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Ternary Polymer Solutions Studied By Dynamic Light Scattering and Ultracentrifugation

**A thesis presented in partial fulfilment
of the requirements for the degree of**

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DEDICATION

To my mother, Veisia Ueleni; my sisters and brothers and to my Church,
"Siasi Tokaikolo 'Ia Kalaisi".

ABSTRACT

Dynamic light scattering has been used to measure the interpenetration diffusion coefficient of ternary polymer solutions formed with 233 000 dalton polystyrene and a trace amount of 330 000 dalton PMMA dissolved in thiophenol. These measurements have been compared with the diffusion coefficients obtained from ultracentrifuge studies of the same solutions by observing the change in shape of the sedimentation boundary curve with time.

This novel use of ultra centrifugation to measure diffusion coefficients in ternary polymer solutions is possible because; (i) the solvent is isorefractive and isopycnic with polystyrene, and (ii) the PMMA was the minority polymer in the solutions studied (concentration 0.001 g/g). Hence only the PMMA was visible and it sedimented through an effective solvent of thiophenol and polystyrene. All measurements were made at 25°C.

The diffusion coefficients obtained from the ultracentrifuge observations are in good agreement with the interpenetration diffusion coefficients obtained from dynamic light scattering studies on the same solutions. Solutions formed at polymer concentrations greater than 0.1 g/g suffered phase separation since PMMA and polystyrene are incompatible polymers. The solution with polymer concentration 0.0755 g/g was too unstable for ultra centrifugation studies, but was susceptible to investigation by dynamic light scattering. The interpenetration diffusion coefficient of this solution was found to be much smaller than those of the more dilute solutions.

The temperature dependence of the interpenetration diffusion coefficient was also investigated on the solution with the largest polymer concentration. The interpenetration diffusion coefficient was found to decrease as the temperature was lowered. This behaviour is consistent with the prediction that the interpenetration diffusion coefficient approaches zero as phase separation is approached. A value for correlation length critical exponent, n , of this ternary solution system was found. This is the first time that dynamic light scattering has been used (successfully) to obtain a value for n .

Dynamic light scattering and ultra centrifugation were also used to investigate the dynamical behaviour of ternary polymer solutions formed with 233 000 dalton polystyrene and a trace amount of 110 000 dalton poly(vinyl methyl ether) (PVME) dissolved in thiophenol. The preparation of this PVME fraction is described here. The fractionation was achieved by batch fractional precipitation from toluene solution with petroleum spirit.

All ultra centrifugation studies carried out on this system were unsuccessful because the solutions phase separated when subjected to strong centrifugal forces. The results of the light scattering measurements are reported and discussed.

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Chapter 1

Introduction

There is great interest in polymer mixtures since it is widely believed that important new polymer materials are likely to be developed from mixtures of known polymers rather than from entirely new ones. This interest in polymer mixtures has in turn stimulated interest in polymer ternary solutions, that is solutions formed from two dissimilar monodisperse random coil polymers dissolved in a low molar mass solvent. The dynamical behaviour of these ternary solutions must be thoroughly understood if stable composite polymer materials are to be developed.

The interaction between polymers is described by the Flory-Huggins interaction parameter χ , which is positive for dissimilar polymers that do not intermix in the melt (but which instead form two separate phases). However if such polymers are dissolved in a suitable low molar mass solvent then single phased solutions can be stable in certain composition, concentration and temperature regimes thus promoting polymer mixing and enabling the parameter χ to be determined. The theoretical development has assumed χ to be constant for any given pair of polymers and that the compatibility of the two polymers is governed solely by χ . However the theory is known to be incomplete for χ is introduced as a constant independent of polymer composition, solvent or temperature which is contrary to experiment [43, 44]. Indeed Saeki et al [41] and Robard et al [39] have separately shown that the compatibility of two polymers in a ternary solution depends on the solvent, even polymers with a negative χ value can form two phased solutions if the solvent has sufficiently dissimilar affinities for the two polymers, thereby implying that the effective polymer-polymer interaction parameter for two polymers is solvent dependent. Nevertheless χ has proved to be a valuable yardstick for describing the thermodynamic behaviour of polymers in combination. The polymer-solvent interactions are described by the single parameter v , the excluded volume parameter which describes the swelling of the random coils due to the finite volume of the polymer monomers.

A convenient measure of the dynamical behaviour of stable polymer ternary solutions can be obtained by considering their transport parameter coefficients. There are many diffusion coefficients which can be defined for a polymer ternary solution but only a few of which are amenable to measurement. These are the self diffusion coefficients of each of the polymers D_{S1} and D_{S2} , the self diffusion coefficient of the solvent, the

interpenetration diffusion coefficient D_I , and the cooperative diffusion coefficient D_C . It is important that these diffusion coefficients be clearly distinguished and that their properties and means of determination be appreciated.

In general there are three self diffusion coefficients in a ternary solution one for each constituent. These describe the motion of a labelled molecule in the solution in the absence of concentration gradients. The interpenetration diffusion coefficient describes the relative motion of the polymers when the total polymer concentration is constant but the relative polymer abundance varies. The cooperative diffusion coefficient describes the combined motion of both polymers under the influence of a total polymer concentration gradient, the relative abundance of the polymers being constant. Pulsed field gradient nuclear magnetic resonance (pfgnmr) can be used to measure the self diffusion coefficients of the constituents of a ternary solution providing two conditions are met. Each constituent must have a magnetic resonance which is sufficiently resolved in the frequency domain, and the concentration of the constituent must be sufficiently high for the collection of adequate data. Dynamic light scattering (dls) can be used to measure the interpenetration and cooperative diffusion coefficients to very small polymer concentrations, in addition dls observations on binary polymer solutions can be used to measure the mutual diffusion coefficient of the solution. The pfgnmr technique is far less sensitive than the dls technique so substantially larger concentrations are required, this usually means that the self diffusion coefficient of the minority polymer cannot be measured at small values of the relative abundance parameter. Nevertheless pfgnmr has provided valuable data for the experimental investigations of ternary polymer solutions because this technique always measures the self diffusion coefficient which is a precisely defined readily identifiable quantity.

Nemoto et al [30] have shown that under special circumstances ultracentrifugation can be used to measure the sedimentation coefficient of one of the polymers in a ternary polymer solution. The majority polymer and the solvent must be isorefractive and also isopycnic so that the sedimentation coefficient of the minority polymer can be obtained. The sedimentation coefficient, s , is a measure of the velocity of the sedimenting polymer molecules with respect to the high centrifugal forces involved in this technique. This technique can also be used to obtain a diffusion coefficient for ternary solutions which meets the special condition described above. A ternary system previously studied by Nemoto et al [30] was PMMA dissolved with polystyrene in thiophenol. This system was chosen because the majority polymer (polystyrene) and thiophenol were not only isorefractive but also isopycnic thus constituting an "effective solvent" through which PMMA sedimented and diffused. The system chosen for the study reported here approximated a system studied by Nemoto et al [30]. Dynamic light

scattering was used to measure the interpenetration diffusion coefficient, D_I , and ultra centrifugation was used to measure the sedimentation coefficient, s , and also a diffusion coefficient of the polymers.

This work has three principle aims:

1. To investigate the proposition that the diffusion coefficient obtained from ultracentrifugation studies of such a solution is the interpenetration diffusion coefficient obtained from dynamic light scattering studies.
2. To investigate the temperature dependence of D_I for the most concentrated sample of the ternary solution. Phase separation occurs as the temperature is lowered to the critical temperature and D_I is expected to diverge since D_I is inversely proportional to the correlation length which increases without limit as phase separation is approached.
3. To investigate the dynamical behaviour of a ternary system of PVME dissolved with polystyrene in thiophenol.