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Flow and Diffusion Measurements on Complex Fluids Using Dynamic NMR Microscopy

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Physics at Massey University

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Abstract

This thesis deals with the measurement of fluid motion by NMR methods and the relationship of that motion both to the molecular organisation and to the fluid boundary conditions. The theory and technique of dynamic NMR microscopy are presented. A specially designed high gradient probe for Pulsed Gradient Spin Echo (PGSE) experiments is described.

First, the time evolution of electroosmotic flow in a capillary is measured. With increasing time after the application of an electrophoretic pulse a transition from plug flow to parabolic flow is found. The agreement of the measured flow profiles with theory is excellent.

Next, a two-dimensional velocity exchange experiment (VEXSY) is described. Experiments on unrestricted Brownian motion, laminar circular flow in a Couette cell and flow through microspheres are performed.

A major aspect of the thesis concerns molecular dynamics in semi-dilute polymer solutions close to a de-mixing transition. Therefore, a description of the Flory-Huggins model for the phase behaviour of polymer solutions is given along with a review of the literature on shear-induced effects in semi-dilute polymer solutions. PGSE experiments were performed in order to measure the temperature dependence of the self-diffusion coefficient of polystyrene in semi-dilute cyclohexane solutions near the de-mixing transition over a wide range of molar masses. The temperature dependence can be described by a Williams-Landel-Ferry (WLF) equation, characteristic of a glass transition. From the self-diffusion coefficients the values for the tube disengagement times were obtained.

NMR rheology experiments were performed on semi-dilute polystyrene/cyclohexane solutions near the de-mixing transition. The flow profiles exhibit power law behaviour, and from the power law index the entanglement formation times are extracted. A consistency of the values for the entanglement formation times and tube disengagement times was found.

As part of the study of polymer solutions at elevated temperatures, strong convectional effects were observed. In order to carry out diffusion measurements these effects were suppressed using better thermal equilibration. However, the
convection process itself was subject to NMR investigation. Convectional flow
in a capillary was measured using PGSE NMR, VEXSY and dynamic NMR mi-
croscopy. The VEXSY experiment shows that the flow is stationary. The velocity
propagator measured using dynamic NMR microscopy was used to calculate the
echo attenuation function $E(q)$. It was found that the pronounced minima and
maxima in the Stejskal–Tanner plots agree well with the measured $E(q)$ values.

Flow profiles of lyotropic liquid crystals are presented. Using deuterium NMR
spectroscopy it is shown that the shear–induced alignment of molecules can be
measured using NMR microscopy.
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