Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

# POLYMER DYNAMICS STUDIED BY NMR AND LIGHT SCATTERING METHODS

A thesis presented in partial fulfilment of the requirements

for the degree of Doctor of Philosophy in Physics

at Massey University

PETER JOHN DAIVIS

1989

Massey University Library. Thesis Copyright Form

Title of thesis: Polymer dynamics studied by NMR and light scattering methods.

(1) (a) I give permission for my thesis to be made available to readers in the Massey University Library under conditions determined by the Librarian.

~~(b)~~ I do not wish my thesis to be made available to readers without my written consent for ________ months.

(2) (a) I agree that my thesis, or a copy, may be sent to another institution under conditions determined by the Librarian.

~~(b)~~ I do not wish my thesis, or a copy, to be sent to another institution without my written consent for ________ months.

(3) (a) I agree that my thesis may be copied for Library use.

~~(b)~~ I do not wish my thesis to be copied for Library use for ________ months.

Signed Peter Davis

Date 26/9/89

The copyright of this thesis belongs to the author. Readers must sign their name in the space below to show that they recognise this. They are asked to add their permanent address.

NAME AND ADDRESS DATE

# DEDICATION

To my grandparents; Bob and Florence Turner, who lived in Narrandera, Jonas Burbulevicius, who lived in Vilnius and Stefanija Fugaru who lives in Adelaide.

# ABSTRACT

Theoretical treatments of static and dynamic properties of polymer solutions are reviewed. Particular emphasis is placed on the discussion of diffusion in polymer solutions. The relationship between the mutual diffusion coefficient defined in non-equilibrium thermodynamics and the diffusion coefficient measured in a dynamic light scattering experiment is discussed. The blob model is applied to the calculation of the concentration and solvent quality dependence of the polymer self diffusion coefficient.

An introduction to the theory of Pulsed Gradient Spin Echo (PGSE) NMR and Dynamic Light Scattering (DLS) is given. The possibility of directly measuring a nonlinear mean square displacement for a diffusing polymer molecule by Pulsed Gradient Spin Echo NMR is considered.

Experimental techniques involved in PGSE NMR and DLS measurements are discussed. The variance of the normalized echo attenuation is derived and related to the weighting of least squares fits to PGSE NMR data. A run rejection scheme is proposed for DLS experiments. This scheme can be used to discriminate against data which may be distorted by the scattering from a small number of strongly scattering particulate contaminants in the sample.

The concentration dependences of the polymer and solvent self diffusion coefficients in polystyrene-cyclohexane solutions have been measured. Cyclohexane is a theta solvent for polystyrene and the measurements were made at a temperature near the theta temperature. The polystyrene molar mass was 350,000 g mol$^{-1}$. The exponent found for the concentration dependence was in good agreement with the theoretical prediction of the reptation model combined with scaling theory. The contribution of local friction effects, which often become apparent near the glass transition, is estimated from the solvent diffusion measurements.

The preparation and characterization of poly(vinyl methyl ether) fractions is described. The fractionation was achieved by batch fractional precipitation from toluene solution with petroleum spirit. Gel permeation chromatography, dynamic light scattering and ultracentrifugation were used to characterize the fractions.

The results of dynamic light scattering measurements on ternary polymer solutions are reported. Three sets of experiments are described. The first set of experiments was performed on the PS-PVME-toluene system. The PS and PVME molar masses were 929,000 g mol$^{-1}$ and 102,000 g mol$^{-1}$. PVME and toluene are very nearly isorefractive and the polystyrene was present only at trace concentrations. It has often been assumed in the literature that the self diffusion coefficient of the "visible" polymer is obtained in such measurements, but the range of the validity of this assumption has not been fully defined. Agreement with results in the literature is found, and the diffusion coefficient measured in these experiments is identified as the self diffusion coefficient of the polystyrene. However, in the second set of experiments, it is shown that the self diffusion coefficient of the polystyrene is not obtained from similar measurements when the solvent, toluene, is replaced by carbon tetrachloride. The difference is attributed to thermodynamic factors.

The third set of experiments on ternary polymer solutions also investigated PS-PVME-toluene solutions. The polystyrene and PVME molar masses were 110,000 g $mol^{-1}$. The effect of an increasing the polystyrene concentration was investigated. Both PGSE NMR and DLS experiments were performed on these samples. A direct comparison of the diffusion coefficients given by these two techniques showed that the self diffusion coefficient of the polystyrene was obtained from the DLS experiments, even when the polystyrene comprised 25% of the total polymer concentration in the samples. Although a cooperative mode of decay was expected to appear in the correlation functions measured in DLS experiments, it was not observed. These experiments are discussed using theoretical results from the literature.

# ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the assistance provided by my supervisors. My chief supervisor, Dr D. N. Pinder, provided encouragement, insight and constructive criticism in the right proportions at the appropriate times. He was always available whenever I needed to discuss any aspect of the project. Prof. P. T. Callaghan gave me the opportunity to expand my toolkit of experimental techniques by offering a project involving PGSE NMR - an opportunity from which I feel that I have profited greatly. His sound advice and his willingness to provide assistance with various different aspects of the project is genuinely appreciated. Dr R. C. O'Driscoll also deserves thanks. Without his active involvement, the improvement of the dynamic light scattering apparatus to its present state would not have been possible.

The staff of the Departments of Physics and Biophysics and Chemistry and Biochemistry have been very helpful throughout the duration of my Ph D project. The close proximity and cooperation of the two departments has been a real advantage.

To all those who made or repaired equipment for me, those who freely loaned equipment, and those who instructed me in the use of various items of specialized apparatus, I offer my thanks. Dr Ken Jolley, Mr Dick Poll and Dr James Lewis deserve special mentions for their help with NMR, GPC and ultracentrifugation experiments.

It has been a pleasure to associate with the postdoctoral fellows and Ph D students I have met here at Massey during the past few years. Their good humour, friendship and cooperation have made my stay an enjoyable one. Some of them have become fearsome adversaries - they must be kept in check!

I am particularly thankful for the encouragement and support given to me by my housemates, present and past; John, Phil, Margaret, Beth and James and also my parents and sister, who, despite distance, have been with me all the way.

For her help with the typing of Chapter Two and her phone calls, letters and postcards which kept my spirits high during the completion of this work, my special thanks go to Jessica.

# TABLE OF CONTENTS

**Acknowledgements** ........ v

**Table of Contents** ........ vi

**List of Figures** ........ ix

**List of Tables** ........ xiii

**1 Introduction** ........ 1

1.1 Background ........ 1

1.2 Research Goals ........ 2

1.3 Thesis Organization ........ 4

**2 Theory** ........ 6

2.1 Static Properties of Polymers ........ 6
  2.1.1 Phase Diagram for a Binary Solution ........ 6
  2.1.2 Infinite Dilution ........ 8
  2.1.3 The Virial Regime ........ 10
  2.1.4 Semidilute Solutions ........ 10
  2.1.5 Polymer Melts ........ 13
  2.1.6 The Glass Transition ........ 14
  2.1.7 Ternary Solutions ........ 14

2.2 Dynamic Properties of Polymers ........ 17
  2.2.1 Diffusion Coefficients ........ 17
  2.2.2 Infinite Dilution ........ 20
  2.2.3 The Virial Regime ........ 21
  2.2.4 Semidilute and Entangled Solutions ........ 22
  2.2.5 Matrix Effects ........ 30
  2.2.6 Solvent Diffusion ........ 32

2.3 Pulsed Gradient Spin Echo NMR ........ 33
  2.3.1 Nuclear Magnetic Resonance ........ 33
  2.3.2 Spin Echoes ........ 37
  2.3.3 The Effect of Gradient Pulses ........ 38
  2.3.4 PGSE and Polymer Solutions ........ 43

2.4 Dynamic Light Scattering........................................................46
  2.4.1 The Dynamic Structure Factor........................................46
  2.4.2 Dynamic Regimes..................................................50
  2.4.3 Scattering from Ternary Solutions..................................52

3 Experimental..............................................................56

3.1 PGSE Experiments..........................................................56
  3.1.1 Apparatus.........................................................56
  3.1.2 Preparation of Samples for PGSE NMR...............................59
  3.1.3 Experimental Technique............................................60
  3.1.4 Data Analysis.....................................................60

3.2 DLS Experiments...........................................................61
  3.2.1 Apparatus.........................................................61
  3.2.2 Preparation of Samples for Light Scattering........................66
  3.2.3 Experimental Technique............................................68
  3.2.4 Data Analysis.....................................................71

4 Polymer and Solvent Self Diffusion in Polystyrene-Cyclohexane Solutions Near the Theta Temperature..................................77

4.1 Polymer Diffusion.........................................................77
  4.1.1 Experimental......................................................77
  4.1.2 Results...........................................................79
  4.1.3 Discussion........................................................82

4.2 Solvent Diffusion.........................................................94
  4.2.1 Experimental......................................................94
  4.2.2 Results...........................................................95
  4.2.3 Discussion........................................................96

5 Fractionation and Characterization of PVME.............................105

5.1 Preparation of PVME fractions...........................................105
  5.1.1 Raw Materials....................................................105
  5.1.2 Fractionation....................................................106

5.2 Characterization of PVME Fractions......................................109
  5.2.1 Gel Permeation Chromatography....................................109
  5.2.2 Dynamic Light Scattering.........................................112

5.2.3 Sedimentation Velocity ..... 120

6. Ternary Solutions ..... 124

6.1. DLS Experiments on PS-PVME-Toluene ..... 124
6.1.1. Experimental ..... 124
6.1.2. Results ..... 126
6.1.3. Discussion ..... 127

6.2. DLS Experiments on PS-PVME-Carbon Tetrachloride ..... 134
6.2.1. Experimental ..... 135
6.2.2. Results ..... 137
6.2.3. Discussion ..... 141

6.3. DLS and PGSE NMR Experiments on PS-PVME-Toluene ..... 144
6.3.1. Experimental ..... 144
6.3.2. Results ..... 159
6.3.3. Discussion ..... 160

7. Conclusion ..... 175
7.1. Conclusions ..... 175
7.2. Suggestions for Further Work ..... 178

Appendix 1 Equivalent Equations for the Mutual Diffusion Coefficient. 179

Appendix 2 Microscopic Expression for the Mutual Diffusion Coefficient ..... 180

Appendix 3 Application of the Blob Model to the Calculation of the Self Diffusion Coefficient ..... 184

Appendix 4 The Free Energy Density in Terms of Osmotic Pressure .... 195

Appendix 5 PGSE NMR in the Narrow Pulse Limit ..... 197

Appendix 6 The Variance of the Mean Count Rate in a Dynamic Light Scattering Experiment ..... 199

References ..... 201

# LIST OF FIGURES

Figure 2.1 Qualitative phase diagram for a polymer solution............................... 7

Figure 2.2 Temperature - concentration diagram according to Daoud and Jannink........ 8

Figure 2.3 Qualitative volume-temperature plot for various liquids ........................15

Figure 2.4 Production of a spin echo by a $\pi/2-\tau-\pi$ rf pulse sequence.....................37

Figure 2.5 The pulsed gradient spin echo NMR pulse sequence..........................40

Figure 2.6 Scattering geometry in a dynamic light scattering experiment..................46

Figure 2.7 Dynamic regimes for the coherent dynamic structure factor....................51

Figure 3.1 Pulsed gradient spin echo NMR apparatus......................................57

Figure 3.2 Dynamic light scattering apparatus ..............................................62

Figure 3.3 Apparatus for cleaning light scattering cells.....................................67

Figure 3.4 Apparatus for filtering light scattering samples .................................67

Figure 3.5 Flow diagrams for program DLS...........................................72, 73

Figure 4.1 Echo attenuation plot for polystyrene diffusion in $C_6D_{12}$ ......................79

Figure 4.2 Echo attenuation plot for polystyrene diffusion in $C_6D_{12}$ ......................80

Figure 4.3 Concentration dependence of PS self diffusion in $C_6D_{12}$ ......................81

Figure 4.4a Low concentration polymer self diffusion data plotted as $1/D_s$ vs C..........83

Figure 4.4b Low concentration polymer self diffusion data plotted as log $D_s$ vs C........83

Figure 4.5 Collected data for PS self diffusion in cyclohexane.............................86

Figure 4.6 The self diffusion coefficient of PS in $C_6D_6$, $CCl_4$ and $C_6D_{12}$................87

Figure 4.7 Polystyrene self diffusion in theta solvents....................................88

Figure 4.8 Collected polystyrene self diffusion data plotted as $D_s/D_0$ vs $C/C^*$ ...........90

Figure 4.9 Kim's self diffusion data plotted as $(D_S M^2 \eta_0/T)/(D_{S\theta} M_\theta^2 \eta_{0\theta}/T_\theta)$............93

Figure 4.10 Echo attenuation plot for a $C_6H_{12}$ diffusion measurement ....................96

Figure 4.11 Echo attenuation plot for a $C_6D_{12}$ diffusion measurement....................97

Figure 4.12 Concentration dependence of $C_6H_{12}$ self diffusion ............................98

Figure 4.13 Concentration dependence of $C_6D_{12}$ self diffusion............................99

Figure 4.14 Concentration dependence of solvent $D_s/D_0$.................................100

Figure 4.15 Polymer $D_s$ before and after correction for local friction effects.............102

Figure 4.16 Solvent self diffusion coefficient plotted as $D/D_0$ vs $\phi$.......................103

Figure 5.1 The structure of poly(vinyl methyl ether).......................................105

Figure 5.2 GPC chromatogram for a solution of mixed polystyrene standards.........110

Figure 5.3 GPC calibration plot for polystyrene standards in chloroform...............111

Figure 5.4 GPC chromatogram for unfractionated Polysciences PVME.................113

Figure 5.5 GPC chromatogram for a fraction of the Polysciences PVME...............113

Figure 5.6 Concentration dependence of D for G-PVME B2 in ethyl acetate ...........115

Figure 5.7 Concentration dependence of D for G-PVME C2 in ethyl acetate ...........116

Figure 5.8a $\langle\Gamma\rangle$ versus $q^2$ for G-PVME fraction C2........................................117

Figure 5.8b Correlation functions plotted against $q^2\tau$ for G-PVME fraction C2.........118

Figure 5.9 Concentration dependence of D for G-PVME E2 in ethyl acetate............119

Figure 5.10 Concentration dependence of D for G-PVME fractions in ethyl acetate.....120

Figure 5.11 Schlieren profiles for G-PVME E2 in ethyl acetate............................123

Figure 5.12 Plot of ln r against time for G-PVME E2 in ethyl acetate .....................123

Figure 5.13 Plot of $s^{-1}$ against concentration for G-PVME E2 in ethyl acetate ...........122

Figure 6.1 Typical correlation function for the PS-PVME-toluene system..............126

Figure 6.2 $D_{eff}$ versus $q^2$ obtained from second order cumulant fits to DLS data......129

Figure 6.3 Concentration dependence of $D_s$ for PS in PS-PVME-toluene..............132

Figure 6.4 DLS data obtained for the PS-PVME-$CCl_4$ system ........................... 138

Figure 6.5 $D_{eff}$ versus $q^2$ for the PS-PVME-$CCl_4$ system................................ 139

Figure 6.6 Concentration dependence of $D_I$ for the PS-PVME-$CCl_4$ system ........... 142

Figure 6.7 DLS data for sample E25-3 and sample E11-4................................ 150

Figure 6.8 Structures and high resolution spectra of PVME and polystyrene........... 152

Figure 6.9 Spectra recorded at low resolution with the PGSE probe..................... 153

Figure 6.10 Spectra from PGSE experiments on samples E6-3, E11-3 and E25-2...... 154

Figure 6.11 Echo attenuation plot for window β for sample E6-2......................... 154

Figure 6.12 Echo attenuation plot for window γ for sample D-1........................... 157

Figure 6.13 Echo attenuation plot for window γ for sample E11-6........................ 157

Figure 6.14 Concentration dependence of diffusion coefficients from DLS experiments on E6, E11 and E25 series samples................................................ 159

Figure 6.15 Concentration dependence of diffusion coefficients obtained from linear fits to PGSE echo attenuation plots for window β.................................. 161

Figure 6.16 Concentration dependence of diffusion coefficients obtained from PGSE echo attenuation plots for window γ................................................. 162

Figure 6.17 Amplitude of the cooperative mode versus x in the q = 0 limit.............. 163

Figure 6.18 Comparison of $D_s$ from DLS experiments with Martin's..................... 164

Figure 6.19 Comparison of diffusion coefficients from DLS with those from PGSE experiments on window β........................................................ 166

Figure 6.20 Comparison of diffusion coefficients from window β data with those from window γ data.................................................................. 171

Figure 6.21 Comparison of $D_s$ for PS in the PS-PVME-(toluene d8) system with PGSE measurements of $D_s$ in PS-(benzene d6) and PS-$CCl_4$ solutions............ 173

Figure 6.22 Comparison of $D_S$ for PVME in PS-PVME-toluene and PS-PVME-$CCl_4$ with $D_S$ for PS from DLS in PS-PVME-toluene and $D_S$ from PGSE experiments on PS-$CCl_4$ ........ 174

Figure A3.1 Expansion factor for the radius of gyration........ 188

Figure A3.2 Universal plot for the blob hydrodynamic radius........ 190

Figure A3.3 Effective exponent for the concentration dependence of $D_S$ from the blob model........ 193

Figure A3.4 Reduced self diffusion coefficient from the blob model........ 194

Figure A6.1 Sampling scheme for digital correlation........ 200

## LIST OF TABLES

Table 2.1 Conformation of long polymers in a bimodal melt................................16

Table 4.1 Properties of polystyrene - cyclohexane solutions................................77

Table 6.1 Results of linear fits to the q dependence of $D_{eff}$................................140

Table 6.2 Components of samples................................145

Table 6.3 Compositions of samples................................146