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SHORT RANGE ORDER IN AMORPHOUS POLYCONDENSATES

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ABSTRACT

The static coherent structure factors $S(Q)$ of the polymer glass Bisphenol-A-Polycarbonate and its chemical variation Bisphenol-A-Polyetherketone – both in differently deuterated versions – have been measured by spin polarized neutron scattering. The method of spin polarisation analysis provided an experimental separation of coherent and incoherent scattering and a reliable intensity calibration. The results are compared to structure factors calculated for model structures which were obtained by "amorphous cell" computer simulations. In general reasonable agreement is found between experiment and simulation; however, certain discrepancies hint at an insufficient structural relaxation in the amorphous cell method.

1. Introduction

The group of polymer glasses known as polycondensates comprises polycarbonates, polyetherketones and polyethersulfones in numerous chemical variations. The most prominent example thereof is Bisphenol-A-Polycarbonate (BPA-PC), a technical thermoplastic with favorable mechanical and thermal properties[1]. Due to its outstanding technical importance short range order in BPA-PC has been investigated in various X-ray and neutron scattering studies in the wide angle range[2, 3, 4]. The advantage of neutrons for scattering experiments on polymers is the possibility to vary the scattering contrast by selective deuteration of particular hydrogen positions in the monomer. This concept was applied in the work of Červinka et al.[4], where the scattering of four differently deuterated versions of BPA-PC was measured and

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compared to calculated structure factors for certain model structures. However, their comparison suffered from the background by incoherent scattering and from the lack of an intensity calibration of the measured data. As shown by Schärpf and Gabryś in several papers[5, 6, 7], these problems can be avoided by the use of spin polarisation analysis, providing an experimental separation of coherent and incoherent scattering, a reliable intensity calibration and thus, a good comparability between measured data and model calculations.

In the work reported here the coherent structure factors of BPA–PC and Bisphenol–A–Polyetherketone (BPA–PEK), both in four differently deuterated versions, have been measured by spin polarized neutron scattering. This study is part of a larger research project which is devoted to the investigation of the correlation between primary chemical structure and macroscopic properties of amorphous polycondensates by a combination of experimental (e. g. dynamic mechanical measurements) and theoretical methods such as static and dynamic computer simulations[8]. The results of the neutron scattering experiments are to be compared to structure factors calculated from so-called "amorphous cell" computer simulations, where model structures of amorphous polymers are generated in chemical detail by filling a cubic box of typically 30 Å cube length with polymer chains and subsequent relaxation of this initial configuration by potential energy minimisation [9, 10, 11]. First comparisons between amorphous cell results and neutron scattering data[12] indicated that this simulation method reproduces the interatomic distances of glassy polycarbonates quite well, whereas correlation lengths are underestimated, most likely due to an insufficient structural relaxation.

In this study the work has been extended to BPA–PEK, where the carbonate group in BPA–PC is replaced by a much bulkier ketone group which has a rather drastic impact on the macroscopic properties reflected in a significantly weaker secondary relaxation in BPA–PEK compared to BPA–PC. For an investigation of such effects by means of amorphous cell simulations it is revealing to learn from neutron scattering experiments in how far the generated model structures are realistic.

2. Experiment

The polycondensate samples for the experiments described here were synthesized by Bayer AG. Table 1 gives a survey of some of the samples used herein by schematic sketches of their monomer structures and the type of deuteration. The degree of deuteration on the supposedly deuterated positions exceeded 90 % in each case according to ^{1}H–NMR investigations. The samples were prepared as hollow cylinders with an outer diameter of 1 cm, a length of 5 cm and a wall thickness of 0.2 mm (in most cases) suitable for neutron scattering experiments.

The measurements were performed with the triple axis spectrometers HB-1 at the Oak Ridge National Laboratory (ORNL)[13] and H4m at the Brookhaven National Laboratory (BNL)[14], both with spin analysis option. The spectrometers were operated in the elastic mode (energy transfer $E = 0$ with a resolution of $\Delta E < 2.0$meV)

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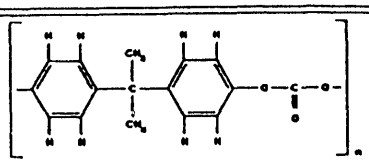
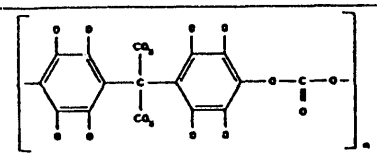
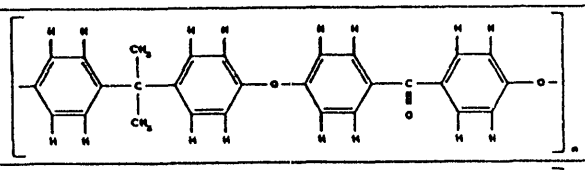
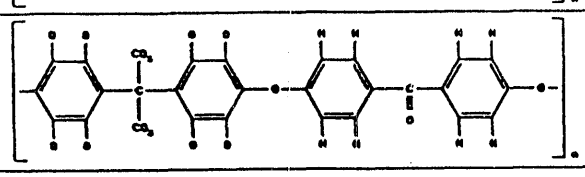
Table 1: Primary chemical structure and type of deuteration for the polycondensate samples referred to in figure 1

Sample	Monomer
H-BPA-PC	
D-BPA-PC	
H-BPA-PEK	
D-BPA-PEK	

with an incoming neutron wavelength $\lambda = 1.53$Å (HB-1) or $\lambda = 2.44$Å (H4m), respectively. In order to suppress the attenuation of the elastic scattering by inelastic or quasielastic processes the samples were cooled down to a few Kelvins during the measurement.

The structure factor was measured by scanning the scattering angle in the interesting region both with spin-flip (SF) of the scattered neutrons and without such a spin-flip ("non-flip" NF). The measured intensities were corrected for background, finite flipping ratio[15] and Debye–Waller factor. From the corrected intensities $\hat{I}_{NF}$ and $\hat{I}_{SF}$ in non-flip and spin-flip mode the (static) coherent structure factor $S(Q)$ was calculated by[6, 12]

$$S(Q) = \frac{2}{3} \cdot \left(\frac{d\sigma}{d\Omega}\right)_{inc} \cdot \frac{\hat{I}_{NF} - \frac{1}{2}\hat{I}_{SF}}{\hat{I}_{SF}} \tag{1}$$

using the incoherent scattering of the sample as an internal calibration standard.

3. Discussion

The measured structure factors are to be compared to the $S(Q)$ computed for model structures which were generated by the amorphous cell simulation method briefly characterized in section 1. Based on the observation of the underestimation of correlation lengths by amorphous cell[12], the simulation algorithm has been modified in order to improve the structural relaxation. For this purpose, the height of the interatomic potentials is lowered during the initial stages of the simulation run and several shorter chains are used instead of one long chain as before. The polymer chains were simulated in full chemical detail except for the methyl groups which were represented by CH_3 superatoms with an increased atom size.

Figure 1 shows the structure factors $S(Q)$ measured by neutron scattering compared to calculated $S(Q)$ from amorphous cell structures for BPA–PC and BPA–PEK in the undeuterated and the fully bisphenol deuterated version, the other partly deuterated samples are omitted here. The agreement between experiment and simulation is fairly good, though not quantitative for H–BPA–PC and H–BPA–PEK, but rather poor for D–BPA–PC and D–BPA–PEK. In general, reasonable agreement between measured and calculated structure factors is found and the number and positions of peaks in the experimental $S(Q)$ is reproduced quite well by the simulation data. However, certain discrepancies reveal deficiencies of the amorphous cell method in its current state: First of all, the strong peaks at $Q \approx 1.3\text{Å}^{-1}$ ("amorphous halos"), in H–BPA–PC and H–BPA–PEK are still too broad in the simulation. This indicates that the afore-mentioned modifications of the amorphous cell algorithm have not been sufficient to solve the problem of the underestimated correlation lengths completely. However, it should be difficult to achieve realistic correlation lengths in polycondensates by amorphous cell simulations, since these lengths are found to be comparable to the cell dimensions[12]. Furthermore, it is observed that the calculated scattering for the fully deuterated D–BPA–PC is much too intense in the simulation. Since in case of full deuteration all scattering atoms have very similar neutron scattering lengths, the diffuse scattering is then mainly determined by the contrast between the atoms on the one hand and the free volume between the atoms on the other hand. The overestimation of the scattering intensity in this case hints at a too inhomogeneous distribution of the free volume in the simulated structure which would be a further indication of an insufficient structural relaxation in the amorphous cell simulation. For H–BPA–PEK (and other BPA–PEK versions as well) the calculated $S(Q)$ exhibits a smaller peak at $Q \approx 0.25\text{Å}^{-1}$ not found in the experiment. In the present state it cannot be excluded that these peaks are artefacts from the finite box size. Finally, it is observed that the calculated scattering deviates significantly from the experiment whenever deuterated methyl groups are involved. Thus it appears questionable if the concept of the methyl group superatoms – although well justified by quantum chemical considerations – is really favorable for a comparison between measured and calculated structure factors as performed here.

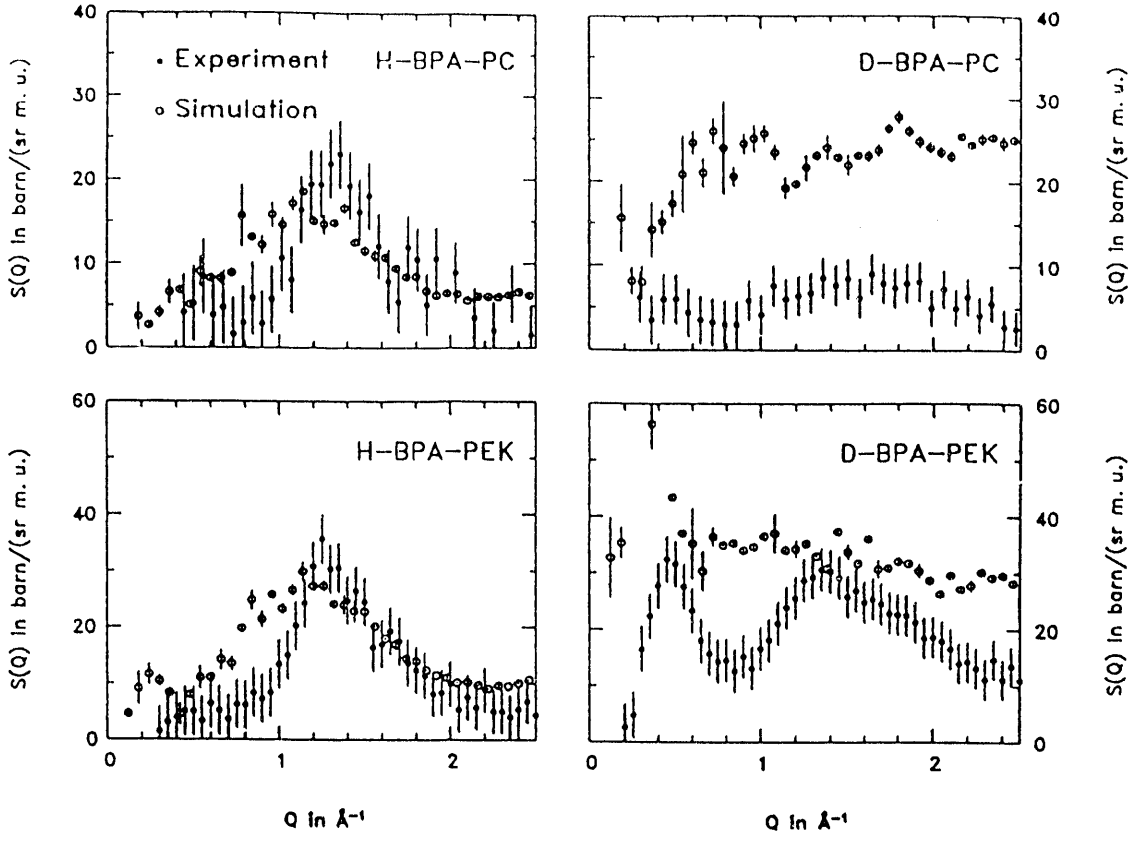


Figure 1: Coherent structure factors of the undeuterated H–BPA–PC and H–BPA–PEK and the fully bisphenol deuterated D–BPA–PC and D–BPA–PEK, measured with the triple axis spectrometers HB-1 (ORNL) or H4m (BNL) using the spin analysis option (•), compared to amorphous cell results (○).

4. Conclusions

Neutron scattering has proved to be an appropriate method for the investigation of short range order in amorphous polymer glasses by comparison with computer generated model structures, since it offers the opportunity to vary the scattering contrast by selective deuteration of particular hydrogen positions in the monomer. Based on measurements of the static coherent structure factor of the polymer glass BPA–PC and its chemical modification BPA–PEK both in four differently deuterated versions, advantages and disadvantages of the amorphous cell simulation method became evident by a comparison with calculated $S(Q)$ for model structures generated by these simulations. In general "amorphous cell" is found to reproduce the intra- and intermolecular arrangement in both polycondensates quite well as reflected in a reasonable agreement between measured and calculated structure factors in most cases. However, the insufficient structural relaxation of the initial structure leads

to a broadening of the amorphous halos for the undeuterated samples and to an overestimation of the scattering from the fully deuterated BPA–PC in the simulation. Furthermore, the poor agreement between experiment and simulation for samples with deuterated methyl groups might be related to the representation of these groups by CH_3 superatoms in the simulation.

Acknowledgement

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