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A New Method for Data Evaluation of Small Angle Neutron Scattering Experiments and Its Application to Amorphous Polycarbonate[*],[**]

W. Gawrisch[***], M.G. Brereton[****] and E.W. Fischer

Institut für Physikalische Chemie, Universität Mainz, 6500 Mainz,
Federal Republic of Germany

SUMMARY

The conformation of single chains in bulk polymer materials can be evaluated from coherent neutron scattering on mixtures of normal and deuterated polymers. It is shown that the single-chain structure factor can be also obtained from measurements of highly concentrated mixtures and the procedure of evaluation is described. The application to amorphous polycarbonate demonstrates the advantages of the method.

INTRODUCTION

In the past the structure factor of the single chain in bulk polymeric materials has been evaluated mostly from measurements of rather diluted mixtures of protonated and deuterated macromolecules because it was assumed that the interchain interferences of the tagged molecules will disturb the evaluation for higher concentrations. It has been demonstrated experimentally, however, that in the case of semicrystalline polymers the single-chain conformation can also be evaluated from measurements on concentrated mixtures (FISCHER et al. 1979, STAMM et al. 1979). This evaluation was based on the conventional scattering theory of X-ray scattering by solid solutions where any concentration can be used. In the following it is shown that also in the general case high concentrations can be used for the evaluation of the single-chain structure factor. The theory is applied to the neutron scattering of polycarbonate in the glassy state.
The idea of using highly concentrated mixtures is already expressed in DE'GENNES book (1979). Independent from our own work (BRERETON et al.(1979), GAWRISCH (1980)) very similar results have been obtained by AKCASU et al. (1980) from a basic theoretical point of view. The treatment of the data is somewhat different however, see e.g. TANGARI et al. (1980).

THEORY

The function of interest is the neutron intensity $I(\kappa)$. We let $\vec{R}_i^{\alpha s}$ denote the position of a monomer with isotope "s" whose position along the α-chain is labelled by i. Associated with this monomer will be a scattering length $b_i^{\alpha s \sigma}$, where σ is the spin state. Then the neutron scattering intensity is

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[***] Hoechst AG, Wiesbaden

[****] University of Leeds, Dept. of Physics, Leeds (England)

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directly related to:

$$I(\vec{\kappa}) = \sum_{\substack{\alpha\beta,\ ij\\ ss',\sigma\sigma'}} \langle b_i^{\alpha s\sigma}\ b_j^{\beta s'\sigma'}\ \exp\ i\vec{\kappa}(\vec{R}_i^{\alpha s} - \vec{R}_j^{\beta s'})\rangle \tag{1}$$

The averaging <"> is done over i) the configurations of all molecules, ii) the isotopic species, iii) the spin states. The average is independent of the isotopic species as long as there are no H-H, H-D or D-D specific interactions. After averaging (i) - iii) we get for the neutron scattering intensity (BRERETON et al. 1981):

$$\begin{aligned} I(\kappa) = {} & c(1-c) \cdot n^2 \cdot (b^H - b^D)^2 \cdot \sum_{\alpha ij} S_{ij}^{\alpha\alpha}(\vec{\kappa}) \\ & + (4\pi)^{-1}((1-c)\sigma_{inc}^H + c\sigma_{inc}^D) \cdot \sum_{\alpha i} S_{ii}^{\alpha\alpha}(\vec{\kappa}) \\ & + (4\pi)^{-1}((1-c)\sqrt{\sigma_{coh}^H} + c\sqrt{\sigma_{coh}^D})^2 \cdot \sum_{\substack{\alpha\beta\\ ij}} S_{ii}^{\alpha\beta}(\vec{\kappa}) \end{aligned} \tag{2}$$

where

$$S_{ij}^{\alpha\beta} = \langle \exp\ i\vec{\kappa}\ (\vec{R}_i^{\alpha} - \vec{R}_j^{\beta}) \rangle_{\text{conf.}} \tag{3}$$

c: concentration of the labelled molecules

n: number of exchanged H-Atoms per monomer

σ_{inc}^H: incoherent cross section of the protonated monomer unit

σ_{coh}^H: coherent cross section of the protonated monomer unit

The dependence of the intensity $I(\kappa,c)$ on the concentration c is given over the entire range of κ by a quadratic form of c:

$$I(\kappa,c) = \alpha(\kappa)\ c\ (1-c) + \beta(\kappa)\ (1-c) + \gamma(\kappa)\ c \tag{4}$$

where the coefficients α, β, γ depend only on κ.

The single chain structure factor $S(\kappa)$, the density fluctuation $\langle\rho\rho\rangle$ in Fourier space and the total number N^* of scatterer in the scattering volume V can be found by fitting the experimental data taken over the entire concentration range at a fixed κ-value to this quadratic form. The κ-dependence of the interesting quantities is then calculated from α, β and γ.

There are three obvious advantages of the method: i) The accuracy of the scattering data is much better due to the high concentrations of the tagged molecules, see for example Fig. 2 and 3, and due to the fact, that no background scattering of the "zero-sample" must be substracted. ii) Besides the structure factor of the single chain also the overall density fluctuation is obtained. iii) Since the experimentally found value of N^* must not depend on κ, the method has an inherent control of self-consistency.

The new technique of evaluation has been applied successfully to polyethylenoxide in the crystalline and amorphous state (KUGLER 1981), and to polycarbonate (GAWRISCH 1980).

EXPERIMENTAL RESULTS FOR POLYCARBONATE

Deuterated amorphous polycarbonate (PC) on the base of 4,4'dioxydiphenyl-2,2 propan was investigated at different concentrations in a protonated matrix. All samples were in the form of films (~1mm) cast from dichlormethane solutions. As usual, the chain conformation was firstly studied with diluted systems (up to 0.04 g/cm^3) of deuterated PC. Later concentrations up to c=0.5 were investigated.

The measurements were performed at the high-flux-reactor in Grenoble using D 11 and D 17 (small angle scattering machines) and D 1B, a wide angle apparatur. Results from the analysis of the scattering curve in the Guinier-range from the diluted systems are summarized in Tab. 1.

sample	$\bar{M}_n$ g/Mol	$\bar{M}_w$ g/Mol	$\bar{M}_w$(SANS) g/Mol	$(<r_w^2>/\bar{M}_w)^{1/2}$ nm/(g/Mol)$^{1/2}$
PC-D1	11300	20300	20100	$4.60 \cdot 10^{-2}$
PC-D2	23500	46100	49000	$4.62 \cdot 10^{-2}$
PC-D3	29200	56100	59700	$4.65 \cdot 10^{-2}$

TABLE I

Molecularweights as measured viscosimetrically, by GPC and by neutron small angle scattering (SANS) and radius of gyration measured from the Guinier-range with diluted mixtures.

It can be noticed that the values of M_w measured by SANS are in good agreement with the viscosimetric data. There exists some discrepancy with regard to the radius of gyration in θ-solvents, however, which was determined by BERRY et al. (1967):

$$(<r_w^2>/M_w)^{1/2} = 3.8 \cdot 10^{-2}\mathrm{nm}/(\mathrm{g/Mol})^{1/2}$$

The reliability of the evaluation method was tested by determining the radius of gyration in dependence on concentration. Fig. 1 shows one example of the results; as expected the measured values do not depend on c.

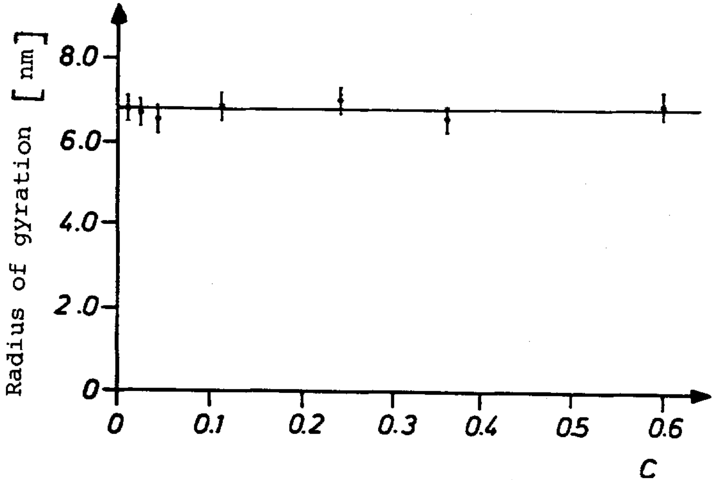

Fig.1: Radius of gyration of sample PC-D1 in dependence on concentration c of deuterated PC.

Fig. 2 shows the reduced intensity $I_{Red}(\kappa)$ in the Kratky plot ($I_{Red}(\kappa) \cdot \kappa^2/c(1-c)$ vs. κ) in the κ-range up to $12nm^{-1}$. In the region up to $1nm^{-1}$ the plot shows the generally observed plateau. However it does possess a slight slope and it is never truly parallel to the κ axis. Above $2.5nm^{-1}$ an increase of the scattering curve is observed. This scattering behaviour is in good agreement with the scattering function calculated by YOON and FLORY (1981) for the unperturbed chain model of polycarbonate. Also, the chain extension thus calculated is in satisfactory agreement with the experimental value of Tab. 1.

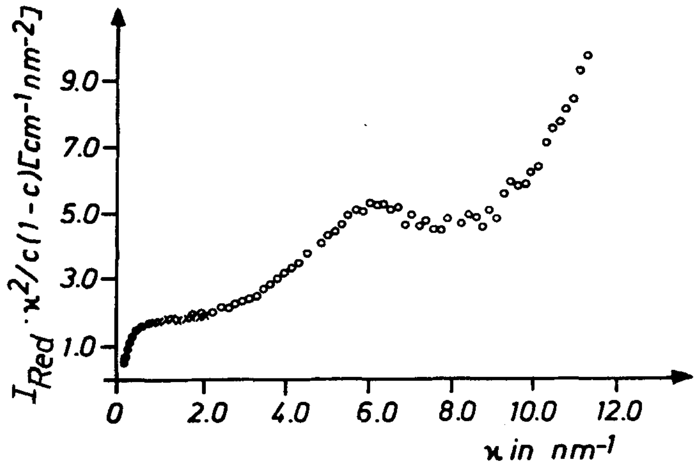

Fig. 2: $J_{Red} \cdot \kappa^2/c(1-c)$ plotted vs. κ for polycarbonat (M_w = 20300). Master curve obtained from highly concentrated mixtures.

The advantage of the new method can be judged from a comparison between Fig. 2 and Fig. 3, which is the Kratky plot of the scattering data obtained with the conventional method of low concentrations.

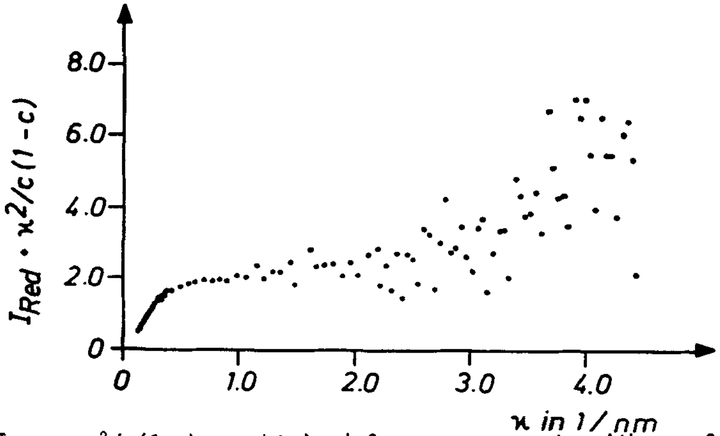

Fig. 3: $I_{Red} \cdot \kappa^2/c(1-c)$ as obtained from measurements with c = 0.02, 0.03 and 0.05

The method also yields the density fluctuation in Fourier-space. It is shown in Fig. 4 and by comparison with the X-ray pattern some valuable informations about the origin of the various halos can be obtained. This work is still in progress.

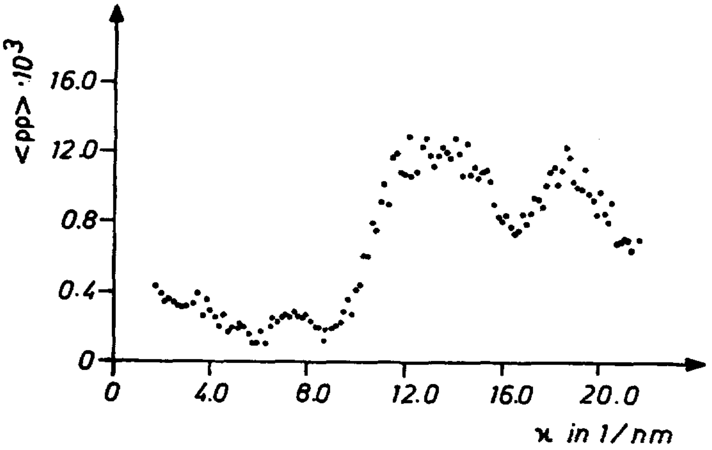

Fig. 4: Density fluctuations of amorphous PC.

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