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Polymer Dynamics Studied by Dynamic Light Scattering

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Abstract

Theoretical treatments of dynamic properties of polymer solutions are reviewed. Particular emphasis is placed on the discussion of diffusion in polymer solutions. The relationship between the slow diffusion coefficient found by Dynamic Light Scattering (DLS) and the Self Diffusion Coefficient is shown.

An introduction to DLS theory is given. The experimental techniques involved in DLS measurements are discussed.

Concentration dependencies of the DLS observed slow diffusion coefficient in ternary polymer solutions of polystyrene-poly vinyl methyl ether-solvent have been measured. Solvents used were toluene, carbon tetrachloride and tetrachloroethylene and the polymer molar masses were 110 000 $gmol^{-1}$ for both polystyrene (PS) and poly vinyl methyl ether (PVME). Solvents were chosen to be very nearly isorefractive with PVME. Toluene is very nearly an equally good solvent for the polymer pair PS and PVME, while tetrachloroethylene is equally poor for both polymers. Carbon tetrachloride is an unequal quality solvent for this polymer pair. The results of these DLS measurements are reported.

Four sets of experiments are described. The first is the effect on the relationship between D_I (the slow mode diffusion coefficient found by DLS) and D_S (the self diffusion coefficient) of different mass fractions in the polymer solution. It is found the mass fraction, x, has little effect on the observed diffusion coefficient. Secondly the effect of the polymer-polymer interaction parameter, χ, on the relationship between D_I and D_S is investigated. It is found solutions formed with equal quality solvents have D_I nearly equal to D_S. But solutions formed with unequal quality solvents have D_I considerably less than D_S and that these solutions suffer phase separation at lower concentration. Thirdly the effect of polymer molar mass on the relationship between D_I and D_S is investigated. These are found to be in line with those expected from literature.

Fourthly the considerable discrepancy between D_I and D_S which is manifest in 110 000 $gmol^{-1}$ PS/ 110 000 $gmol^{-1}$ PVME/ toluene solutions at polymer volume fractions greater than 0.4 is investigated. The diffusion coefficient found, D_I, does not fit a unique concentration power law. Two unique regions are seen with concentration exponents of -11±4 and -14.9±0.7 for the low and high concentration regions respectively. This is found to agree with results found in literature.

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Chapter 1
Introduction

1.1 Polymers and Dynamic Light Scattering

Since the dawn of the laser, Laser Light Scattering has allowed the investigation of molecular size movements within solutions. Recently ternary polymer solutions containing two polymers and a single solvent have been investigated using Dynamic Light Scattering (DLS). The lack of suitable theory, and apparatus of sufficient quality has limited these investigations to diffusion coefficient dependence on molar mass and concentration. Generally these investigations have utilised special polymers and solvents in order to reduce the complexity of the results found.

Benmouna and Borsali et al [1] [2] [3] [4] have recently produced a theory of diffusion specifically for polymer solutions, which they have extended in ternary polymer solutions. This theory makes several predictions which are easily verifiable by experiment. Daivis [5] has briefly examined various aspects of this theory experimentally, however these results require confirmation and expansion, as well as experimental investigation into recent theoretical advances of this theory.

Daivis's work advanced understanding of diffusion in polymer solutions, however understanding was left incomplete in several areas. In his work Daivis compared diffusion in an equally good solvent for the polymer pair polystyrene (PS) and poly vinyl methyl ether (PVME) with that for the same polymer pair in an unequal quality solvent. The comparison of this diffusion data with data collected with the same polymer pair in an equally poor quality solvent would reveal much about polymer motion in solutions, yet this work was not attempted by Daivis. Daivis noted that the diffusion coefficient measured by DLS deviated from that obtained by Pulse Gradient Spin Echo Nuclear Magnetic Resonance Spectroscopy (PGSE NMR) at high polymer concentrations. This work was not pursued by Daivis. This work investigates aspects of

Daivis's work which have been left incomplete or require further investigation for resolution.

1.2 Thesis Organisation

Chapter 2 summarises existing theories of diffusion in polymer solutions, and DLS theory. This chapter also explains what polymers are and gives a basic understanding of the properties of polymers critical to understanding this thesis.

Chapter 3 summarises experimental procedures for both the DLS equipment and also for solution preparation. This chapter also summarises some of the theoretical background for the DLS equipment, and the sources of polymers and solvents utilised in this work.

Chapter 4 summarises investigations into four aspects of the work previously presented by Daivis et al [5] [6] [7] [8] [9]. The first is the effect on the relationship between D_I and D_S of different mass fractions in the polymer system 110 000 Dalton PS/ 110 000 Dalton PVME/ solvent (where three different solvents were utilised:- toluene, carbon tetrachloride and tetrachloroethylene). Secondly the effect of the polymer-polymer interaction parameter, χ, on the relationship between D_I and D_S is investigated. Thirdly the effect of polymer molar mass on the relationship between D_I and D_S is investigated. Fourthly the considerable discrepancy between D_I and D_S which is manifest in 110 000 Dalton PS/ 110 000 Dalton PVME/ toluene solutions at polymer volume fractions greater than 0.4. The results presented in this chapter are also discussed and compared to results found in literature.

Chapter 5 summarises the main conclusions which can be drawn from this study.