

DETERMINATION OF THE TRIAD SEQUENCE DISTRIBUTION AND THE *cis/trans* LINKAGE CONFIGURATIONS AT THE CYCLIC ANHYDRIDE UNITS IN THE ALTERNATING COPOLYMERS OF MALEIC ANHYDRIDE AND CITRACONIC ANHYDRIDE WITH STYRENE AND OTHER DONOR MONOMERS

A Thesis submitted for the degree of Master of Science of the University of New England

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I certify that the substance of this thesis has not already been submittied for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis, and all sources used, have been acknownledged in this thesis.



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Abstract

Copolymers of maleic anhydride (MA or 0) with styrene (ST or 1) and copolymers of citraconic anhydride (CA or 0) with ST(1) were prepared with a radical initiator at 50°C in CCl₄ (the dielectric constant $\varepsilon = 2.24$) and in highly polar N,Ndimethylformamide (DMF, $\varepsilon = 36.7$). ¹³C NMR spectroscopy was used to determine the ST(1) centred triad mole fractions (F_{010} , $F_{(011+110)}$ and F_{111}) and the mole fraction of the *cis/trans* linkage configuration at the cyclic anhydride units (F_{cis} and F_{trans}).

Non-linear least squares (NLLS) minimisation techniques was applied for the examination of the applicability of various copolymerisation models; the terminal model, the penultimate unit effect model, the complex participation model, the complex dissociation model and the so-called "*comppen*" model. The triad distribution data and the overall copolymer composition were used for the NLLS examination of the copolymerisation models, in combination with the test functions **a** and **b**. For both MA-ST copolymers and CA-ST copolymers, the copolymerisation models which incorporated a participation of the complex were most consistent with the data; for the MA-ST copolymers, the complex participation model, while for the CA-ST copolymers the *comppen* model showed the best fit.

It was found that a large and significant proportion of the linkage configurations at the cyclic monomer units was in the *cis* linkage; in MA-ST copolymers $F_{cis}=0.57$ and in CA-ST copolymers $F_{cis}=0.58$, in both CCl₄ and DMF. This evidence is significant because only a mechanism which includes a complex participation can provide an explanation. It was also concluded that the same copolymerisation mechanism operated in CCl₄ and in DMF.

The proportion of the *cis* linkage configuration was determined for other related alternating and semi-alternating copolymers. It was found that a large proportion of the linkages were in the *cis* configuration supporting the results in the MA-ST and CA-ST copolymers: for a MA-stilbene copolymer, F_{cis} = 0.56±0.02, for a MA- α -methylstyrene

copolymer, F_{cis} = 0.465, for a MA-allylbenzene copolymer, F_{cis} = 0.74±0.02, for a bromomaleic anhydride-ST copolymer, F_{cis} = 0.55±0.02, for a dichloromaleic anhydride-ST copolymer, F_{cis} = 0.59±0.02, for a maleimide-ST copolymer, F_{cis} = 0.30±0.02 for a MA-(2-chloroethyl vinyl ether) copolymer, F_{cis} = 0.44±0.02, and for MA-(n-butyl vinyl ether) copolymer, F_{cis} = 0.46±0.02.

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