correlation length of the scattering particles.

For most of the samples, which we studied, we could characterize the system by a correlation function  $C(r)$

$$C(r) = \exp(-r/a)$$

which defines a correlation length  $a$ . Debye used this correlation function for the characterization of the hole distribution in dried gels. The intensity function which corresponds to this correlation function in the case of a slit-like primary beam is

$$I(s) = \text{const.} (1 + s^2 a^2)^{-3/2}.$$

Thus a plot of  $I(s)^{-2/3}$  versus  $s^2$  gives a straight line and the correlation length can be calculated from

$$a = (\text{slope/intercept } (s = 0))^{1/2}.$$

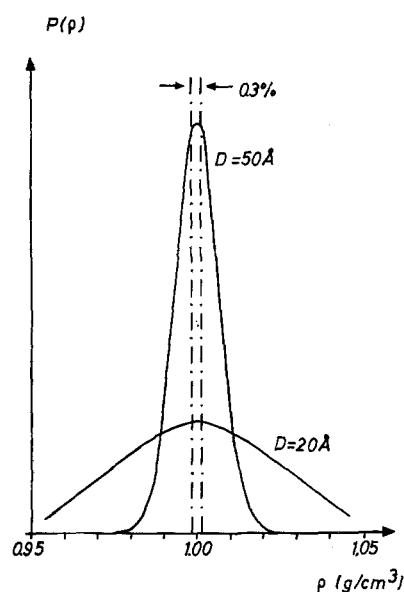


Fig. 4. Dependence of the probability density  $P(\varrho)$  on the reduced density  $\varrho = (\varrho'/\bar{\varrho}')$  for the case of PMMA, as calculated from the fluctuation theory. Parameter is the diameter  $D$  of the volume considered

As an example, fig. 5 shows these plots for the case of different PET-samples, the correlation length is of the order of 40 Å to 60 Å. The deviations at small angles can be attributed to the presence of large holes and in one case to the presence of small amounts of pigments.

The macroscopic distribution can also be checked by the small angle X-ray method. This can be done by determining the scattering curve at different parts of the sample. From this we can calculate the distribution of the amount and

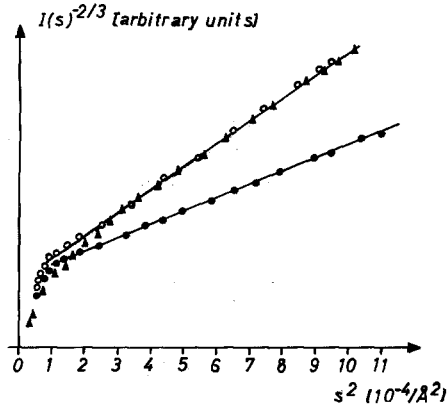


Fig. 5. Debye plot  $I(s)^{-2/3}$  versus  $s^2$  for PET-samples with different additives

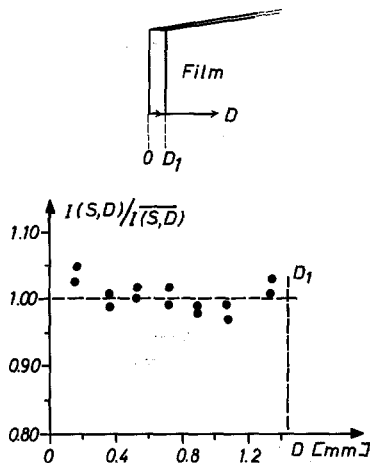


Fig. 6. Dependence of the relative intensity  $I(D)/I(\bar{D})$  on the position  $D$ , measured perpendicular to the surface of a PET-film

size of the particles in the sample. We measured the scattering curves at different parts of a PET-film perpendicular to the surface of the film and along the film surface. As an example fig. 6 shows the distribution of the amount of additives perpendicular to the film surface. The conclusion is that this method can be a useful tool for the characterization of the distribution of additives in a polymer sample.

#### Acknowledgements

This research was supported by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich Makromoleküle (SFB 41) Mainz-Darmstadt. The samples were kindly supplied by Dr. C. G. Vonk (Stamylan), the Kalle Company/Wiesbaden (PET) and Dr. Heinze, BASF (PE-Lupolen).

We are indebted to Prof. R. G. Kirste, and Dr. G. F. Schmidt for helpful discussions.

#### Summary

The small angle X-ray scattering of glassy polymers (PET, PC, PVC, PMMA) and of polymer melts (PE) was studied. The dependence of the intensity scattered at small angles on the sample treatment suggests that neither the inherent structure of the pure polymer phase nor microholes are the origin of the scattering. In agreement with all experimental facts the scattering can be attributed to foreign particles such as for instance stabilizers in the polymer matrix. The consequence of this result is discussed with respect to the nodular structure of the amorphous phase and with respect to structural models of the amorphous phase. The nodular structure is not related to regions of different densities within the pure amorphous phase.

The small angle X-ray scattering can be used to characterize the microscopic and macroscopic distribution of additives in polymer samples.

#### Zusammenfassung

Es wurden Röntgenkleinwinkeluntersuchungen an glasig erstarrten Polymeren (PÄT, PC, PVC, PMMA) und an Polymerschmelzen vorgenommen (PÄ). Die Abhängigkeit der bei kleinen Winkeln beobachteten Streuung von der Probenbehandlung weist darauf hin, daß weder die innere Struktur der amorphen Phase noch Mikrolöcher die Ursache für die Streuung sein können. In Übereinstimmung mit allen Ergebnissen wird die Streuung Fremdpartikeln wie z.B. Stabilisatoren in der Polymermatrix zugeschrieben. Die Folgerungen, die sich hieraus ergeben, werden hinsichtlich der „Körnerstruktur“ der amorphen Phase und der Strukturmodelle diskutiert. Die Körnerstruktur kann nicht durch Bereiche unterschiedlicher Dichte in der amorphen Phase erklärt werden.

Die Röntgenkleinwinkelstreuung kann zur Charakterisierung der makroskopischen und der mikroskopischen Verteilung der Zusätze im Polymeren herangezogen werden.

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