1. Introduction

The mechanical properties of materials such as, for instance, the strength or the elongation at break are not only determined by molecular interactions but also by the presence of defects in the material. These defects may be surface flaws, microscopic or macroscopic voids, heterogeneities such as stabilizers or pigments or crystal defects in the crystalline regions of partially crystalline materials. The influence of these defects is described in statistical theories in which certain assumptions are made about the distribution of defects and about the distribution of the strength of the defects (1, 2).

The experimental analysis of defects in a material and of their properties is difficult for various reasons. Often the concentration of defects is low, furthermore defects of different sizes and variable structures can occur. This makes it impossible to study defects just by one experimental method. Crazes in amorphous polymers, for instance, can be studied by optical methods such as elastic light scattering or optical microscopy (3), if their size approaches a critical value. Crazes below this critical dimension as well as crazes in partially crystalline polymers cannot be analyzed by this method. Electron microscopical studies have been used in this case (4), this technique, however, also meets with difficulties due to a low concentration of defects and due to the fact that preparation techniques may lead to the introduction of new defects.

The method of acoustic emission can be used to detect the formation of defects under strain, the spectra obtained do not contain direct information on the character of the defects, their distribution and their strength (5—7). Defects arising from main-chain breakage have been studied using the method of ESR-spectroscopy (8). Indirect methods of obtaining information on flaws have been used by Retting (9).

Small angle X-ray scattering can be employed to obtain information on defects with dimensions ranging from several Å up to several 1000 Å in amorphous as well as partially crystalline materials, if the density of the defects differs from the density of the matrix. Using small angle scattering defects were studied in a variety of polymers including amorphous PMMA and partially crystalline polypropylene by Zhurkov, Kuksenko, Slutsker et al. (10—13). They analyzed the concentration, size and shape of the defects and tried to correlate these results with results on failure of the materials. It seems, however, that the analysis of their scattering curves contains some mistakes, this will be discussed in subsequent papers (14, 17).

It is the purpose of this work to analyze for the specific case of partially crystalline polyoxymethylene in which way defects may be created in a material, which properties are exhibited by the defects and in which way the macroscopic properties of the material may be influenced by the presence of these defects.

II. Experimental

The material studied was partially crystalline polyoxymethylene (Copolymer Hostaform T 1020, Hoechst AG, W.-Germany). Different samples were obtained by crystallization from the melt at 155°C (sample A) by quenching in cold water (sample B) and by quenching in liquid nitrogen (sample C). These different samples were subjected to uniaxial stress-strain experiments at room temperature in which the ultimate strain was varied. The strain rate was varied between 0.5 mm/min and 500 mm/min. The samples were kept in the stress-free state for at least one day at room temperature after
the stress-strain experiment. The small angle X-ray scattering was measured by means of a Kratky small angle apparatus after this period. The scattering curves were determined in the direction of the applied stress and perpendicular to this direction. Absolute intensities were gained by comparing the scattering of the sample with the scattering of a calibration sample which was supplied by Prof. Kratky. The samples could also be subjected to stresses in the small angle apparatus, only constant stress experiments were performed in this case.

### III. Results

If a stress strain experiment was performed on a partially crystalline polyoxymethylene sample one observed the occurrence of particle scattering in addition to the scattering which was due to the two-phase structure of the material. The intensity of the particle scattering was found to increase with increasing strain (Fig. 1). The shape of the particle scattering curve could be described on the basis of an exponential electron density autocorrelation function \( C(r) \).

\[
C(r) = \frac{\langle \varrho(u) \varrho(u+r) \rangle}{\langle \varrho(u)^2 \rangle} \quad [1]
\]

where \( a \) is the correlation length, \( \varrho \) the electron density. This correlation function leads to the following expressions for the pinhole scattering curve and the smeared scattering curve, which is obtained by the Kratky camera:

\[
I_{\text{pinhole}} \sim (8\pi a^2)/(1 + \tilde{h}^2 a^2)^2 \quad [2]
\]

\[
I_{\text{smeared}} \sim (4\pi a^2)/(1 + \tilde{h}^2 a^2)^{3/2} \quad [3]
\]

where \( \tilde{h} \) is the distance between the origin and the position of the detector slit in the plane of registration. In the case of the smeared scattering curve a plot of \( I^{-2/3} \) versus \( h^2 \) should yield a straight line, the slope and intercept of which can be used to calculate the correlation length \( a \).

\[
a = \left( \frac{\text{slope}}{\text{intercept}} \right)^{1/2}. \quad [4]
\]

Figure 2 gives an example of this plot. The average dimension of a structure is related to the correlation length \( a \). In the case of particles with a distribution of their sizes it is a measure of the average particle size. The value of the invariant, defined by

\[
\int I(\tilde{h}) \tilde{h} d\tilde{h} = \text{Inv.} \quad [5]
\]

gives information about the concentration of the particles \( V \). It was found that the correlation length depended on the direction within the sample, relative to the direction of the applied stress. Apparently particles exist in the material which did not possess a constant average dimension in all directions (Fig. 2). The experimental results showed that the particles had on the average the shape of an ellipsoid. The small axis of the ellipsoid, which turned out to be the rotational axis, was oriented in the direction of the applied stress.

![Fig. 1. Small angle X-ray scattering curves of strained polyoxymethylene samples](image-url)