Polymer Weight Distribution measured by PGSE NMR

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The molecular weight distribution (MWD) and the polydispersity index (PDI) are important numbers for characterizing polymers. They reflect the type of polymerization reaction and thus are related to the physical and mechanical properties of polymer mixtures. Currently size exclusion chromatography (SEC), also known as gel permeation chromatography, is one of the most common methods used to directly determine MWD based on the hydrodynamic volume of the dissolved polymer. However, SEC measurements require special sample preparation and a large amount of solvent, and they are time consuming. Such drawbacks can be avoided by an NMR method using the pulsed field gradient spin echo diffusion technique (PFG- or PGSE-diffusion) as an alternative method to SEC. This method has a simplified sample preparation, less solvent consumption, and can be less time consuming.

The PGSE-NMR experiments require strong gradients, because the signal must be attenuated by 3 orders of magnitude. Therefore, using a high-power gradient diffusion probe like the DiffBB shown in fig. 1 is recommended.

This application note is mainly based on "Diffusion in Polymer Solutions: Molecular Weight Distribution by PFG-NMR and Relation to SEC" by Guo et al. [1]. Details about the experimental work, calculations and all references can be found there.

Figure 1

Bottom part of a DiffBB probe equipped with a WB adaptor.

Experimental

The first sample was mono-disperse polystyrene, certified for GPC from Sigma Aldrich at different concentrations dissolved in deuterated dichloromethane. The second sample was 29kD PMMA synthesized at KIT [1] dissolved in deuterated chloroform.

The polystyrene experiments were performed on an AVANCE ™ III HD at 500 MHz using a DiffBB diffusion probe. The PMMA experiments were performed on a 200 MHz system using a Diff30 probe.

The pulse sequence used in both cases was a PGSTE [2] (Pulsed Gradient Stimulated Echo) sequence. For the very low concentrations in the polystyrene experiment the double stimulated echo sequence, PGDSTE [3] was used to avoid convection.

Results and discussion

Diffusion profiles of non-monodisperse polymer solutions show a deviation from the mono-exponential behavior indicating a distribution of diffusion coefficients. The degree of deviation depends on the width of the distribution. The data is analyzed using the Gamma-distribution model [4] to derive the probability distribution of diffusivities, as shown in fig. 2.

The diffusivity of polymer molecules in solution depends on the concentration. As soon as the concentration is above a certain level the molecules can "sense" each other. In polymer solutions clustering is not expected, just spatial obstruction of the free pathway. Therefore, the first step is to investigate the concentration dependence of a monodisperse polymer solution. As shown in fig. 3 a), the diffusivity is approximately independent of the concentration below 1 g/l. Above 1g/l the diffusivity is reduced as a function of the concentration.

Figure 2
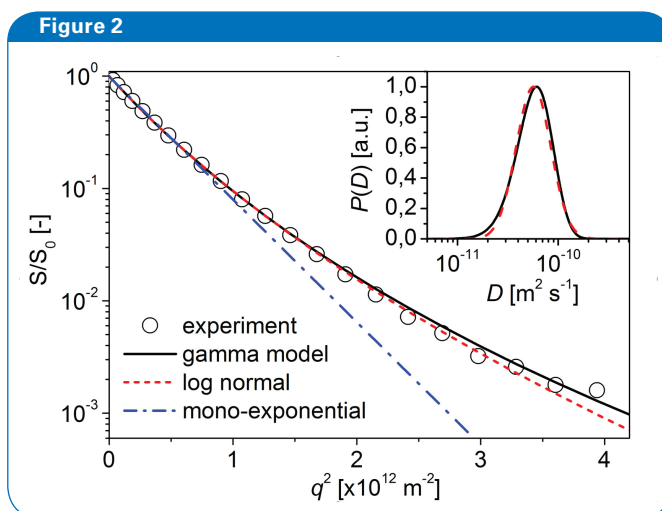
Diffusion profile of a PMMA in CDCl3 solution. The experimental data points show a strong deviation from the mono-exponential behavior indicated by the blue dash-and-dot line. The red dashed line indicates the fit to a log-normal model, the solid line the fit to the Gamma distribution model. The inset picture shows P(D) the probability distribution as a function of the diffusion coefficients calculated using the 2 different models.

This can be phenomenologically described by an exponential decay with k as a fit parameter. Fig. 3 b) shows that the mean diffusivities of the non-monodisperse PMMA solution reveal a similar behavior as the monodisperse.

$$D = D_0 \exp(\kappa c) \quad (1)$$

To calculate the molecular weight distributions (MWD) from the probability distributions of the diffusion coefficients (P(D)), the relation of the diffusion coefficient to the mass, generally described by the Stokes-Einstein relation must be considered first:

$$D = \frac{k_B T}{6\pi\eta r_H} = \frac{k_B T}{6\pi\eta} M_W^{-\alpha} \quad (2)$$

Figure 3
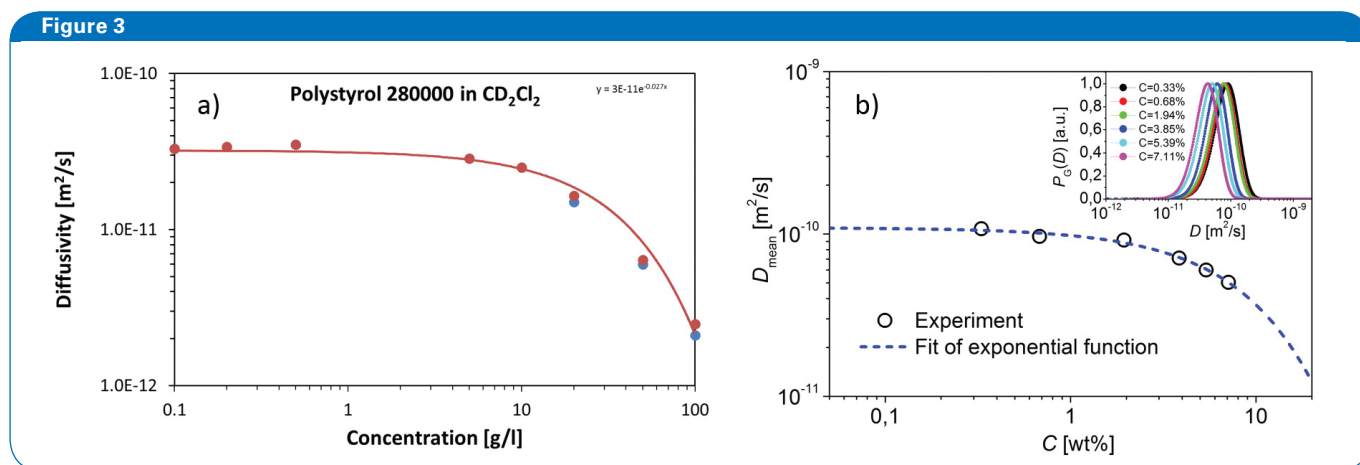
a): Concentration dependence of the diffusivity in a solution of polystyrene (molecular weight 280 kD, mono-disperse standard for GPC) in Dichloromethane (Double-log plot). The red dots are corrected for the viscosity change of the solvent derived from the change of the diffusivity of the solvent. b): Concentration dependence of the mean values of the distributions in the non-monodisperse PMMA solution (open dots) and the fit to an exponential function (dashed line). The mean values are taken from the probability distributions shown in the inset.
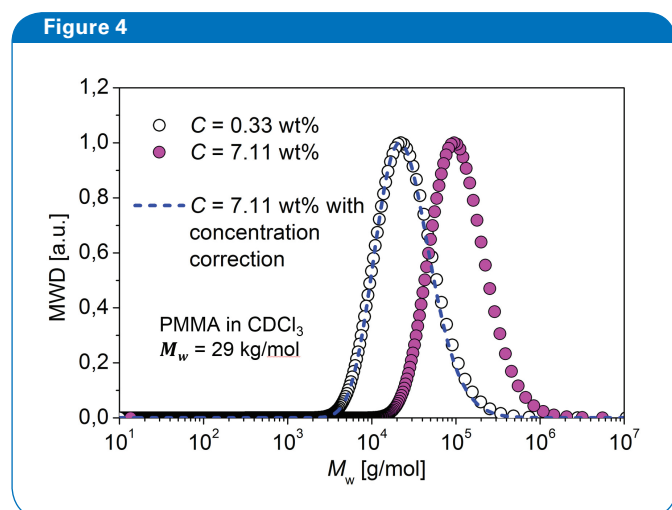
In eq. 1 k_B stands for the Boltzmann constant, T for the absolute temperature, η for the viscosity of the solution, r_H for the hydrodynamic radius of the molecule assuming spherical molecules. For a more general shape definition of the molecule, also r_H is replaced by $M_W^{-\alpha}$. M_W stands for the molecular weight and the exponent α describes the shape of the molecule in the solution. A spherical shape corresponds to $\alpha = 1/3$. Assuming constant temperature equation (2) can be simplified:

$$D = KM_W^{-\alpha} \quad (3)$$

K covers all constant terms. The shape parameter α was experimentally determined by measuring the diffusion coefficients of PMMA molecules with different molecular weights in the concentration regime, where the diffusion coefficient is concentration independent. The values of α are in the range of 0.52 to 0.55, which is in good agreement with the literature [5], [6]. With eq. (1) and (3) the molecular weight distribution function $P_M(M)M$ can be calculated as a function of the probability distribution of the diffusion coefficients $P(D)$:

$$P_M(M)M = \propto Kexp(\kappa c)M_W^{-\alpha}P(D) \quad (4)$$

The results for 2 concentrations are shown in Fig. 4. The width of the distribution is independent of the concentration. The effect of the non-zero concentration can be purged by making use of the know concentration dependence of the mean diffusivity.

Conclusion

PGSE Diffusion NMR measurements performed with high-power gradient diffusion probes give straightforward access to the MWD. The gamma-distribution model used, proved to be a robust tool for analyzing the molecular weight distributions of polymers. The experiments are easy to perform and on the long term faster, cheaper, and more environmentally friendly than conventional methods.

References:

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Figure 4

Molecular weight distribution (MWD) at low concentration (0.33 wt%, open dots), at high concentration (7.11 wt%, pink dots), and the concentration corrected MWD calculated from the high concentration data (dashed line).

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