



PHYSICOCHEMICAL STUDY OF
POLY (ISOPRENE:STYRENE) BLOCK COPOLYMERS

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Thesis presented for the degree of Doctor
of Philosophy in the Department of Physical
and Inorganic Chemistry University of Adelaide

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SUMMARY

PHYSICO CHEMICAL STUDY OF POLY(ISOPRENE:STYRENE) BLOCK COPOLYMERS

Anionic polymerization using the 'living' polymer method founded by Szwarc was employed to synthesize a series of A-B block copolymers of polyisoprene and polystyrene. By meticulous care in purging all glassware, solvents, monomers and initiator a technique of synthesis was achieved which enabled 'tailoring' of these copolymers to the required specifications. Polymerization was carried out in benzene, initiated by n-butyllithium. A series of ten block copolymers were prepared: five of them having a constant molecular weight of 100,000 and a composition range of 11-78% by weight of polystyrene, three others with a molecular weight of 250,000 and a composition range of 11-50% by weight of polystyrene and two others of molecular weight 500,000 and composition of 25% and 50% by weight of polystyrene.

The microstructure of the polyisoprene sequence was investigated by using nuclear magnetic resonance spectroscopy (NMR). Unfortunately the aliphatic protons of the polystyrene sequence absorbed in the same region as the polyisoprene. This made the estimation of the microstructure for the high polystyrene blocks difficult. However, it was found that an arbitrary correction could be applied to allow for this background signal. The microstructure of the polyisoprene sequence was virtually the same for all the blocks and

corresponded to the microstructure of the polyisoprene homopolymers. The composition of the block copolymers was determined by using ultra-violet spectroscopy.

Gel permeation chromatography (GPC) proved the absence of any homopolymer in the blocks and enabled the calculation of a complete molecular weight distribution curve from which the values of \bar{M}_w , \bar{M}_n and \bar{M}_w/\bar{M}_n could be obtained. These values were compared with those obtained from the classical light scattering and osmometric methods. Also, a GPC 'universal' calibration curve was constructed for the copolymers based on the hydrodynamic volume as the universal size-parameter.

Configurational and thermodynamic parameters were determined from viscosity, light scattering and osmometry data. These parameters were studied as a function of the nature of the solvent, the molecular weight and the composition of the block copolymers. Three intrinsically different solvents were employed. Toluene - a good solvent for both parent homopolymers, cyclohexane - a good solvent for polyisoprene but poor for polystyrene; and methyl isobutyl ketone - a poor solvent for both parent homopolymers. Measurements under theta conditions were also made. The results in solvents equally good or equally poor for both parent homopolymers suggested that the distribution of segments is similar to that of normal homopolymers. This means that in non-preferential solvents the copolymer chain can be considered as a random

distribution of segments. For this reason solution theories developed for homopolymers and based on this type of distribution, are also applicable to the copolymer systems. In preferential solvents, such as cyclohexane, a different behaviour was indicated. The results could be best explained by assuming that some degree of intramolecular phase separation was occurring.

Intrinsic viscosity against temperature plots for the block copolymers in cyclohexane, methyl cyclohexane and decalin confirmed the general behaviour of the copolymers in preferential solvents. The results were explained by assuming that a phenomenon of intramolecular phase transition was occurring at a characteristic temperature T_p .

The results of the hydrodynamic studies provided support for the validity of two-parameter semi-empirical theories, developed originally for flexible homopolymers. Such theories were applicable even in preferential solvents provided the operational temperature was above the transition temperature T_p .

The morphology of solvent cast films of the copolymers was studied by measuring the glass transition temperature using a differential scanning calorimeter (DSC). In all cases multiple glass transitions were observed. Depending on the casting conditions, the multiple transitions were assigned either to the pure homopolymer phase, or to a mixed phase.

The mixed phase transition was found to be a function of composition. The results suggested domain formation in the bulk copolymer.

This thesis contains no material previously submitted for a degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously written by another person, except when due reference is made in the text.

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ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. J.R. Urwin for his advice and encouragement shown throughout the course of this work. I would also like to express my gratitude to the personnel of the Glass Blowing, Mechanical and Electronic Workshops, and to the other ancillary staff, especially Mrs. J. Walsh, who have assisted me from time to time.

I am indebted to the Commonwealth Postgraduate Research Studies Board for the Award of a Commonwealth Postgraduate Scholarship.