# 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

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*I certify that the subsıance 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 $CCl_4$ (the dielectric constant $\varepsilon$ =2.24) and in highly polar N,N-dimethylformamide (DMF, $\varepsilon$=36.7). $^{13}C$ 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 $CCl_4$ 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 $CCl_4$ 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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