Chapter 4. Results and Discussion

4.1. Copolymerisation of maleic anhydride with styrene in carbon tetrachloride and in N,N-dimethylformamide and in solvents of different polarities.

The equilibrium constant of the electron donor acceptor (EDA) complexation (*K*) of ST and MA in CCl_4 was determined by UV spectroscopy using Ketelaar equation [69] to be K=0.208±0.015 l/mol at room temperature. The Ketelaar plots are shown in Fig.4.1.1 . In DMF all the attempts to obtain a reliable *K*-value failed because the amount of the complex was too small and probably because DMF solvated MA very strongly.

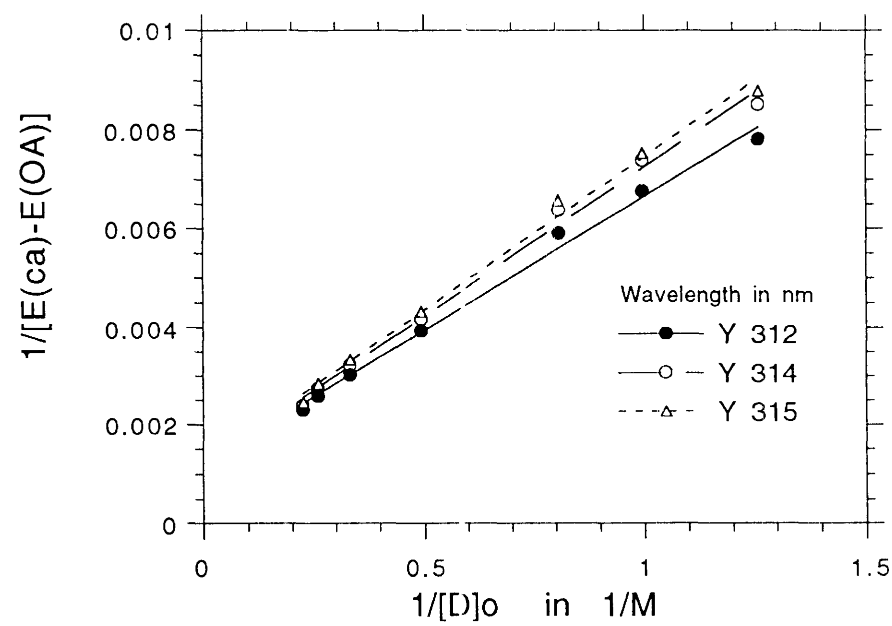


Fig.4.1.1 Determination of the equilibrium constant (*K*) of MA-ST complexation in CCl_4 at room temperature by UV spectroscopy using the Ketelaar equation. E(ca) and E(OA) are the molar extinction coefficients of complex and acceptor and of acceptor alone, respectively.

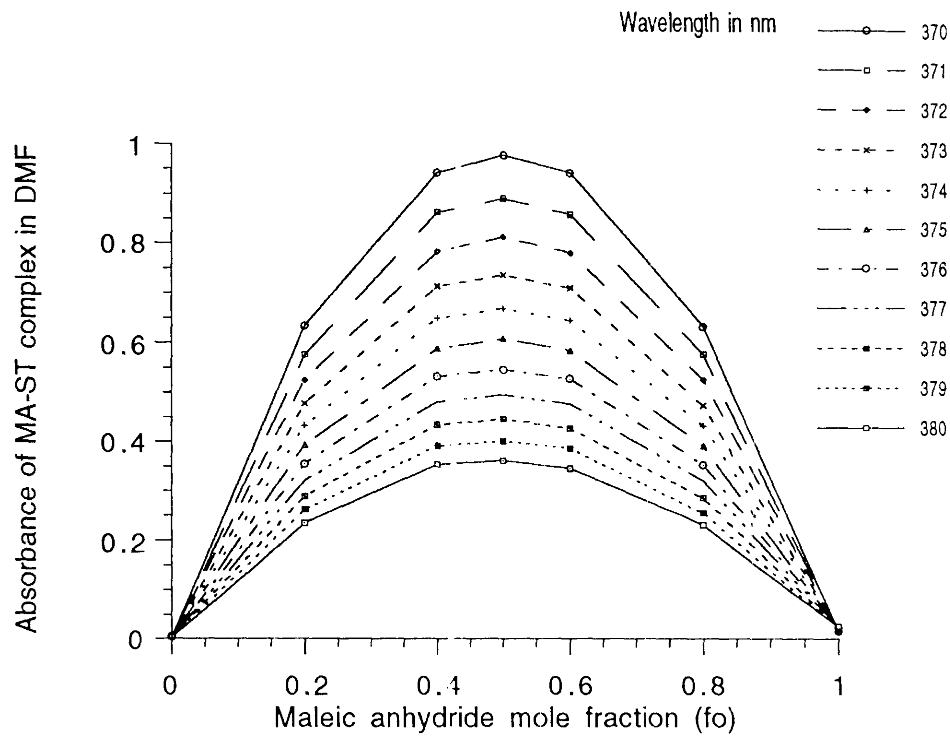


Fig.4.1.2 The UV absorbance of MA-ST complex in DMF vs. MA mole fraction in MA+ST/DMF solutions. [MA+ST]=2.000M.

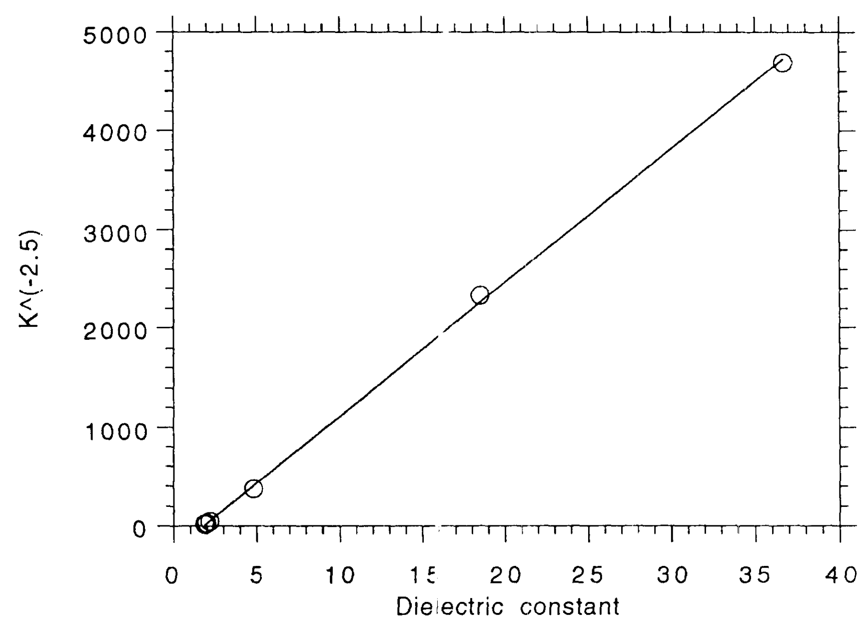


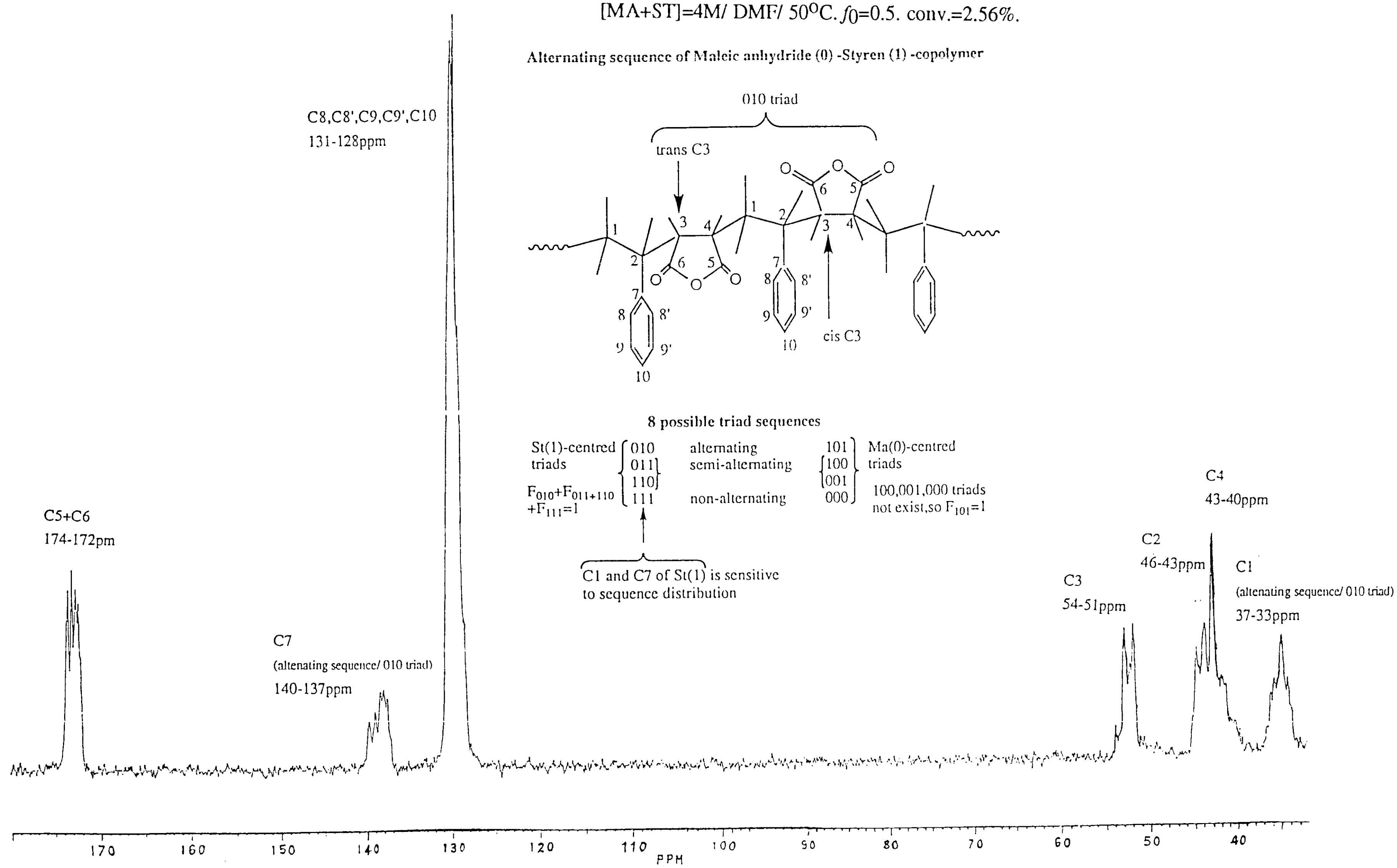
Fig.4.1.3 The empirical estimation of the equilibrium constant (K) of the MA-ST complexation in DMF based only on the dielectric constant (ε).

The continuous variation plots of the UV absorbance of MA-ST complex in DMF solutions shows a maximum when the mole ratio of MA: ST is equal to 1:1 (Fig.4.1.2). This indicates a 1:1 EDA complexation between MA and ST in DMF. In order to estimate the magnitude of the K-value in DMF a purely empirical correlation between the reported values of the equilibrium constants of the complexation and the dielectric constant (ε) of the solvents is plotted in Fig.4.1.3. The K of the complexation between ST and MA in DMF is thus estimated to be K=0.035$\pm$0.015 l/mol according to this empirical extrapolation.

Three values of thus estimated K for the complexation of MA-ST in DMF, namely 0.015, 0.025 and 0.035 l/mol, were used to run the non linear least squares (NLLS) curve fitting of the equations which were based on the copolymerisation models : the complex participation- , the complex dissociation- and the comppen model to the experimental data. The sum of squares (SS) and the standard error (S_y) consistently gave the smallest values for K= 0.035 l/mol (Tab.4.1.3).

The copolymers of ST and MA were prepared in a wide range of MA mole fractions in feed (f_0) from 0.01 to 0.60 in CCl_4 and from 0.01 to 0.90 when prepared in DMF, at 50°C. Fig.4.1.4 shows a typical ^{13}C NMR spectrum of an alternating MA-ST copolymer. The peak assignments were taken according to Butler et al.[31] . The DEPT ^{13}C NMR subspectra of methylene C1 carbons were used for determining the ST(1) centred triad mole fractions (F_{010}, $F_{(011+110)}$, F_{111})[15] . Because MA does not homopropagate[1] , the sequence of MA-MA (or 00) is considered to be absent in the copolymers. Those of the methine C3 carbons were used for determination of the mole fraction of the *cis* linkage configuration at the cyclic MA units (F_{cis}) in the MA-ST copolymers. Fig.4.1.5 and Fig.4.1.6 show the variation with respect to the monomer composition in feed of the methylene C1 and the methine C3 carbons in the MA-ST copolymers prepared in CCl_4 , and in DMF, respectively. *Linesim*[68] peak simulation

Fig.4.1.4 Typical ^{13}C NMR spectrum of MA(0) - ST(1) copolymer.
[MA+ST]=4M/ DMF/ 50°C. f_0=0.5. conv.=2.56%.



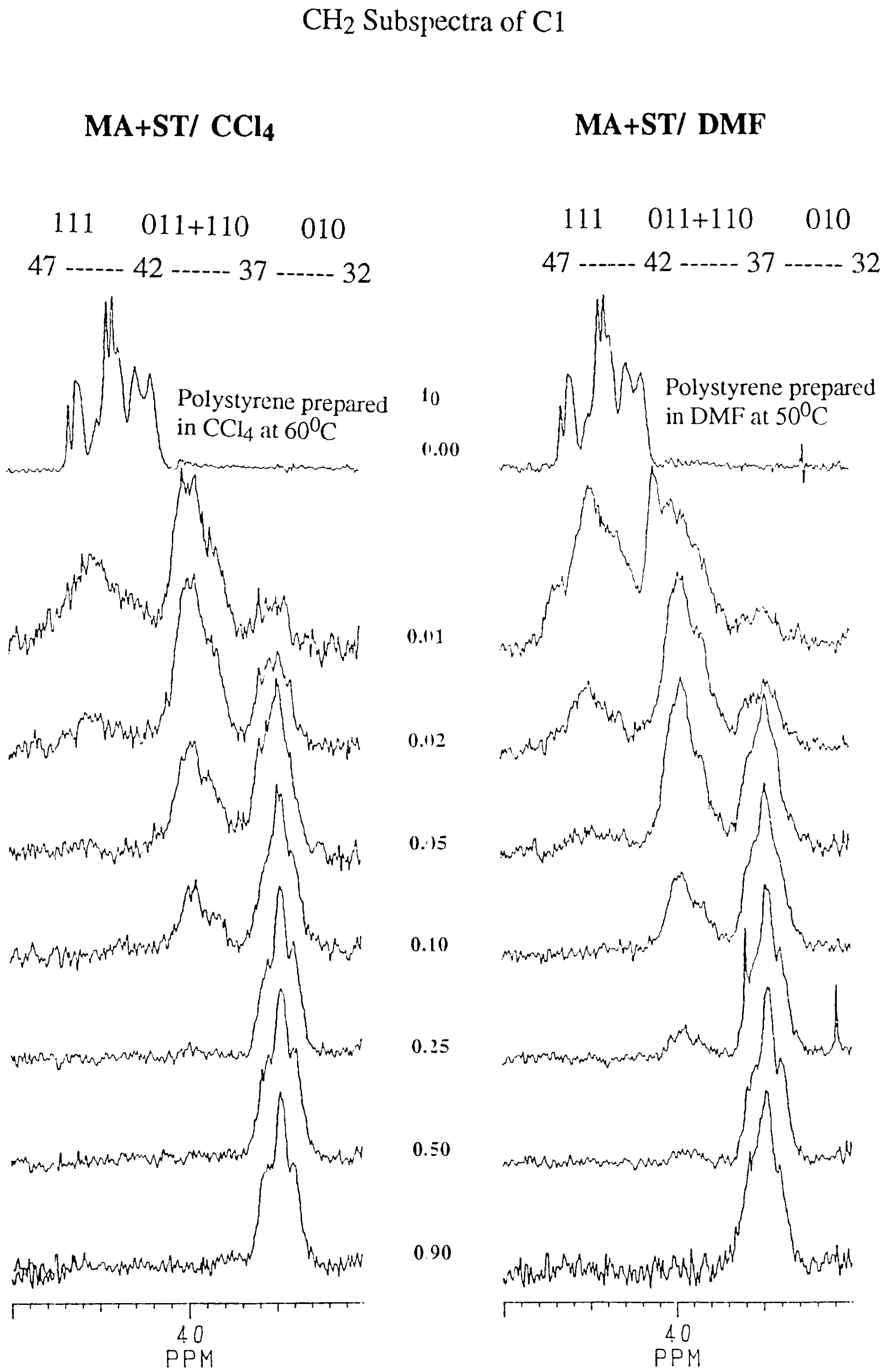


Fig.4.1.5 Selected DEPT ^{13}C NMR subspectra of methylene(CH_2) C1 of the MA(0)- ST(1) copolymers prepared in CCl_4 and in DMF.

CH Subspectra of C3

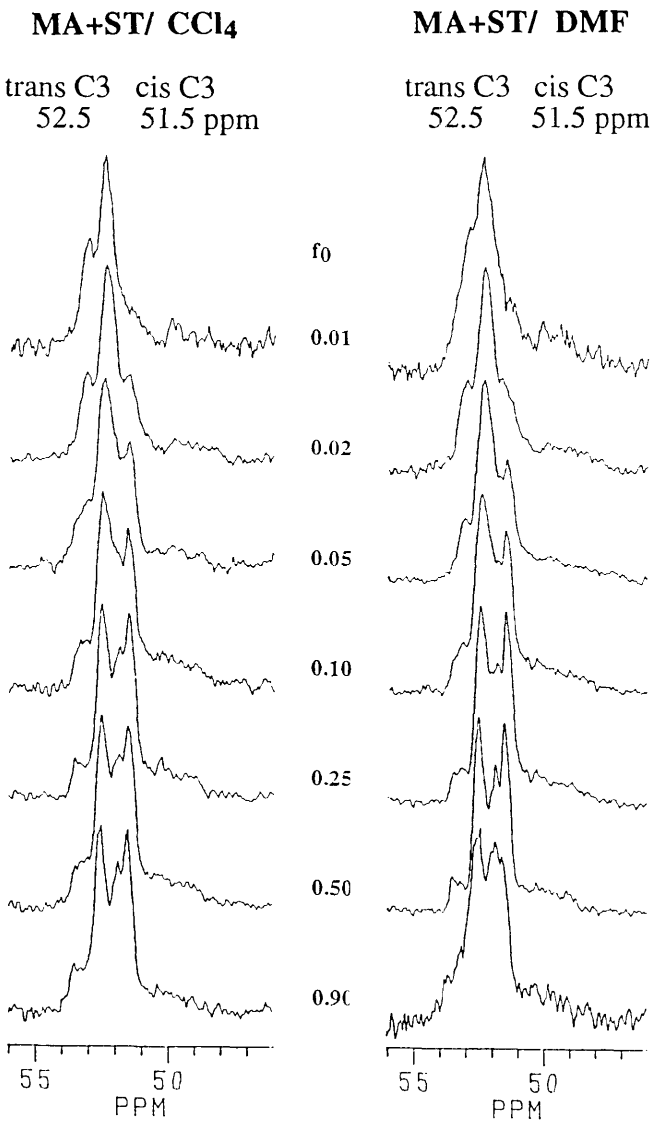


Fig.4.1.6 Selected DEPT ^{13}C NMR subspectra of methine(CH) C3 of the MA- ST copolymers prepared in CCl_4 and in DMF.

program was used to analyse the peak areas. The overall MA mole fraction in copolymer (F_0) was calculated from the triad mole fractions [15] according to the following equation:

$$\frac{F_1}{F_0} = 1 + \frac{2F_{111} + F_{(011+110)}}{2F_{010} + F_{(011+110)}} \quad \text{, where } F_0 + F_1 = 1$$

The triad sequence distribution data, the copolymer composition data and the mole fraction of the cis linkage configuration at the cyclic MA units in the MA-ST copolymers prepared in CCl_4 and in DMF are collected in Tab.4.1.1.

Tab.4.1.1 The experimental triad and composition data and the mole fraction of the *cis* linkage configurations at the cyclic MA units (F_{cis}) in MA-ST copolymers prepared in CCl_4 and in DMF. The triad mole fractions and the mole fraction of the *cis* linkages were determined from DEPT ^{13}C NMR CH_2-subspectra of C1 and CH- subspectra of C3, respectively.

f_0	Copolymer of MA+ST prepared in CCl_4					Copolymer of MA+ST prepared in DMF				
	F_{010}	$F_{(011+110)}$	F_{111}	F_0	F_{cis}	F_{010}	$F_{(011+110)}$	F_{111}	F_0	F_{cis}
0.01	0.099	0.512	0.390	0.262	0.230	0.074	0.460	0.467	0.233	0.252
0.02	0.274	0.582	0.144	0.361	0.311	0.189	0.592	0.219	0.327	0.329
0.05	0.527	0.453	0.018	0.430	0.309	0.416	0.529	0.054	0.405	0.364
0.10	0.681	0.298	0.020	0.454	0.428	0.663	0.331	0.006	0.453	0.432
0.15	0.803	0.195	0.002	0.474	0.465	0.781	0.291	0.000	0.471	0.502
0.20	0.836	0.131	0.034	0.474	0.525	0.844	0.157	0.000	0.480	0.481
0.25	0.986	0.015	0.000	0.498	0.612	0.870	0.130	0.000	0.483	0.548
0.30	1.000	0.000	0.000	0.500	0.622	0.902	0.098	0.000	0.487	0.589
0.35						0.968	0.032	0.000	0.496	0.640
0.40	0.98	0.020	0.000	0.498	0.592	0.958	0.042	0.000	0.495	0.612
0.50	1.000	0.000	0.000	0.500	0.587	0.965	0.035	0.000	0.496	0.586
0.60	1.000	0.000	0.000	0.500	0.595	1.000	0.000	0.000	0.500	0.594
0.70						1.000	0.000	0.000	0.500	0.536
0.80						1.000	0.000	0.000	0.500	0.583
0.90						1.000	0.000	0.000	0.500	0.527

f_0 = MA(0) mole fraction in feed

F_0 = MA(0) mole fraction in MA(0)-ST(1) copolymers. The uncertainties (Δ)were estimated to be ±0.015

F_{010}, $F_{(011+110)}$, F_{111} = ST(1) centred triad mole fraction in MA(0)-ST(1) copolymer. $\Delta(F_{triad})$= ±0.03.

F_{cis} = mole fraction of the *cis* linkage congigurations at the cyclic MA units in copolymers. $\Delta(F_{cis})$= ±0.06.

[MA+ST]=4.000M. [AIBN]=0.0305M. copolymerised at 50°C.

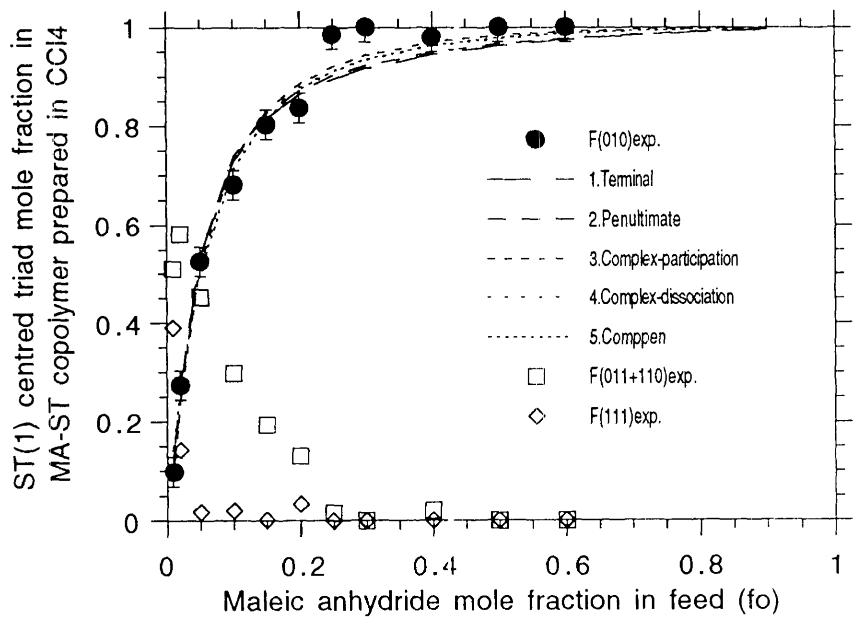


Fig.4.1.7 NLLS curve fitting of F_{010} experimental data to 5 models. (MA+ST/CCl_4)

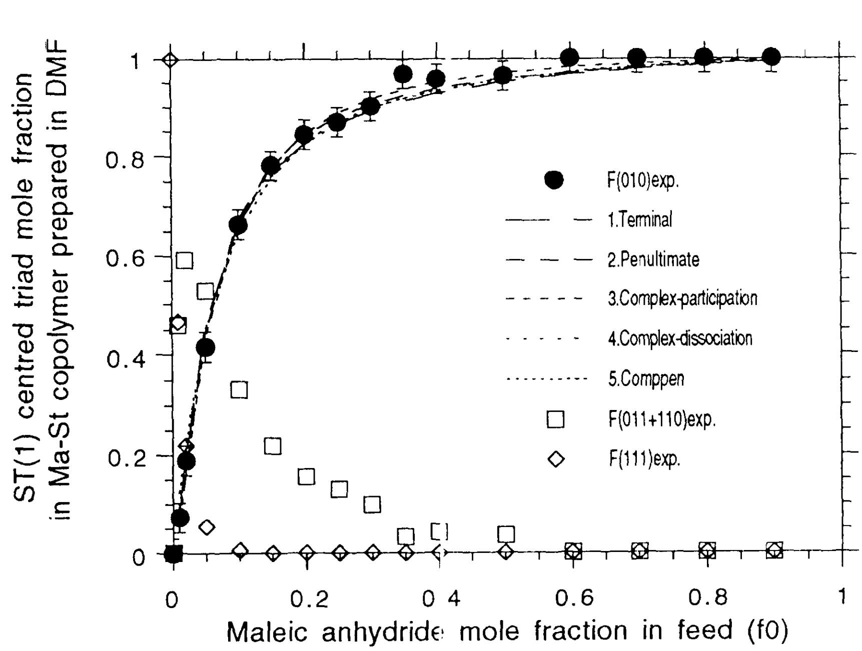


Fig.4.1.8 NLLS curve fitting of F_{010} experimental data to 5 models. (MA+ST/DMF)

The non linear least squares (NLLS) curve fitting of the theoretical equations based on each copolymerisation model to the experimental data was run for the following five models; the terminal model , the penultimate unit effect model , the complex participation model, the complex dissociation model and the comppen model. The alternating triad fraction equations in Scheme 2 (Chapter 2) were used to obtain the experimental alternating triad data (F_{010}). Fig.4.1.7 and Fig.4.1.8 present the experimental ST(1) centred triad mole fractions and the best fit calculated alternating triad mole fraction (F_{010}) for the five above mentioned copolymerisation models for the copolymers of MA and ST prepared in CCl_4 and in DMF, respectively. Tab.4.1.2 lists the SS and S_y values from the NLLS curve fitting process for the triad mole fraction data for copolymerisation in CCl_4 and in DMF. The smallest SS and S_y values among the five models for F_{010} data set would indicate the model which best fits to the experimental data. It can be seen from Tab.4.1.2 that the complex participation model is the marginally better model for the copolymerisation of ST with MA in both CCl_4 and DMF. The SS and S_y values indicate no apparent advantage for the comppen model over the penultimate unit effect or the complex participation model.

Tab.4.1.2 The sum of squares (SS) and the standard error (S_y) values of the NLLS curve fitting of the 1.Terminal-, 2.Penultimate-, 3.Complex- Participation-, 4. Complex-Dissociation- and 5. Comppen- model to the experimental triad mole fraction data. MA-ST copolymers prepared in CCl_4 and in DMF. The triad mole fractions were determined from DEPT ^{13}C NMR CH_2-subspectra of C1. K_{CCl4}= 0.208 (l/mol). K_{DMF}= 0.035 (l/mol)-estimated.

Model	Solvent used	SS F_{010}	SS $F_{(011+110)}$	SS F_{111}	S_y F_{010}	S_y $F_{(011+110)}$	S_y F_{111}
1.	CCl_4	$\underline{2.23\text{x}10^{-2}}$	$3.47\text{x}10^{-2}$	$4.31\text{x}10^{-3}$	$\underline{4.16\text{x}10^{-2}}$	$5.17\text{x}10^{-2}$	$1.82\text{x}10^{-2}$
	DMF	$\underline{8.54\text{x}10^{-3}}$	$2.68\text{x}10^{-2}$	$1.20\text{x}10^{-3}$	$\underline{2.46\text{x}10^{-2}}$	$4.38\text{x}10^{-2}$	$1.25\text{x}10^{-2}$
2.	CCl_4	$\underline{2.16\text{x}10^{-2}}$	$2.46\text{x}10^{-2}$	$1.33\text{x}10^{-3}$	$\underline{4.24\text{x}10^{-2}}$	$4.52\text{x}10^{-2}$	$1.05\text{x}10^{-2}$
	DMF	$\underline{5.52\text{x}10^{-3}}$	$1.37\text{x}10^{-2}$	$9.93\text{x}10^{-5}$	$\underline{2.06\text{x}10^{-2}}$	$3.24\text{x}10^{-2}$	$2.76\text{x}10^{-3}$
3.	CCl_4	$\underline{1.50\text{x}10^{-2}}$	$2.86\text{x}10^{-2}$	$1.33\text{x}10^{-3}$	$\underline{3.87\text{x}10^{-2}}$	$5.35\text{x}10^{-2}$	$1.15\text{x}10^{-2}$
	DMF	$\underline{2.65\text{x}10^{-3}}$	$2.58\text{x}10^{-2}$	$1.04\text{x}10^{-4}$	$\underline{1.55\text{x}10^{-2}}$	$4.84\text{x}10^{-2}$	$3.38\text{x}10^{-2}$
4.	CCl_4	$\underline{1.64\text{x}10^{-2}}$	$2.88\text{x}10^{-2}$	$4.03\text{x}10^{-3}$	$\underline{4.05\text{x}10^{-2}}$	$5.37\text{x}10^{-2}$	$2.01\text{x}10^{-2}$
	DMF	$\underline{6.37\text{x}10^{-3}}$	$2.58\text{x}10^{-2}$	$2.08\text{x}10^{-3}$	$\underline{2.41\text{x}10^{-2}}$	$4.84\text{x}10^{-2}$	$1.37\text{x}10^{-2}$
5.	CCl_4	$\underline{1.62\text{x}10^{-2}}$	$1.86\text{x}10^{-2}$	$3.37\text{x}10^{-3}$	$\underline{4.81\text{x}10^{-2}}$	$5.16\text{x}10^{-2}$	$2.19\text{x}10^{-2}$
	DMF	$\underline{1.02\text{x}10^{-2}}$	$2.44\text{x}10^{-2}$	$5.83\text{x}10^{-2}$	$\underline{3.57\text{x}10^{-2}}$	$5.52\text{x}10^{-2}$	$8.54\text{x}10^{-2}$

Tab.4.1.3 The sum of squares (SS) values of the NLLS curve fitting of the 3.Complex- Participation-, 4. Complex-Dissociation- and 5.Comppen- model to the experimental triad mole fraction data. MA-ST copolymers prepared in DMF. The triad mole fractions were determined from DEPT ^{13}C NMR CH_2-subspectra of C1. K=0.015, 0.025, 0.035 (l/mol)- estimated alternative values.

Model	K	F_0	F_{010}	$F_{(011+110)}$	F_{111}
3	0.015	1.35×10^{-4}	2.72×10^{-3}	2.32×10^{-2}	1.08×10^{-4}
	0.025	1.35×10^{-4}	2.68×10^{-3}	2.24×10^{-2}	1.05×10^{-4}
	0.035	1.33×10^{-4}	2.65×10^{-3}	2.58×10^{-2}	1.04×10^{-4}
4	0.015	1.44×10^{-4}	7.45×10^{-3}	2.63×10^{-2}	2.14×10^{-3}
	0.025	1.40×10^{-4}	6.88×10^{-3}	2.60×10^{-2}	2.11×10^{-3}
	0.035	1.35×10^{-4}	6.37×10^{-3}	2.58×10^{-2}	2.08×10^{-3}
5	0.015	7.90×10^{-3}	1.15×10^{-2}	2.55×10^{-2}	5.89×10^{-2}
	0.025	1.00×10^{-2}	1.09×10^{-2}	2.49×10^{-2}	5.85×10^{-2}
	0.035	9.93×10^{-3}	1.02×10^{-2}	2.44×10^{-2}	5.83×10^{-2}

The reactivity ratios calculated from the overall copolymer composition (F_0) data for the five models are summarised in Tab.4.1.4 and Tab.4.1.5 for the MA-ST copolymerisations in CCl_4 and in DMF, respectively.

Tab.4.1.4 The reactivity ratios of MA-ST copolymerisation in CCl_4, calculated from composition data (F_0) for 5 models. The triad mole fractions were determined from DEPT ^{13}C NMR CH_2-subspectra of C1. K=0.208(l/mol).

				SS
1.Terminal Model	$\underline{r_0=0}$	$r_1=0.0174$		6.15×10^{-4}
2.Penultimate Model	$\underline{r_{00}=r_{10}=0}$	$r_{11}=0.0183$	$r_{01}=0.0165$	6.07×10^{-4}
3.Complex Participation	$\underline{K=0.208}$			
Model	$\underline{r_0=q_0=0}$ $s_0=10.6$	$r_1=0.0106$ $q_1=0.155$	$s_1=0.208$	5.73×10^{-4}
4.Complex Dissociation	$\underline{K=0.208}$			
Model	$\underline{r_0=q_0=0}$ $s_0=0$	$r_1=0.0100$ $q_1=0.0129$	$s_1=0.0486$	6.00×10^{-4}
5.Comppen Model	$\underline{K=0.208}$			
	$\underline{r_{00}=r_{10}=0}$	$r_{11}=0.0158$	$r_{01}=0.0300$	5.67×10^{-3}
	$\underline{q_{00}=q_{10}=0}$	$q_{11}=0$	$q_{01}=0$	
	$\underline{s_{00}=0}$ $s_{10}=25.9$	$s_{11}=2.12$	$s_{01}=0$	

(The underlined values are the fix values, the K was determined independently and the reactivity ratios involved homopropagation of MA were assigned zero due to non-homo-polymerization of MA)

Tab.4.1.5. The reactivity ratios of MA-ST copolymerisation in DMF, calculated from composition data (F_0) for 5 models. The triad mole fractions were determined from DEPT ^{13}C NMR CH_2-subspectra of C1. K=0.035(l/mol).

					SS
1.Terminal Model	$\underline{r_0=0}$		r_1=0.0227		1.54×10^{-4}
2.Penultimate Model	$\underline{r_{00}=r_{10}=0}$		r_{11}=0.0229	r_{01}=0.0225	1.53×10^{-4}
3.Complex Participation	$\underline{K = 0.035}$				
Model	$\underline{r_0=q_0=0}$	s_0=4.3327	r_1=0.0265 q_1=0	s_1=2.22	1.33×10^{-4}
4.Complex Dissociation	$\underline{K = 0.035}$				
Model	$\underline{r_0=q_0=0}$	s_0=0.01	r_1=0.0201 q_1=0	s_1=0.00580	1.37×10^{-4}
5.Comppen Model	$\underline{K = 0.035}$				
	$\underline{r_{00}=r_{10}=0}$		r_{11}=0.0279	r_{01}=0.0611	9.93×10^{-3}
	$\underline{q_{00}=q_{10}=0}$		q_{11}=0	q_{01}=0	
	$\underline{s_{00}=0}$	s_{10}=74.8	s_{11}=10.8	s_{01}=0	

(The underlined values are the fix values, the K was determined independently and the reactivity ratios involved homopropagation of MA were assigned zero due to non-homo-polymerization of MA)

The definitions of the test functions and their use for testing the applicability of the terminal-, penultimate-, complex participation- and complex dissociation models were summarised in scheme 4 (Chapter 2). Fig.4.1.9a-d and Fig.4.1.10a-d show the test functions **a** and **b** calculated from the triad mole fraction data of the MA-ST copolymers prepared in CCl_4 and in DMF. In both cases function **b**> function **a**. This indicates the non-applicability of the terminal model and the complex dissociation model. While function **a** changes slightly with the copolymer composition (F_0), function **b** seems to fluctuate around a constant but not equal to the corresponding r_{01} of the penultimate model in which r_{01}=0.0165 and 0.0225 in the MA-ST copolymerisation in CCl_4 and in DMF, respectively. Therefore the complex participation model appears to be the most likely model.

Because the copolymerisation of ST with MA gives strongly alternating copolymers, the number of the meaningful data points which can be used effectively for the NLLS regression analysis for the copolymerisation models is limited; the copolymers of ST and MA are rigidly alternating (F_{010}= 1) when prepared with f_0 >0.2 in CCl_4 and f_0 >0.4 in DMF. When copolymer units are rigidly alternating all the copolymerisation

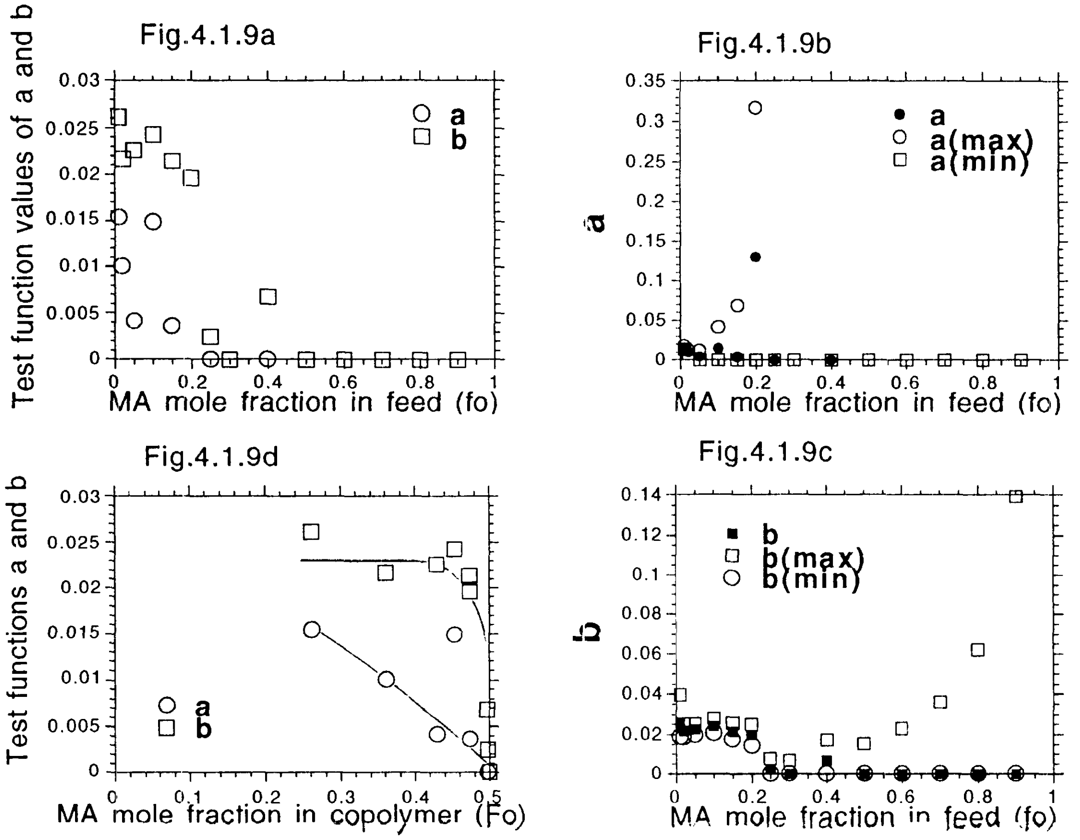


Fig.4.1.9a Testfunction quantities **a** and **b** vesus composition in feed. (MA+ST/CCl_4)
Fig.4.1.9b Test function **a** value with its absolutely calculated error range. (MA+ST/CCl_4)
Fig.4.1.9c Test function **b** value with its absolutely calculated error range. (MA+ST/CCl_4)
Fig.4.1.9d Test function quantities **a** and **b** vesus copolymer composition. (MA+ST/CCl_4)

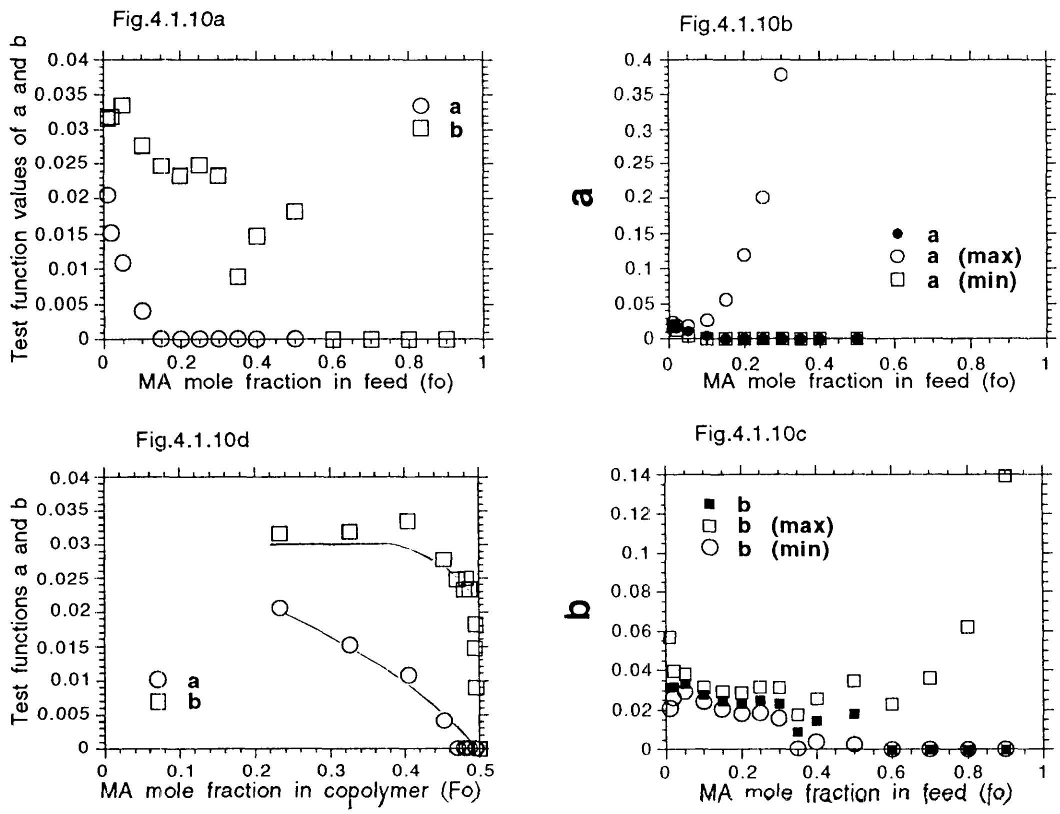


Fig.4.1.10a Test function quantities **a** and **b** vesus composition in feed. (MA+ST/DMF)
Fig.4.1.10b Test function **a** value with its absolutely calculated error range. (MA+ST/DMF)
Fig.4.1.10c Test function **b** value with its absolutely calculated error range. (MA+ST/DMF)
Fig.4.1.10d Test function quantities **a** and **b** vesus copolymer composition. (MA+ST/DMF)

models merge together and any difference will disappear.

The concept of the "bootstrap model" [72,73,74] is demonstrated by the plot of the triad mole fraction versus the copolymer composition (Fig.4.1.11). The "bootstrap effect" was first proposed by Harwood [72] which assumes that the composition of the copolymer is formed at an identical local comonomer ratios[74] characterized by the "partition coefficient" [72,73], and that the growing polymer radical can control its own environment and therefore the propagation mechanism is the same in any solvent [72,73] .

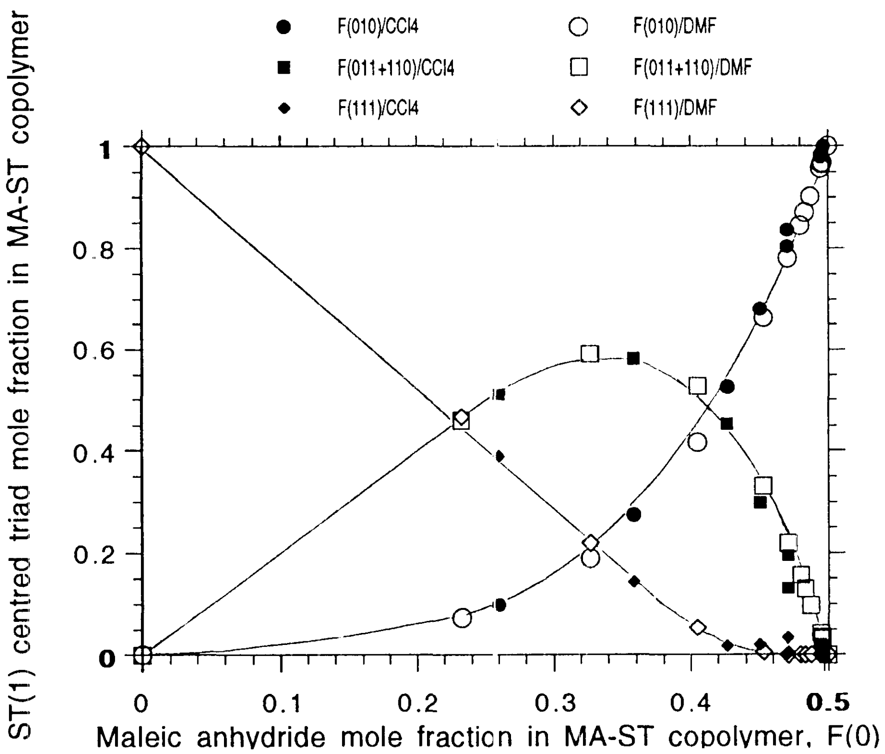


Fig.4.1.11 The ST(1) centred triad sequence distribution with respect to the copolymer composition (F_0). The copolymers of MA with ST were prepared in the nearly non-polar CCl_4 and the highly polar DMF at 50°C. [MA+ST]=4.000M. [AIBN]=0.0305M. The triad mole fractions were determined from the DEPT ^{13}C NMR CH_2 subspectra of C1 carbon.

Fig.4.1.11 shows the solvent independence of monomer sequence distribution (F_{010}, $F_{(011+110)}$, F_{111}) with respect to the copolymer composition (F_0) for the copolymerisation of MA with ST in the nearly non-polar CCl_4 (dielectric constant ε=2.24) and the highly polar DMF (ε=36.7). That is in agreement with the same copolymerisation prepared in $CHCl_3$ (ε=4.8) and in MEK (ε=18.5)[74] . However, because the F_0 was calculated from the triad mole fractions and because the chemical reactivity of the comonomers dominates over the largely very small and physical effects of various solvents, it is easily to understand that the triad mole fraction and the copolymer composition (F_0) correlate so well for a particular comonomer pair.

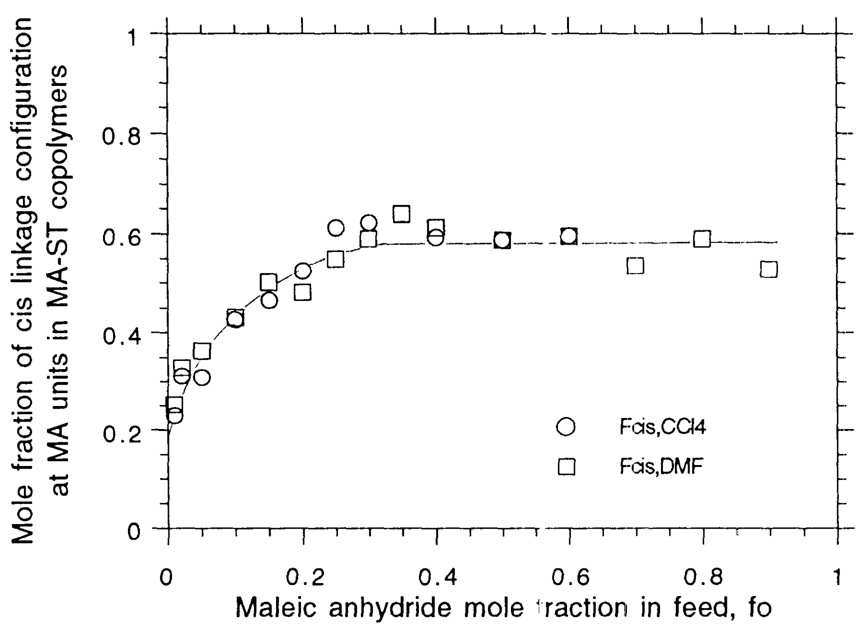


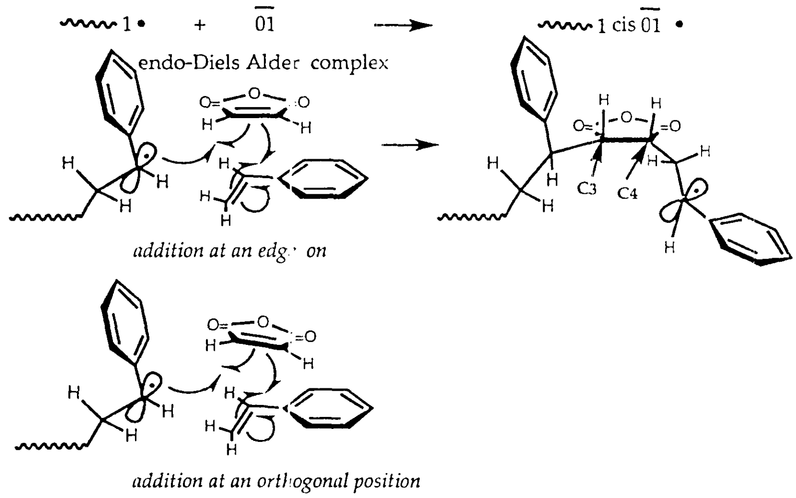
Fig.4.1.12 Mole fraction of the *cis* linkage configurations at the cyclic MA units (F_{cis}) in MA(0)-ST(1) copolymers prepared in CCl_4 and in DMF vs. MA mole fraction in feed (f_0).

The mole fractions of the *cis* linkage configurations at the cyclic MA units (F_{cis}) in MA-ST copolymers prepared in less polar CCl_4 and in highly polar DMF are shown in Fig.4.1.12. The effect of the solvent polarities is too little to be observed. That indicates that the chemical property of the comonomers plays a greater roll than the solvent polarities in the copolymerisation of MA with ST. The amount of the *cis* linkage configuration (F_{cis}) increases along with the increasing MA mole fraction in feed (f_0) when f_0 =0.01-0.30 and then seems to reach a constant value when f_0 >0.30. An average value of F_{cis}=0.57±0.07 is calculated for the copolymers prepared with f_0=0.20-0.90 .

More than half of the linkages at the MA units in MA-ST copolymers are determined to be in *cis* configuration. It is possible to explain this by a mechanism which involves an addition of the electron donor acceptor (EDA) complex formed between the comonomers. The free monomer addition would result mostly *trans* linkage configurations because the radical intermediates, being a non-ionic species, are susceptible to steric hindrance to a relatively large extent. A low activation reaction path of less steric hindrance will be followed by the formation of a thermodynamically more stable *trans* linkage.

Scheme 6 shows the most possible mechanism leading to a *cis* linkage configuration at the cyclic MA units in the MA-ST copolymer. A propagating ST radical (~1·) attacks the MA(0) side at an orthogonal position of a MA-ST complex (01), followed by a concerted addition of the ST monomer in the same complex , will result in a cis linkage at the MA unit in the copolymer. According to this scheme *cis* linkage configuration at MA units would result in the sequence 101.

Scheme 6 : The most likely propagating reactions leading to the *cis* linkage configuration at the cyclic MA units in MA-ST copolymer.



In the copolymerisation of ST with MA free monomer propagation would create mostly the *trans* linkage configurations. A growing copolymer ending with MA radical can only attack to the ST side of MA-ST complex which more possibly creates *trans* linkages. A growing ST radical can attack both MA or ST side of MA-ST complex. Because the cross addition is generally more likely due to the polar effect than the homo addition, it may be considered that, in the copolymerisation of polar monomers such as ST with MA, it is more likely that, a growing ST radical attacks the MA side of the MA-ST complex more often than the ST side of the complex. This reaction, if it takes place at the orthogonal or at an edge-on position of MA-ST complex, would be the main source of creating the *cis* linkages. That also means that there may be a good correlation between the *cis* content and the alternating triad mole fraction.

If all of the alternating sequences were formed by addition of the EDA complex, a relation $F_{cis}=(p_{cis}).F_{010}$ stands, where the p_{cis} is the probability of a single complex addition resulting in *cis* linkage configuration at the MA units. Therefore, this relation may be constant to be applicable to an "ideal" alternating copolymerisation, where all the alternating sequences are due to the addition of the EDA complex. The correlation between the mole fraction of the alternating triad (F_{010}) and the cis linkage (F_{cis}) is plotted in Fig.4.1.13. The extrapolation at $F_{010}=1$ has the value of $F_{cis}=0.61$ which coincides with p_{cis} value of copolymerisation of MA and ST in MEK [40].

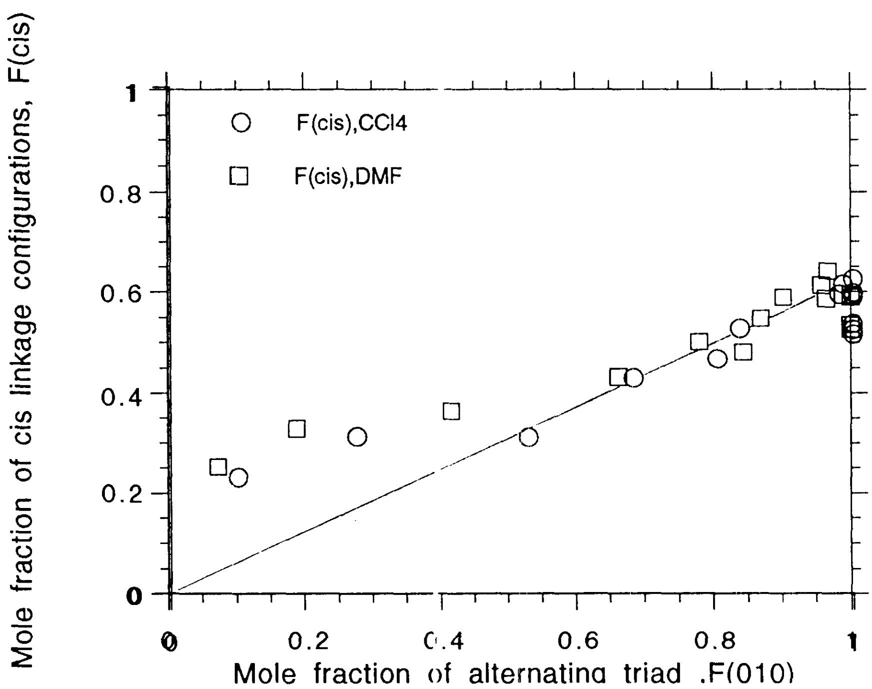


Fig.4.1.13 Mole fraction of the *cis* linkage configurations at the cyclic MA units (F_{cis}) in MA(0)-ST(1) copolymers prepared in CCl_4 and in DMF vs. mole fraction of the alternating triad (F_{010}).

Fig.4.1.14 plots the mole fraction of *cis* linkage configuration (F_{cis}) at the cyclic MA units in MA-ST copolymers with respect to the dielectric constant (ε) of the solvents used. All the ten copolymers were prepared with an equal comonomer concentration of [MA] = [ST] = 1.000±0.001 mol/l and the initiator concentration of [AIBN]=0.0153±0.0001mol/l. The DEPT ^{13}C NMR subspectra of C3 and C1 carbons in the copolymers are shown in Fig.7.3.3 (Appendix). These spectra indicate almost all the monomer unit sequences are rigidly alternating in all the copolymers examined here. The values of F_{cis} of the ten MA-ST copolymers prepared in ten different solvents, with the dielectric constants ranging from 2.24 (CCl_4) to 36.7 (DMF) are listed in Tab.4.1.6.

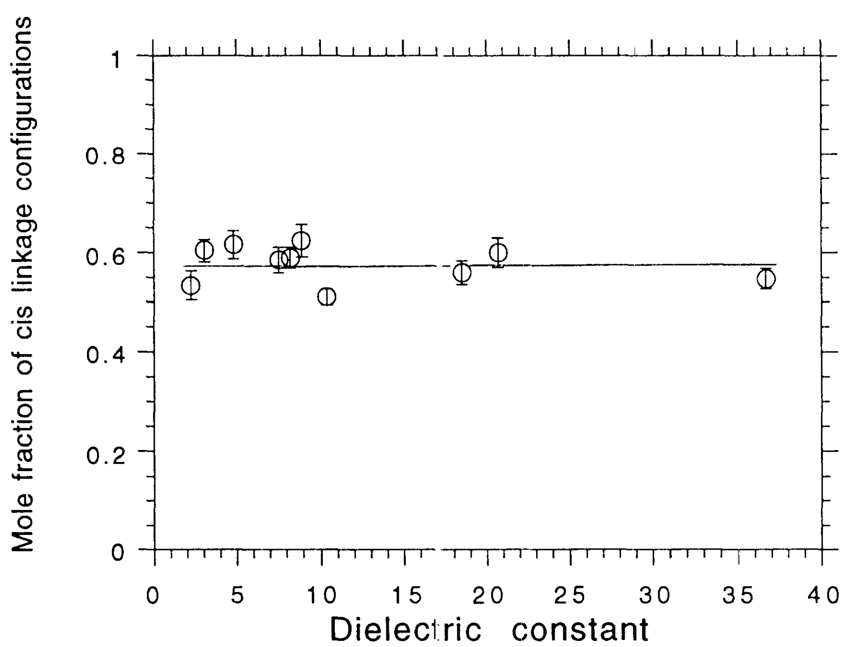


Fig.4.1.14 The mole fraction of *cis* linkage configuration at the cyclic MA units (F_{cis}) in MA-ST copolymers prepared in ten different solvents of the dielectric constants (ε) range from 2.24 to 36.7. F_{cis} was determined from DEPT ^{13}C NMR CH subspectra of C3. [MA]=[ST]=1.000M.

Although the equilibrium constant (K) of the comonomer complexation varies from 0.208 l/mol in CCl_4 to 0.035 l/mol in DMF due to the polarity of the solvents, the amount of the *cis* linkage configurations in resulting MA-ST copolymers seems to be the same. An average value of F_{cis}= 0.577±0.065 is determined for these ten MA-ST copolymers. As mentioned above, in the radical copolymerisation of ST with MA, the chemical property of the comonomer pair plays a dominating roll in forming the copolymer over the solvent polarities, which only contributes by causing different concentrations of the comonomer complex in the polymerisation mixture.

Tab.4.1.6 Correlation between the mole fraction of the *cis* linkage configuration at the cyclic MA units (F_{cis}) in MA-ST copolymers prepared in ten solvents with the dielectric constants(ε) ranged from 2.24 (CCl_4) and 36.7 (DMF). $[MA]_0=[ST]_0=1.000\pm0.001M$. $[AIBN]=0.0153\pm0.0001M$. T=50°C. F_{cis} determined by DEPT ^{13}C NMR CH suspectra of C3

No.	Solvent	Dielectric constant (ε)	F_{cis}	Equilibrium constant of MA-ST complexation (l/mol)
1	Carbon tetrachloride (CCl_4)	2.24	0.534	0.208 (23°C / UV)this work
2	Di-n-butyl ether (C_4H_9-O-C_4H_9)	3.06	0.604	
3	Chloroform ($CHCl_3$)	4.8	0.616	0.093 (23°C / UV) [43]
4	1,1,1-Trichloroethane (CCl_3-CH_3)	7.52	0.585	
5	1,1,2,2-Tetrachloroethane ($CHCl_2$-$CHCl_2$)	8.2	0.589	
6	Methylenechloride (CH_2Cl_2)	8.9	0.624	
7	1,2-Dichloroethane (CH_2Cl-CH_2Cl)	10.36	0.511	
8	Methyl ethyl ketone (MEK)	18.51	0.56	0.045 (23°C / UV) [24]
9	Acetone (CH_3-O-CH_3)	20.7	0.599	
10	N,N-Dimethylformamide (DMF)	36.7	0.547	0.035 (23°C / determined empirically)this work

Average value of F_{cis}= 0.577±0.065

4.2. Copolymerisation of citraconic anhydride with styrene in carbon tetrachloride and in N,N-dimethylformamide.

The equilibrium constants of the EDA complexation of styrene (ST) and citraconic anhydride (CA) in CCl_4 and in DMF were determined by UV spectroscopy using Ketelaar equation [69] to be $K_{CCl4}=0.142\pm0.015$ l/mol and $K_{DMF}=0.021\pm0.015$ l/mol , respectively. The Ketelaar plots for the determination of the equilibrium constant are shown in Fig.4.2.1 and Fig.4.2.2.

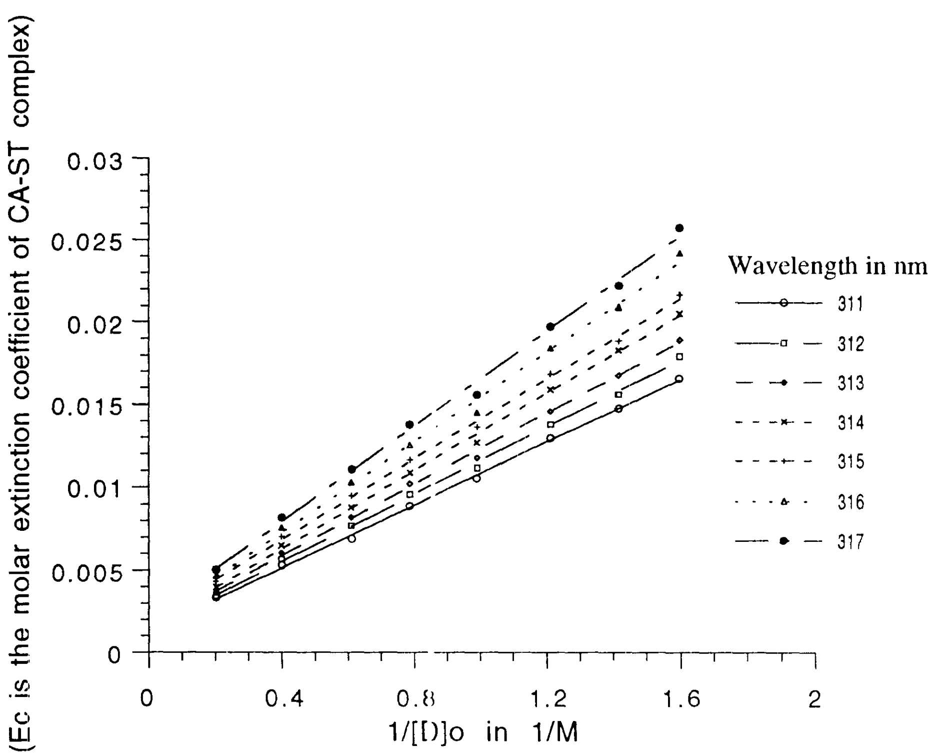


Fig.4.2.1 Determination of the equilibrium constant (K) of CA-ST complexation in CCl_4 at room temperature by UV spectroscopy using the Ketelaar equation.

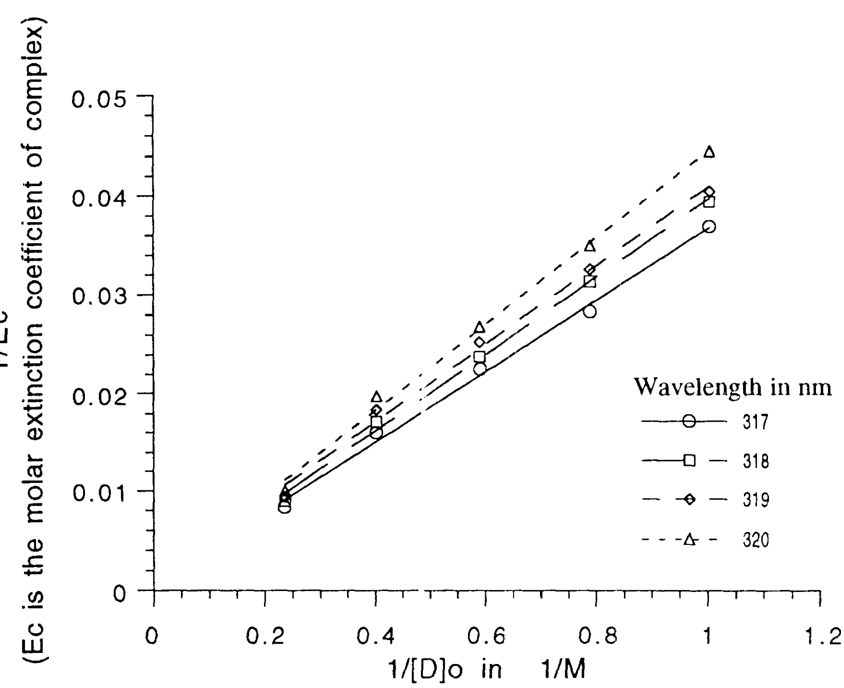
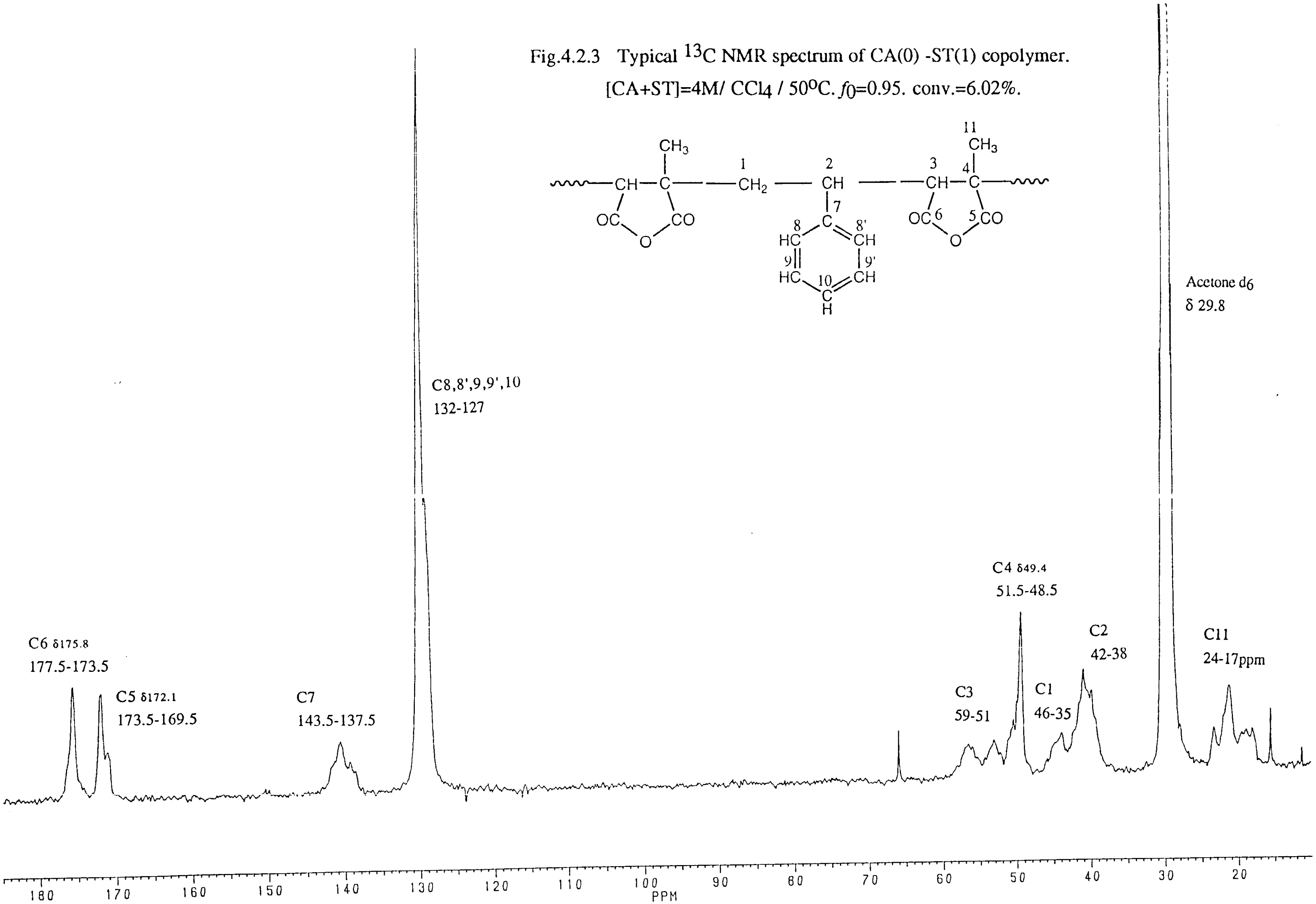


Fig.4.2.2 Determination of the equilibrium constant (K) of CA-ST complexation in DMF at room temperature by UV spectroscopy using the Ketelaar equation.

Fig.4.2.3 Typical ^{13}C NMR spectrum of CA(0) -ST(1) copolymer.
[CA+ST]=4M/ CCl_4 / 50°C. f_0=0.95. conv.=6.02%.



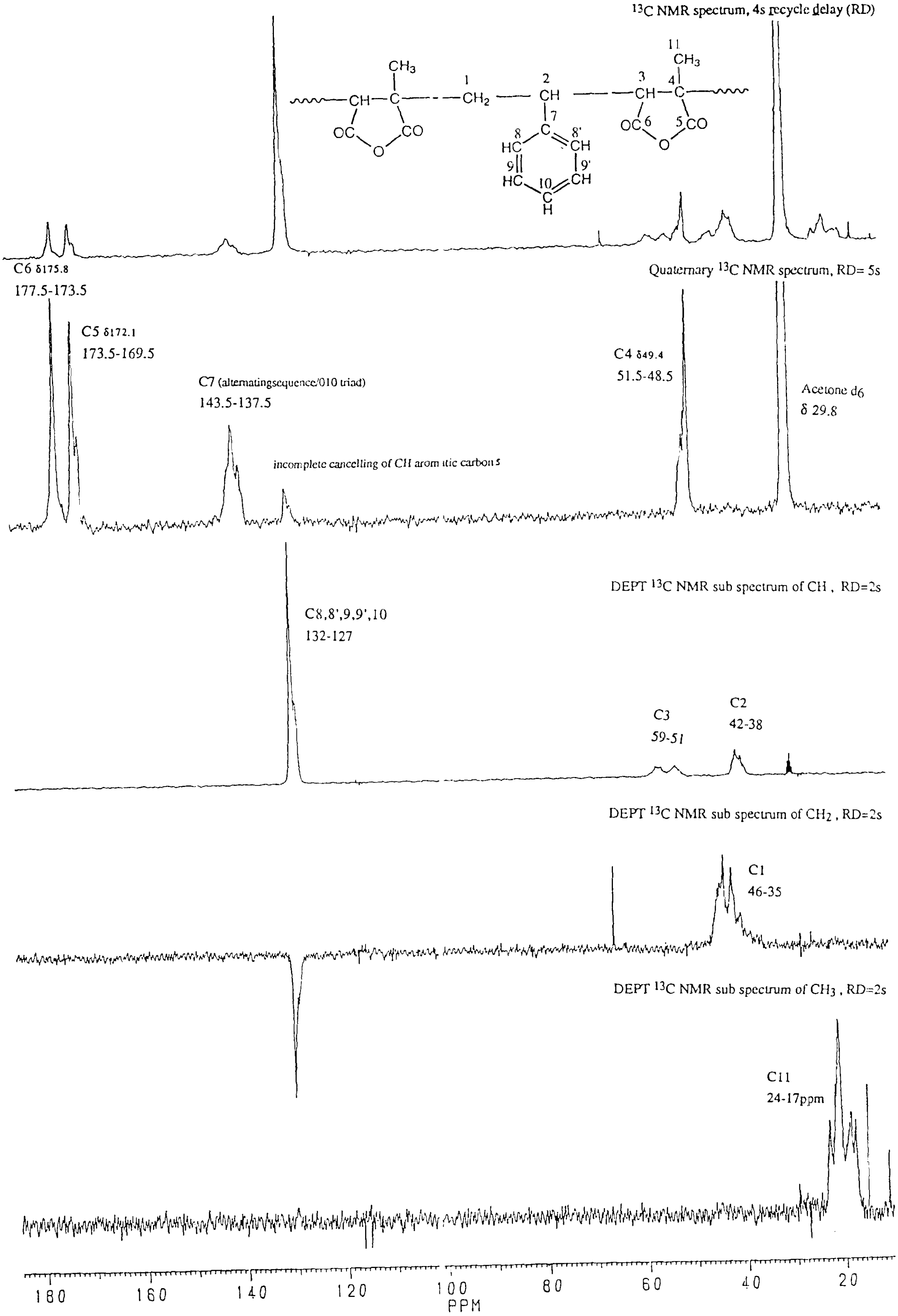


Fig.4.2.4 ^{13}C -, Quaternary ^{13}C -, DEPT ^{13}C - NMR spectra of the alternating CA(0) -ST(1) copolymer. [CA+ST]=4M/ CCl_4 / 50°C. f_0=0.95. conv.=6.02%.

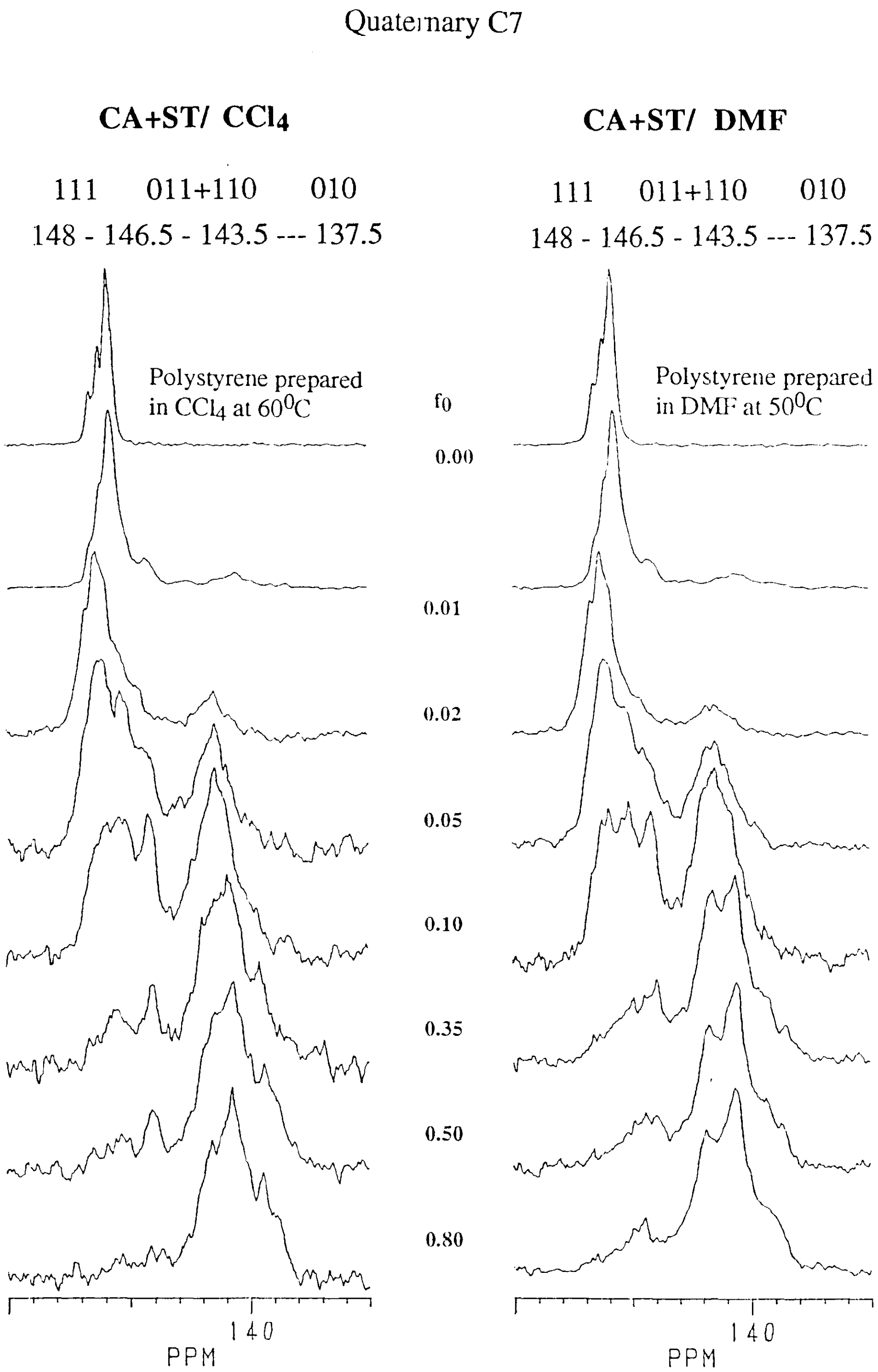


Fig.4.2.5 Selected Quaternary ^{13}C NMR spectra of C7 of CA(0) -ST(1) copolymers prepared in CCl_4 and in DMF.

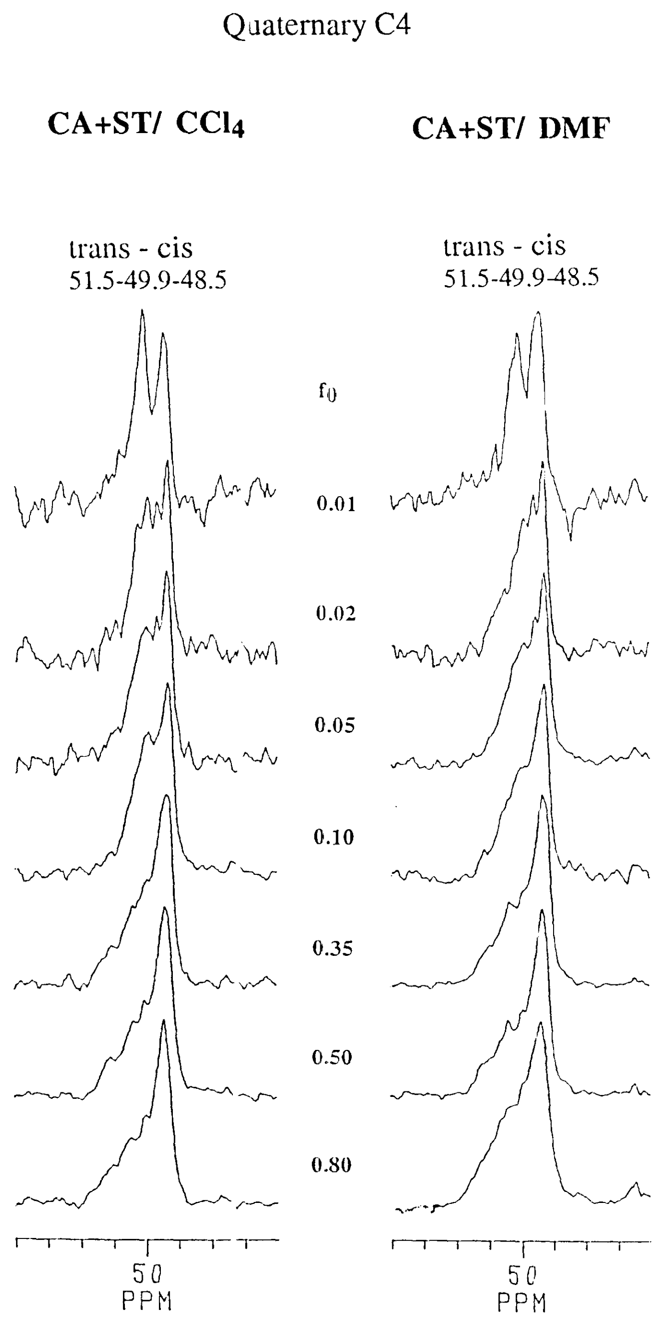


Fig.4.2.6 Selected Quaternary ^{13}C NMR spectra of C4 of CA(0) -ST(1) copolymers prepared in CCl_4 and in DMF.

The copolymers of ST and CA were prepared in a wide range of CA mole fractions in feed (f_0) ranging from 0.01 to 0.95 in CCl_4 and from 0.01 to 0.80 in DMF at 50°C. Fig.4.2.3 shows a typical ^{13}C NMR spectrum of an alternating CA-ST copolymer, which was prepared in CCl_4 with f_0=0.95. Fig.4.2.4 shows the spectra of the general, quaternary, CH-, CH_2- and CH_3- DEPT ^{13}C NMR spectra, where the chemical shifts of the overlapped methylene C1 and methine C2 peaks can be clearly assigned. The quaternary ^{13}C NMR spectra of C7 carbons were used for determining the ST(1) centred triad mole fractions (F_{010}, $F_{(011+110)}$, F_{111}). Those of C4 carbons were used for the determination of the mole fraction of the *cis* linkage configuration at the cyclic CA units (F_{cis}) in the CA-ST copolymers. Fig.4.2.5 and Fig.4.2.6 show the variation of the resonance of the quaternary C7 and C4 carbons in the CA-ST copolymers prepared in CCl_4 and in DMF with respect to the monomer composition in feed (f_0), respectively. *Linesim* [68] peak simulation program was used to determine the peak areas. The composition of CA units in the copolymers (F_0) was calculated from the triad mole fractions [Scheme 5 or reference [15]].

The experimental mole fractions of triad sequences and the overall copolymer composition data are collected in Tab.4.2.1 for the copolymers prepared in CCl_4 and in DMF. It is seen that a fully alternating CA-ST copolymer was formed only when the proportion of CA in feed was extremely large (f_0=0.90-0.95 in copolymerisation of CA and ST in CCl_4 at 50° C). ST and citraconic anhydride(CA) copolymerise only sluggishly because of the effect of the α substituted methyl group in CA. The methyl group of the tertiary CA radical may hinder an approach of a monomer. Alternatively, if the complex is actually participating, the methyl group may reduce the reactivity of the EDA complex toward a growing radical.

The non linear least squares (NLLS) curve fitting of the theoretical equations based on various copolymerisation models to the experimental triad data was performed for the five models; 1.terminal model , 2.penultimate unit effect model, 3.complex participation model, 4.complex dissociation model and 5.comppen model. Fig.4.2.7 and Fig.4.2.8 present the experimental ST(1) centred triad mole fractions and the calculated best fit alternating triad mole fractions (F_{010}) for the five above mentioned

Tab.4.2.1 The experimental triad and composition data and the mole fraction of the *cis* linkage configurations at the cyclic CA units in CA-ST copolymer prepared in CCl_4 and in DMF. The triad mole fractions the mole fraction of the *cis* linkages were determined from Quaternary ^{13}C NMR spectra of C7 and C4, respectively.

f_0	Copolymer of CA+ST prepared in CCl_4					Copolymer of CA+ST prepared in DMF				
	F_{010}	$F_{(011+110)}$	F_{111}	F_0	F_{cis}	F_{010}	$F_{(011+110)}$	F_{111}	F_0	F_{cis}
0.01	0.100	0.253	0.646	0.185	0.395	0.107	0.173	0.721	0.162	0.482
0.02	0.178	0.332	0.490	0.256	0.456	0.166	0.371	0.463	0.260	0.493
0.05	0.338	0.331	0.331	0.335	0.486	0.317	0.403	0.280	0.342	0.517
0.10	0.494	0.342	0.164	0.399	0.494	0.493	0.356	0.112	0.401	0.564
0.15	0.611	0.283	0.106	0.429	0.572	0.597	0.294	0.109	0.427	0.599
0.20	0.654	0.305	0.042	0.446	0.572	0.639	0.285	0.076	0.439	0.618
0.25	0.694	0.283	0.024	0.455	0.534	0.657	0.297	0.046	0.446	0.536
0.30	0.777	0.221	0.003	0.470	0.564	0.728	0.249	0.023	0.460	0.584
0.35	0.484	0.212	0.004	0.471	0.571	0.750	0.223	0.027	0.463	0.579
0.40	0.781	0.210	0.008	0.470	0.578	0.779	0.195	0.026	0.467	0.527
0.50	0.860	0.136	0.008	0.481	0.594	0.822	0.169	0.009	0.476	0.607
0.60	0.859	0.134	0.007	0.481	0.593	0.851	0.139	0.011	0.479	0.618
0.70	0.896	0.103	0.000	0.487	0.588	0.880	0.114	0.000	0.484	0.645
0.80	0.903	0.097	0.000	0.488	0.553	0.859	0.129	0.012	0.480	0.567
0.90	0.988	0.025	0.000	0.500	0.573					
0.95	0.991	0.009	0.000	0.499	0.582					

f_0 = CA(0) mole fraction in feed

F_0 = CA(0) mole fraction in CA(0)-ST(1) copolymers. The uncertainties (Δ)were estimated to be $\pm$0.02

F_{010}, $F_{(011+110)}$, F_{111} = ST(1) centred triad mole fraction in CA(0)-ST(1) copolymer.

Δ (F_{111}, $F_{(011+110)}$)= $\pm$0.04. Δ (F_{010})= $\pm$0.02.

F_{cis} = mole fraction of the *cis* linkage congiguratic ns at the cyclic CA units in copolymers.

Δ (F_{cis})= $\pm$0.06.

[CA+ST]=4.000M. [AIBN]=0.0305M. copolymerised at 50°C.

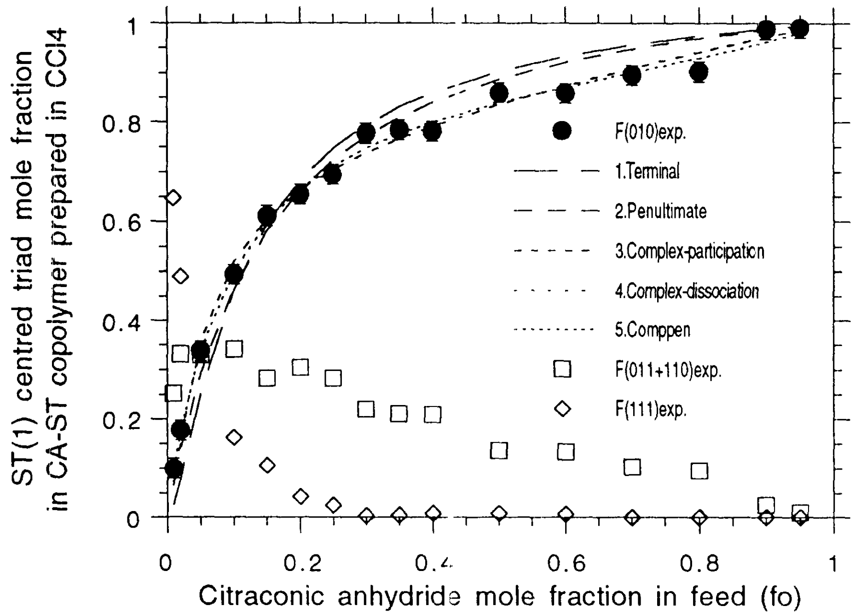


Fig.4.2.7 NLLS curve fitting of F_{010} experimental data to 5 models. (CA+ST/CCl_4)

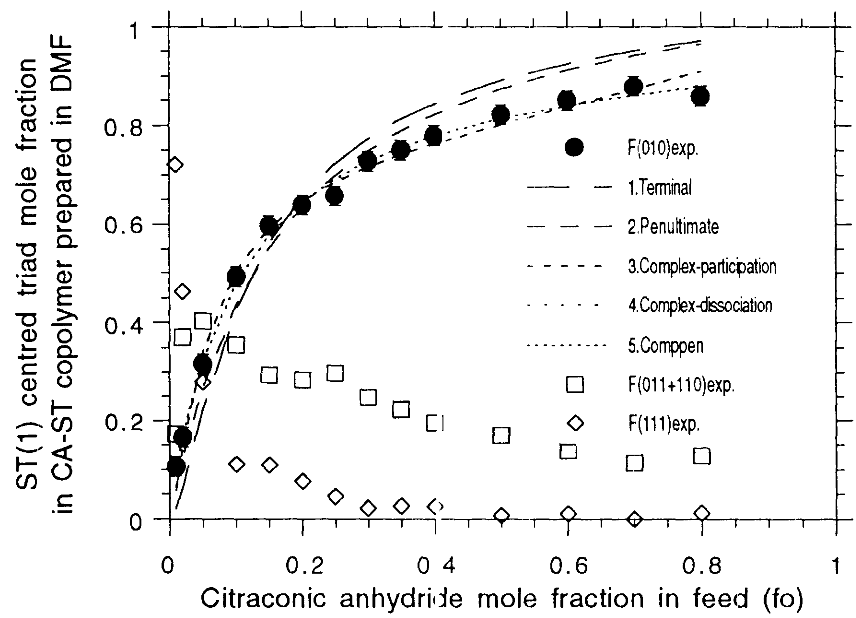


Fig.4.2.8 NLLS curve fitting of F_{010} experimental data to 5 models. (CA+ST/ DMF)

copolymerisation models for the CA-ST copolymers prepared in CCl_4 and in DMF, respectively. Tab.4.2.2 collects the SS and S_y values calculated from the NLLS regression analyses for the triad mole fraction data for both copolymerisation systems. The smallest SS and S_y values among the five models on the F_{010} data set would indicate the model best fit to the experimental data. It can be seen from the Tab.4.2.2, that three models, which involve the complex addition seem to be the better fitting than the terminal and the penultimate unit effect models, which are based on free monomer additions. The SS and S_y values are the smallest for the comppen model. The SS value of the NLLS regression analysis on the overall copolymer composition data (F_0) shows the smallest value for the complex participation model and the greatest value for the comppen model (Tab.4.2.3 and Tab.4.2.4) in both the CA-ST copolymerisations in CCl_4 and in DMF.

Tab.4.2.2 The sum of squares (SS) and the standard error (S_y) values of the NLLS curve fitting of the 1.Terminal-, 2.Penultimate-, 3.Complex- Participation-, 4. Complex-Dissociation- and 5.Comppen- model to the experimental triad mole fraction data. CA-ST copolymers prepared in CCl_4 and in DMF. The triad mole fractions were determined from Quaternary ^{13}C NMR spectra of C7. K_{CCl4}= 0.142 (l/mol). K_{DMF}= 0.021 (l/mol)

Model	Solvent used	SS F_{010}	SS $F_{(011+110)}$	SS F_{111}	S_y F_{010}	S_y $F_{(011+110)}$	S_y F_{111}
1.	CCl_4	5.27×10^{-2}	6.92×10^{-2}	1.68×10^{-2}	5.93×10^{-2}	6.79×10^{-2}	3.35×10^{-2}
	DMF	7.44×10^{-2}	5.84×10^{-2}	1.15×10^{-2}	7.56×10^{-2}	6.70×10^{-2}	2.98×10^{-2}
2.	CCl_4	2.29×10^{-2}	4.87×10^{-2}	6.81×10^{-3}	4.05×10^{-2}	5.90×10^{-2}	2.20×10^{-2}
	DMF	2.29×10^{-2}	4.66×10^{-2}	5.75×10^{-3}	5.66×10^{-2}	6.23×10^{-2}	2.20×10^{-2}
3.	CCl_4	7.57×10^{-3}	1.20×10^{-2}	7.61×10^{-3}	2.51×10^{-2}	3.16×10^{-2}	2.52×10^{-2}
	DMF	8.25×10^{-3}	4.09×10^{-2}	5.06×10^{-3}	2.87×10^{-2}	6.40×10^{-2}	2.25×10^{-2}
4.	CCl_4	7.59×10^{-3}	5.50×10^{-2}	9.56×10^{-3}	2.51×10^{-2}	6.77×10^{-2}	2.82×10^{-2}
	DMF	8.26×10^{-3}	4.11×10^{-2}	5.00×10^{-3}	2.87×10^{-2}	6.41×10^{-2}	2.24×10^{-2}
5.	CCl_4	4.01×10^{-3}	1.08×10^{-2}	1.78×10^{-2}	2.11×10^{-2}	3.47×10^{-2}	1.41×10^{-1}
	DMF	2.79×10^{-3}	3.55×10^{-2}	2.16×10^{-2}	1.99×10^{-2}	7.12×10^{-2}	1.76×10^{-1}

Tab.4.2.3 The reactivity ratios of CA-ST copolymerisation in CCl_4, calculated from composition data (F_0) for 5 models. The triad mole fractions were determined from Quaternary ^{13}C NMR spectra of C7. K=0.142(l/mol).

					SS
1.Terminal Model	$r_0=0$	$r_1=0.0446$			2.92×10^{-3}
2.Penultimate Model	$r_{00}=r_{10}=0$	$r_{11}=0.0296$	$r_{01}=0.0749$		3.24×10^{-4}
3.Complex Participation	K = 0.142				
Model	$r_0=q_0=0$ $s_0=35.0$	$r_1=0.159$	$q_1=12.3$	$s_1=0.000100$	3.04×10^{-4}
4.Complex Dissociation	K = 0.142				
Model	$r_0=q_0=0$ $s_0=0.0011$	$r_1=0.0230$	$q_1=0.311$	$s_1=0.00$	7.52×10^{-4}
5.Comppen Model	K = 0.142				
	$r_{00}=r_{10}=0$	$r_{11}=1.86$	$r_{01}=0.131$		1.64×10^{-2}
	$q_{00}=q_{10}=0$	$q_{11}=0.000200$	$q_{01}=0.0000$		
	$s_{00}=0$ $s_{10}=26.9$	$s_{11}=202$	$s_{01}=0.0000$		

(The underlined values are the fix values, the K was determined independently and the reactivity ratios involved homopropagation of CA were assigned zero due to non-homo-polymerization of CA)

Tab.4.2.4 The reactivity ratios of CA-ST copolymerisation in DMF, calculated from composition data (F_0) for 5 models. The triad mole fractions were determined from Quaternary ^{13}C NMR spectra of C7. K=0.021(l/mol).

					SS
1.Terminal Model	$r_0=0$	$r_1=0.047$			3.49×10^{-3}
2.Penultimate Model	$r_{00}=r_{10}=0$	$r_{11}=0.0317$	$r_{01}=0.0801$		9.42×10^{-4}
3.Complex Participation	K = 0.021				
Model	$r_0=q_0=0$ $s_0=0.599$	$r_1=0.0472$	$q_1=2.26$	$s_1=1.677$	3.70×10^{-4}
4.Complex Dissociation	K = 0.021				
Model	$r_0=q_0=0$ $s_0=0.0108$	$r_1=0.0450$	$q_1=2.15$	$s_1=3.20$	3.70×10^{-4}
5.Comppen Model	K = 0.021				
	$r_{00}=r_{10}=0$	$r_{11}=44.3$	$r_{01}=0.186$		2.14×10^{-2}
	$q_{00}=q_{10}=0$	$q_{11}=0.001$	$q_{01}=0.0000$		
	$s_{00}=0$ $s_{10}=143$	$s_{11}=23700$	$s_{01}=0.0000$		

(The underlined values are the fix values, the K was determined independently and the reactivity ratios involved homopropagation of CA were assigned zero due to non-homo-polymerization of CA)

The reactivity ratios calculated from the overall CA(0) unit composition (F_0) for the five copolymerisation models are collected in Tab.4.2.3 and Tab.4.2.4 for the CA-ST copolymerisations in CCl_4 and in DMF, respectively.

Considering the SS and S_y values the complex participation and the complex dissociation copolymerisation models were expected in the copolymerisation model discrimination by test function. Fig.4.2.9a-d and Fig.4.2.10a-d show the test function quantities **a** and **b** calculated from the triad mole fraction data of the copolymerisation of ST with CA in CCl_4 and in DMF. In both cases function **a** is larger than function **b** in the most of the useable data points. This indicates the terminal model and the complex dissociation models are not applicable. Both functions **a** and **b** vary slightly with the copolymer composition (F_0) (Fig.4.2.9d and Fig.4.2.10d). According to the values of the function **a** and the function **b** , the complex participation model appears to be the most applicable model because the value of **a** as well as the value of **b** does not seem to be converged to a constant value of r_{11} and r_{01} of the penultimate model, respectively. The complex participation model appears to be more applicable model for the copolymerisation of ST and CA in CCl_4.

It is found that the CA-ST copolymers are mostly semi alternating. The Alfred-Price e value of CA (e=1.75) is smaller than that of MA (e=3.69) [50]. This implies that CA is an weaker acceptor monomer in forming EDA complex than MA is. The relative reactivity of MA toward a poly (ST) radical is about 6.8 times higher than that of CA [37]. The alternating tendency of the system of CA and ST is not so strong as mentioned above. The copolymerisation models which involve the complex addition seem to fit better to the experimental data. However this is by no means conclusive and it is only vague and marginal.

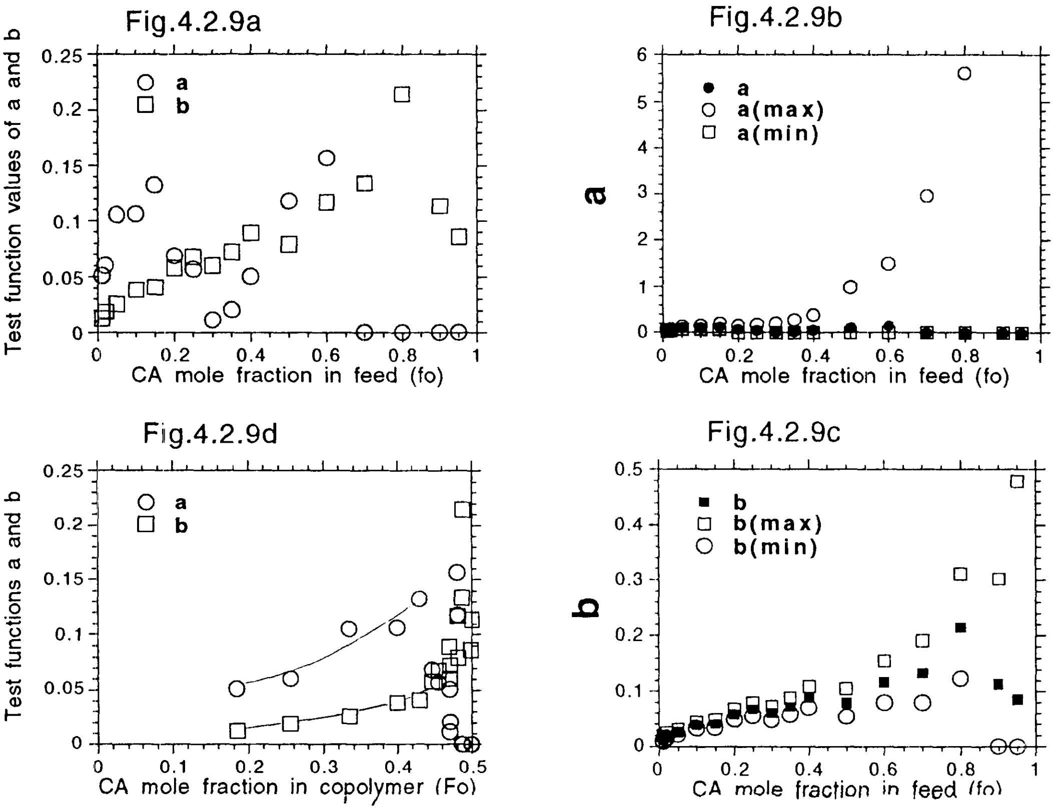


Fig.4.2.9a Test function quantities **a** and **b** vesus composition in feed. ($CA+ST/CCl_4$)
Fig.4.2.9b Test function **a** value with its absolutely calculated error range. ($CA+ST/CCl_4$)
Fig.4.2.9c Test function **b** value with its absolutely calculated error range. ($CA+ST/CCl_4$)
Fig.4.2.9d Test function quantities **a** and **b** vesus copolymer composition. ($CA+ST/CCl_4$)

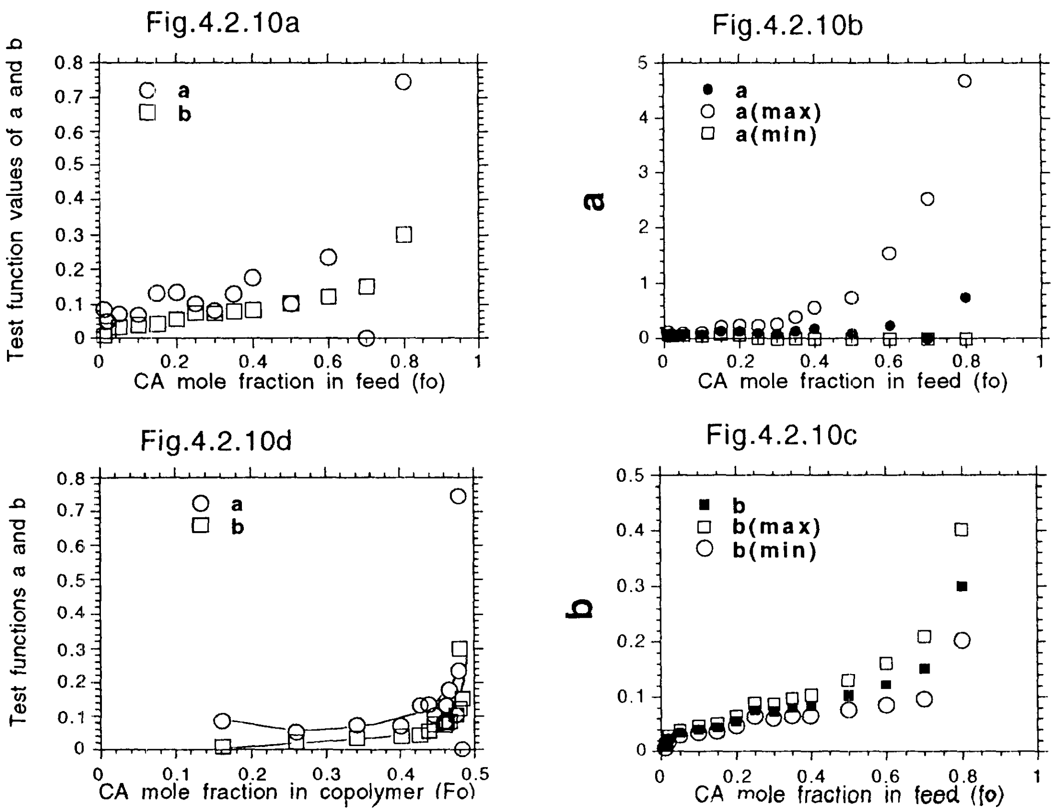


Fig.4.2.10a Test function quantities **a** and **b** vesus composition in feed. (CA+ST/DMF)
Fig.4.2.10b Test function **a** value with its absolutely calculated error range. (CA+ST/DMF)
Fig.4.2.10c Test function **b** value with its absolutely calculated error range. (CA+ST/DMF)
Fig.4.2.10d Test function quantities **a** and **b** vesus copolymer composition. (CA+ST/DMF)

Fig.4.2.11 shows the solvent independence of monomer sequence distribution (F_{010}, $F_{(011+110)}$, F_{111}) versus the copolymercomposition (F_0) for the copolymerisation of CA with ST in the nearly non polar CCl_4 (dielectric constant ε=2.24) and the highly polar DMF (ε=36.7). This can be explained by the "bootstrap model" [72,73]. However as already mentioned in Section 4.1, that the copolymer composition (F_0) was determined from the triad mole fractions and that the solvent effect was dominated by the chemical properties of the comonomer pair, this excelent correlation is in expectation.

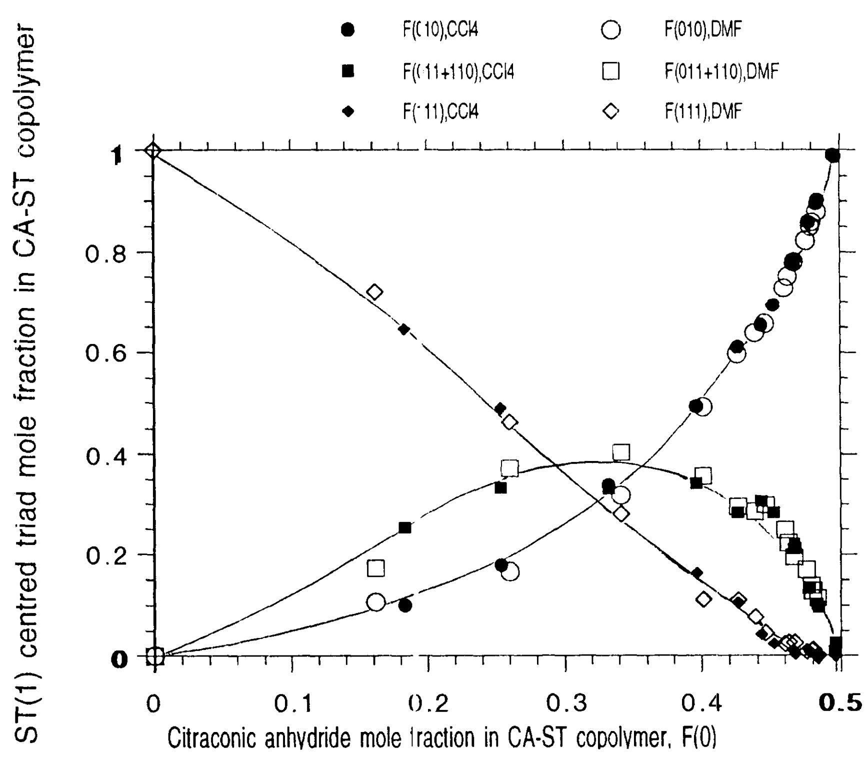


Fig.4.2.11 The ST(1) centred triad sequence distribution with respect to the copolymer composition (F_0). The copolymers of CA with ST were prepared in the nearly non-polar CCl_4 and the highly polar DMF at 50°C. [CA+ST]=4.000M. [AIBN]=0.0305M. The triad mole fractions were determined from the quaternary ^{13}C NMR spectra of C7 carbon.

The similarities between the mole fraction of the *cis* linkage configurations at the cyclic CA units (F_{cis}) in the CA-ST copolymers prepared in less polar CCl_4 and in highly polar DMF is observed in Fig.4.2.12. That implies that there is little difference in the solvent effects on the propagating step between CCl_4 and DMF. The amount of the *cis* linkage configuration (F_{cis}) increases along with the increasing CA mole fraction in feed (f_0) when f_0 =0.01-0.15 and then it seems to assume a constant value when f_0 is larger than 0.15. An average value of F_{cis}=0.58±0.06 is calculated for f_0=0.15-0.95 .

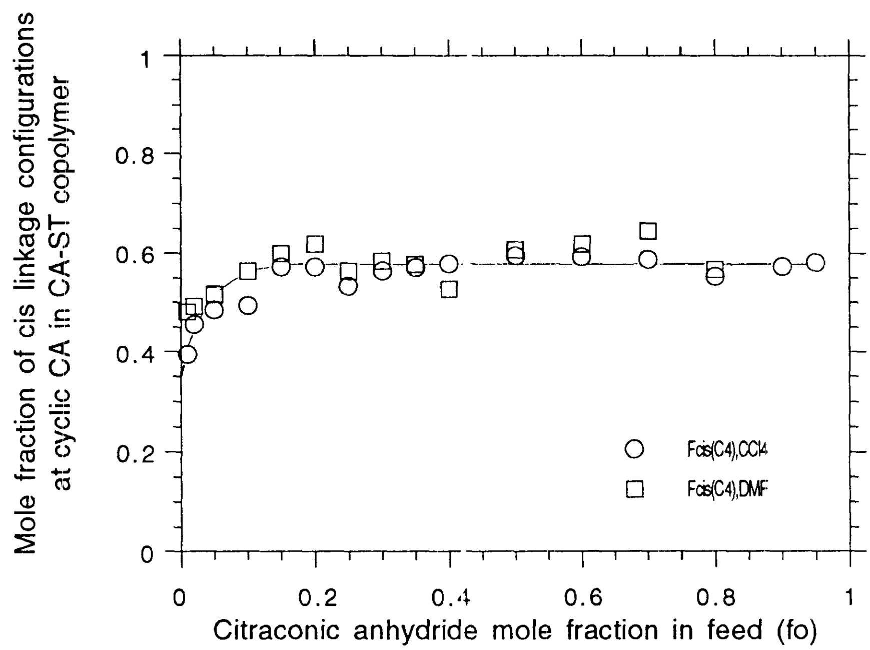
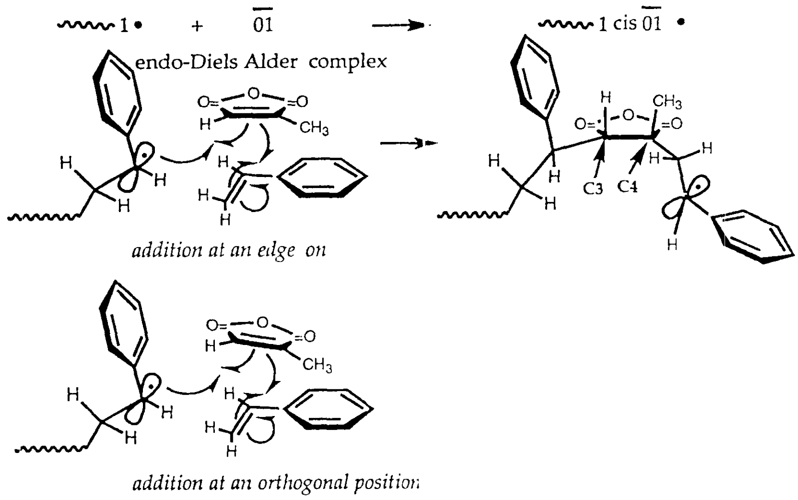


Fig.4.2.12 Mole fraction of the *cis* linkage configurations at the cyclic CA units (F_{cis}) in CA(0)-ST (1) copolymers prepared in CCl_4 and in DMF vs. CA mole fraction in feed (f_0).

More than half of the linkages at the CA units in CA-ST copolymers are found to be in *cis* configuration. This can be explained by a mechanism involving an electron donor acceptor (EDA) complex of ST and CA in the propagating step, while the free monomer additions would result in mostly the *trans* linkage configuration, which is kinetically of a lower activation energy process and the resulting configuration is more thermodynamically stable.

Scheme 7 shows a most likely mechanism leading to a *cis* linkage configuration at the cyclic CA units in the CA-ST copolymers. A propagating ST radical (~1·) attacks the CA(0) side at an orthogonal position and/ or at an edge-on position of a CA-ST complexation (01). A following concerted addition of the ST side of the complex within the complex may explain the large amount of *cis* linkage configuration at the cyclic CA-units.

Scheme 7 : The most likely propagating reactions leading to the *cis* linkage configuration at the cyclic CA units in CA-ST copolymer.



4.3. Mole fraction of *cis* linkage configuration at the cyclic anhydride monomer units in the copolymer and the implication for the propagating mechanism of some other related copolymerisation systems.

Copolymerisations of styrene with bromomaleic anhydride (BMA), styrene with dichloromaleic anhydride (DCMA) and of styrene with maleimide (MI) were carried out with the mole fraction of ST in the feed monomer mixture of 0.5 at 50.0$\pm$ 0.1°C. To obtain conversions of less than 5% , the copolymerisation time of ST-MI system was set around 45 min while that of ST-BMA was set 4hrs and that of ST-DCMA was set 24hrs. Steric hindrance due to the two chlorine atoms on the C=C double bond in DCMA may explain the extremely slow copolymerisation rate of ST with DCMA.

Tab.4.3.1. Mole fraction of *cis* linkage configuration of the cyclic anhydride acceptor monomer units (0) (F_{cis}) in Styrene (ST or 1) copolymers with maleic anhydride (MA or 0), citraconic anhydride (CA or 0), bromomaleic anhydride (BMA or 0), dichloromaleic anhydride (DCMA or 0) and maleimide (MI or 0) prepared at 50°C. F_{cis} determined by DEPT ^{13}C NMR CH sub-spectra of C3 of MA-ST-, CA-ST-, BMA-ST- and MI-ST- copolymers and by quaternary ^{13}C NMR spectrum of DCMA-ST copolymer.

[0+1]/ Solvent	f_0	K(l/mol)	e-Q scheme values of monomer 0 e	Q	F_{cis}
[MA+ST]=4M/ CCl_4	0.5	0.208	3.69	0.86 [50]	0.587
/ DMF	0.5	0.035	2.25	0.23 [75]	0.586
[CA+ST]=4M/ CCl_4	0.5	0.142	1.75	0.87 [50]	0.535
/ DMF	0.5	0.021			0.577
[BMA+ST]=1M/ CCl_4	0.5				0.553
[DCMA+ST]=2M/ $CHCl_3$	0.5				0.595
[MI+ST]=2M/ CCl_4	0.5		2.86	0.94 [75]	0.305

f_0= Mole fraction in feed of monomer 0
K= Equilibrium constant of comonomer complexation, determined by UV, at room temperature.
[0+1]= Total monomer concentration

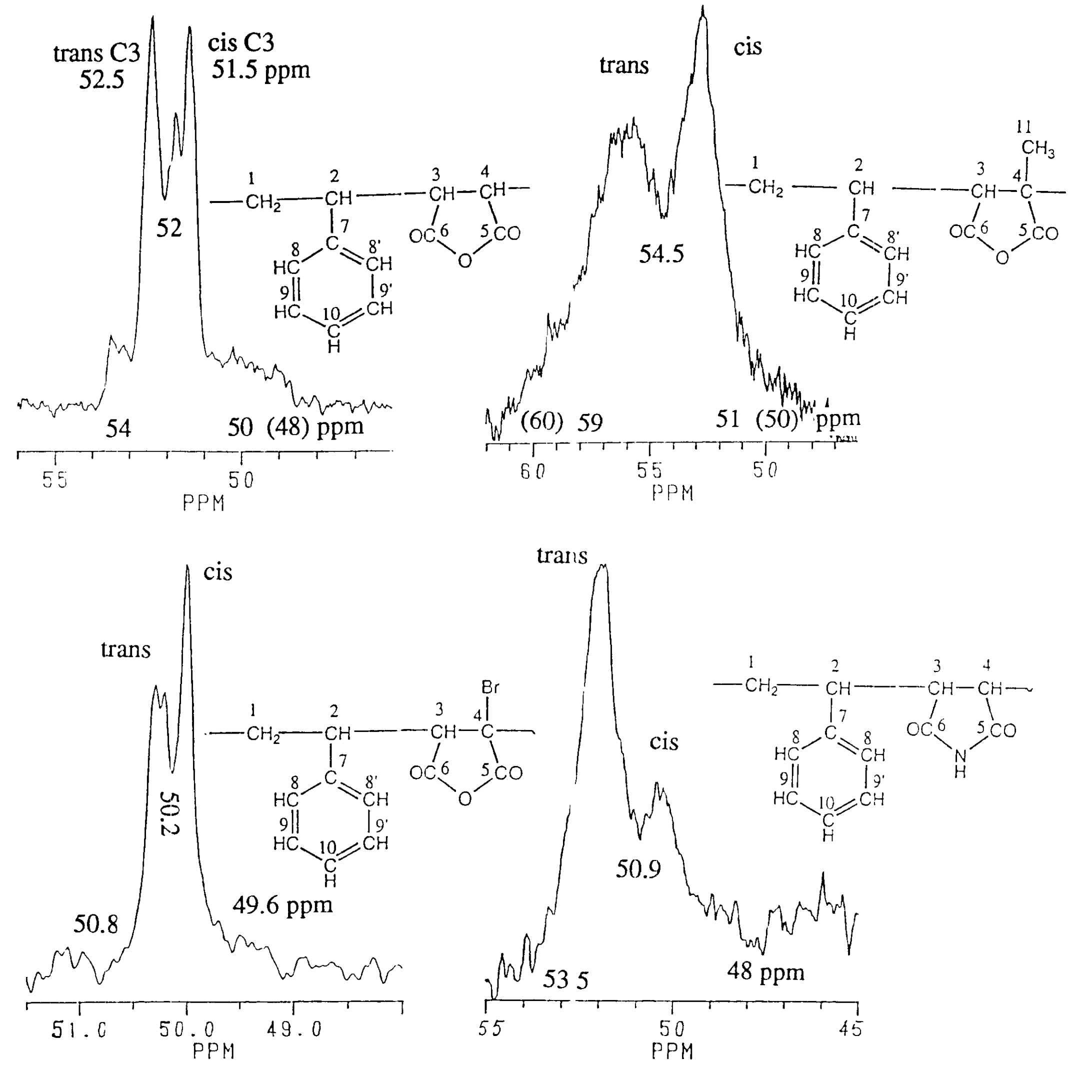
Tab.4.3.1. shows the mole fraction of *cis* linkage configuration at the cyclic acceptor monomer units (F_{cis}) in the copolymers with ST. Due to the bulky methyl substituent, CA is an weaker acceptor compared to MA to ST, which is a donor monomer. The equilibrium constant, K, of the EDA complexation of ST in CCl_4 was determined to be 0.208 l/mol with MA and it was measured to be 0.142 l/mol with CA. In contrast, the BMA and DCMA, due to the large electro negativity of Cl and Br atoms, are supposed to be stronger electron acceptors than MA in complexation with ST. An example of the acceptor characteristic of the anhydride monomers used here can be seen in the relative magnitude of the equilibrium constant in the EDA complexation with a donor monomer, divinyl ether, determined in the same solvent. Tab.4.3.1a shows the reported K values of CA, MA, BMA and CMA in complexing with divinyl ether in $CHCl_3$.

Tab.4.3.1a. The equilibrium constant of the EDA complexation of divinyl ether with acceptor monomers in $CHCl_3$ at 25°C, determined by UV.[76]

Acceptor monomer	K in l/mol
Citraconic anhydride (CA)	0.032
Maleic anhydride (MA)	0.036
Bromomaleic anhydride (BMA)	0.103
Chloromaleic anhydride (CMA)	0.15

The spectra of methine C3 carbons are shown in Fig.4.3.1 where the resonance of the C3 carbon appears very similarly in the MA-ST copolymer and the MI-ST copolymer at around 54-50ppm, sharply in the BMA-ST copolymer at 50.8-49.6ppm, widely spreaded in the CA-ST copolymer at 59-50ppm and both widely spreaded and quite down field shifted in the DCMA-ST copolymer at 82.5-75.5ppm. The difference reflects the chemical structure of the acceptor monomer units in their copolymers with ST; The resonance of the C3 carbon, which is next to chlorine atom (in the DCMA-ST copolymer) is shifted down field while the resonance of the methine(CH) C3 carbon of the other copolymers seem to be not shifted and they all appear at around 60-50 ppm.

All the four copolymers of MA-ST, CA-ST, BMA-ST and DCMA-ST have a very comparable mole fractions of the *cis* linkage configuration (F_{cis}) which are determined to be around 0.54-0.59 (Tab.4.3.1). As mentioned above the large electronegativities of Cl and Br atoms would increase the electron accepting character of MA in its lowest unoccupied molecular orbital (LUOMO) and, possibly, stronger complexations between ST and BMA and between ST and DCMA are formed. The larger size of Cl- and Br- atom compared to a hydrogen (H) atom may create a steric hindrance when the complex tries to be added to a growing radical, resulting in a slower copolymerisation rate. It is interesting to find that the anhydride monomers, which are the derivatives of MA, copolymerise with ST to give copolymers in which the proportion of the cis linkage configurations of the cyclic anhydride monomer units is very comparable each other ranging between 0.54 and 0.59. This may indicate that the propagation mechanism is very similar each other in the copolymerisation of ST with MA derivatives.



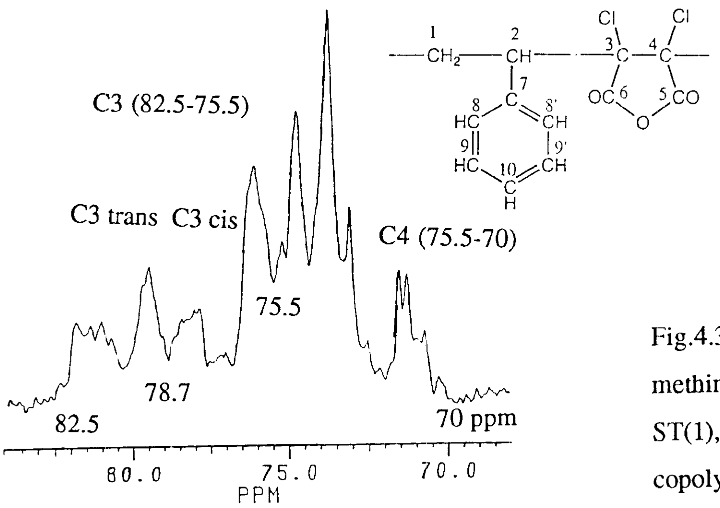


Fig.4.3.1 DEPT ^{13}C NMR subspectra of methine(CH) C3 of MA(0)-ST(1), CA(0)-ST(1), BMA(0)- ST(1) and MI(0)-ST(1) copolymer. Quaternary ^{13}C NMR spectra of C3 and C4 of DCMA(0)-ST(1) copolymer.

The mole fraction of the *cis* linkage configuration in the fully alternating maleimide(MI)- styrene(ST) copolymer is found to be 0.305 , which is much smaller than that in the MA-ST alternating copolymer (F_{cis}=0.59).

The spectra used for the determination of the mole fraction of the *cis* linkage configuration (F_{cis}) are shown in Fig.4.3.2 and the values of F_{cis} are collected in Tab.4.3.2 for copolymers of maleic anhydride (MA) with various aromatic donor comonomers; *trans*-stilbene (STI), α -methylstyrene (MST) and allylbenzene (AB).

Tab.4.3.2. Mole fraction of *cis* linkage configuration of the cyclic MA (0) units (F_{cis})in copolymer of MA with several aromatic donors: styrene (ST or 1), *trans*-stilbene (STI or 1), α-methylstyrene (MSt or 1) and allylbenzene (AB or 1). F_{cis} determined by DEPT ^{13}C NMR CH suspectra of C3 except MA-STI copolymer.

[0+1] / Solvent /T/ f_0	e-Q scheme values of monomer 1 e	Q	K (l/mol) (solvent/T/method)	F_{cis}
[MA+ST]=4M / DMF / 50°C/ 0.5	- 0.80	1.00[50 75]	0.208 (CCl_4/23°C/UV) 0.035 (DMF/23°C)*	0.586
[MA+STI]=1.5M / MEK / 60°C/ 0.6	- 0.08	0.03 [50]	0.15($CHCl_3$/25°C/NMR) [77] 2.02(THF/25°C/NMR) [77]	0.549 a) 0.577 b)
[MA+MST]=4M / MEK / 50°C/ 0.6	- 1.27	0.98 [50]	0.23 (CCl_4/27.5°C/NMR) [79]	0.465
[MA+AB]=3M / MEK / 60°C/ 0.5 0.6	+ 0.40	0.038 [75]		0.754 0.733

f_0= Mole fraction in feed of MA (0) [0+1]= Total monomer concentration
a) = determined by quaternary C(5+6) of MA units in fully alternating MA-STI copolymer
b) = C(17+27) of STI
K= Equilibrium constant of comonomer complexation (in solvent/ at temperature/ determined by the method)
* estimated by an exptrapolation.

The MA and STI should create a fully alternating copolymer at every monomer ratio [77,78] since both MA and STI do not homo polymerise. The structures of MA and STI are both symmetrical. The ^{13}C NMR spectra of the copolymers of MA and STI show a strongly overlapped lump of methine chain carbons, C1 and C2 carbons of the STI units and C3 and C4 carbons of the MA units. However the peaks of the "next to chain" quaternary carbons of both carbonyl C(5+6) and aromatic C(17+27) carbons show very

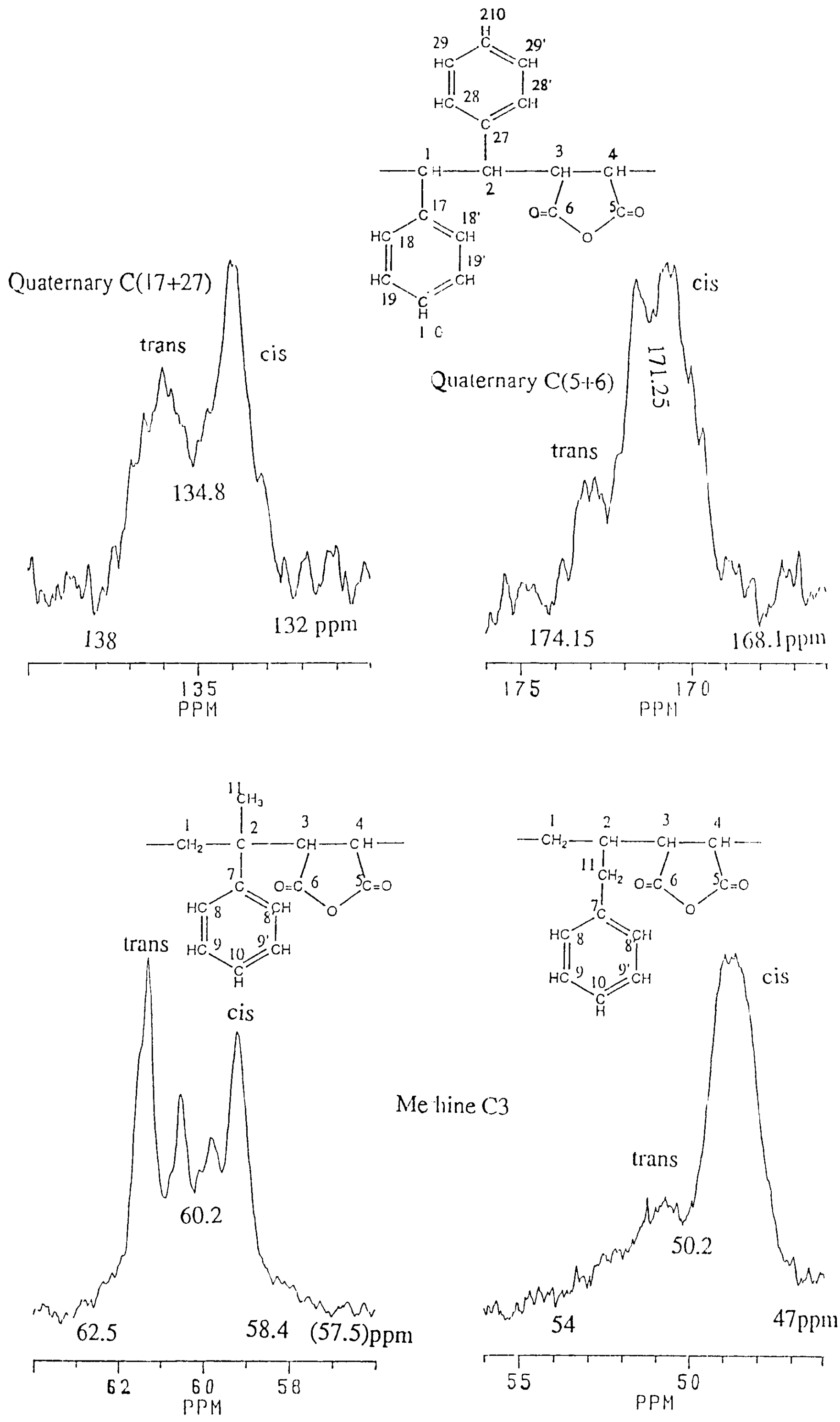
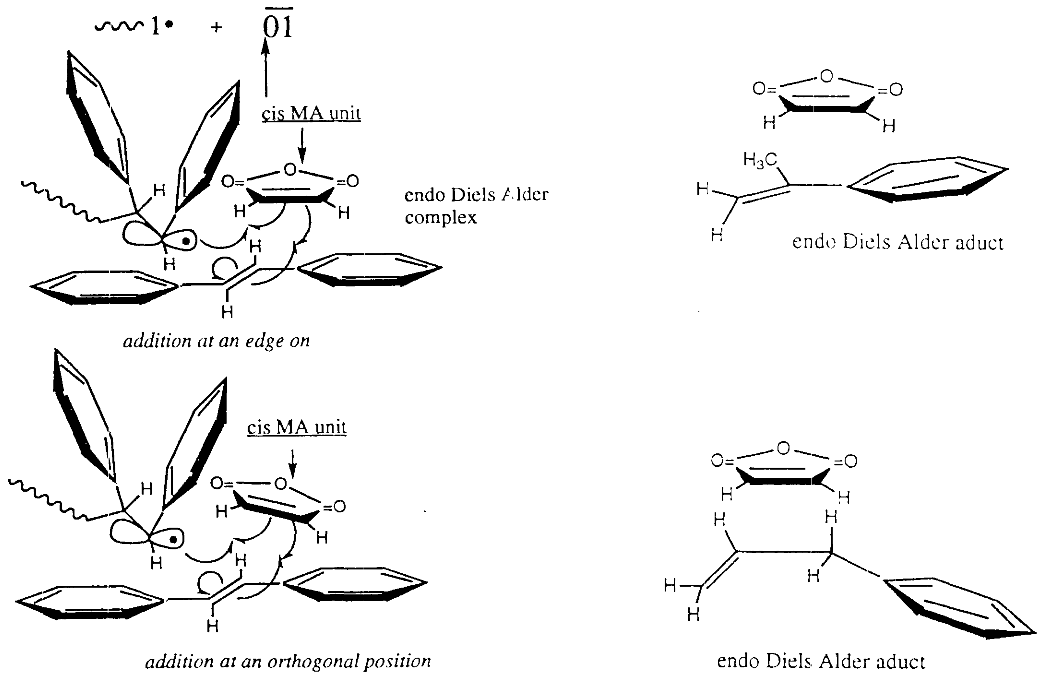


Fig.4.3.2. Quaternary ^{13}C NMR spectra of C(17+27) and C(5+6) of MA(0)-STI (1) copolymer. DEPT ^{13}C NMR subspectra of methine(CH) C3 of MA(0)- MST(1) and MA(0)-AB(1) copolymer.

clear splits indicating the *cis* and *trans* linkage configurations at the cyclic MA units in MA-STI copolymers, which is consistent with what has been reported by Butler et al.[31] for MA-ST copolymers. The mole fraction of the cis configuration in the STI-MA copolymer is determined to be F_{cis}=0.57±0.02, which is very comparable to the F_{cis} of the strong alternating copolymers of MA and ST, where F_{cis} is determined to be between 0.51 and 0.64. When the alternating copolymer is formed majorly by the complex addition, the inserting addition of a ST radical in between the comonomer complex would be the main cause of the greater amount of the *cis* linkage configuration in the MA-STI copolymers. Looser coordinative endo Diels Alder adduct of MA and STI compared to that of MA and ST is expected due to the smaller negative e value of STI (e=-0.08) than that of ST(e=-0.80). Looser MA-STI complex compared to MA-ST complex would even favour this kind of inserting addition (Scheme 8).

Scheme 8 : The most likely propagating reactions leading to the *cis* linkage configuration at the cyclic MA units in MA-*trans* stilbene copolymer. The coordinative endo Diels Alder adducts formed by MA-α-methylstyrene and MA-allylbenzene



α-Methylstyrene (MST) may be a stronger donor than ST due to its greater negative e value[50]. MST forms a marginally stronger complex with MA. Its *K* value (0.23 l/mol in

CCl_4)[79] is only slightly larger than that of ST (K=0.21 l/mol in CCl_4)[this work]. The bulky α-methyl substituent (Scheme 8) may hinder an orthogonal addition of the MST polymer radical in between the MA-MST complex. That conveniently explains for the lower F_{cis} of 0.465 in the MA-MST copolymer while, F_{cis} is found to be between 0.51 and 0.64 in the MA-ST copolymers, which are almost completely alternating .

The steric hindrance in the MA-allylbenzene (AB) endo Diel Alder complex is much smaller than that in the MA-ST complex due to the structure of AB (Scheme 8). The C=C double bond is not directly bonded to the aromatic ring but by a methylene (CH_2) carbon. The smaller steric hindrance in the MA-AB complex may allow more efficient inserting addition by the propagating AB radical in between the MA-AB complex resulting in a higher amount of the *cis* linkage configuration of F_{cis} ,which is found to be 0.74±0.01.

Tab.4.3.3. Mole fraction of *cis* linkage configuration of the cyclic MA (0) units (F_{cis}) in copolymers of MA with 2-chloroethyl vinyl ether (CEV or 1) and with *n*- butyl vinyl ether (BVE or 1). F_{cis} determined by DEPT ^{13}C NMR CH spectra of C3 and C4.

[0+1] / Solvent /T/ f_0	e-Q scheme values of monomer 1: e	Q	K (l/mol) (solvent/T/method)	F_{cis} determined by C3	C4
[MA+ST]=4M/ DMF/ 50°C/ 0.5	- 0.80	1.00[50,75]	0.208 (CCl_4/23°C/UV)	0.586	
			0.035 (DMF/23°C)*		
			0.336(n-Hexan/30°C/NMR)[11]		
[MA+CEV]=4M/ MEK/ 50°C/ 0.5	- 1.64	0.019[75]	0.105($CHCl_3$/25°C/NMR)[80]	0.415	0.456
0.9			0.295(n-Hexan/30°C/NMR)[11]	0.444	0.428
[MA+BVE]=2.25M/ MEK/ 50°C/0.4	- 1.5	0.038[75]	0.56(CCl_4/20°C/UV) [81]	0.455	0.475
	- 1.2	0.087[50]	0.3 (CCl_4/37°C/NMR) [82]		

f_0= Mole fraction in feed of MA (0) [0+1]= Total monomer concentration
K= equilibrium constant of comonomer complexation (in solvent/ at temperature/ determined by the method)
* estimated by an extrapolation.

The mole fractions of *cis* linkage configuration (F_{cis}) in the MA(0)- chloroethyl vinyl ether (CEV (1)) and in the MA(0)- n-butyl vinyl ether (BVE (1)) copolymers were determined and the results are shown in Tab.4.3.3. The spectra of methine C3 and C4 carbons, which were used for the determination of amount of the *cis* linkage configurations, are shown in Fig.4.3.3. The resonance of the C4 carbon splits very clearly into two peaks which are corresponding to the *cis* and *trans* linkage configurations at the cyclic MA units in these two copolymers, while the resonance of C3 carbon seems to be composed of overlapping multiplets of the *cis* and *trans* linkage configurations, where the border between the *cis* and *trans* peaks is estimated to be around 50.8 ppm. Despite the differences in appearance of the spectra of carbons C3 and C4 , the F_{cis} was determined for both copolymers from both the C3 and the C4 spectra to the values of 0.44±0.04 in MA-CEV copolymer and 0.46±0.04 in MA-BVE copolymer. The values of F_{cis} of the copolymer of MA and vinyl ether monomers are thus found to be very similar.

The Alfrey-Price e values of CEV and BVE are both negative and greater than that of ST. That means CEV and BVE are more strongly polarised donor than ST. The e values also imply that CEV is less negatively polarised than BVE. However, as noticed above (Section 4.1) the chemical property of the monomers may play a more important roll in copolymerisation than the concentration of the copolymer complex. Butler et.al.[33-35] suggested the addition of a propagating radical on the inner side of the complex that is *syn* to vinyl ether in the copolymerisation of N-phenyl maleimide(NPM)- 2-chloroethyl vinyl ether (CEV) and in the copolymerisation of N-phenyl citraconimide (NPC)- CEV copolymerisation. Similarly, Brown et al.[40] proposed an orthogonal addition of ST polymer radical on the MA side of the MA-ST complex. The formation of the *cis* linkage configuration in the MA-CEV copolymer and in the MA-BVE copolymer can be explained by a similar mechanism (Scheme 9). A propagating vinyl ether radical attacks the MA side on the orthogonal position of the MA-vinyl ether complex followed by the concerted addition of the MA molecule to its vinyl ether partner in the MA-vinyl ether complex would provide the major amount of the cis linkage configurations. However, the mole fraction of *cis* linkage configuration of 0.44±0.04 in the MA-CEV copolymers and that of 0.46±0.04 in MA-BVE copolymer are smaller than that in the alternating MA-ST copolymer in which F_{cis} has been determined to be 0.57±0.06. Because the vinyl group of the vinyl ethers are not conjugated with a phenyl group like in ST molecule, an orthogonal attack on the EDA

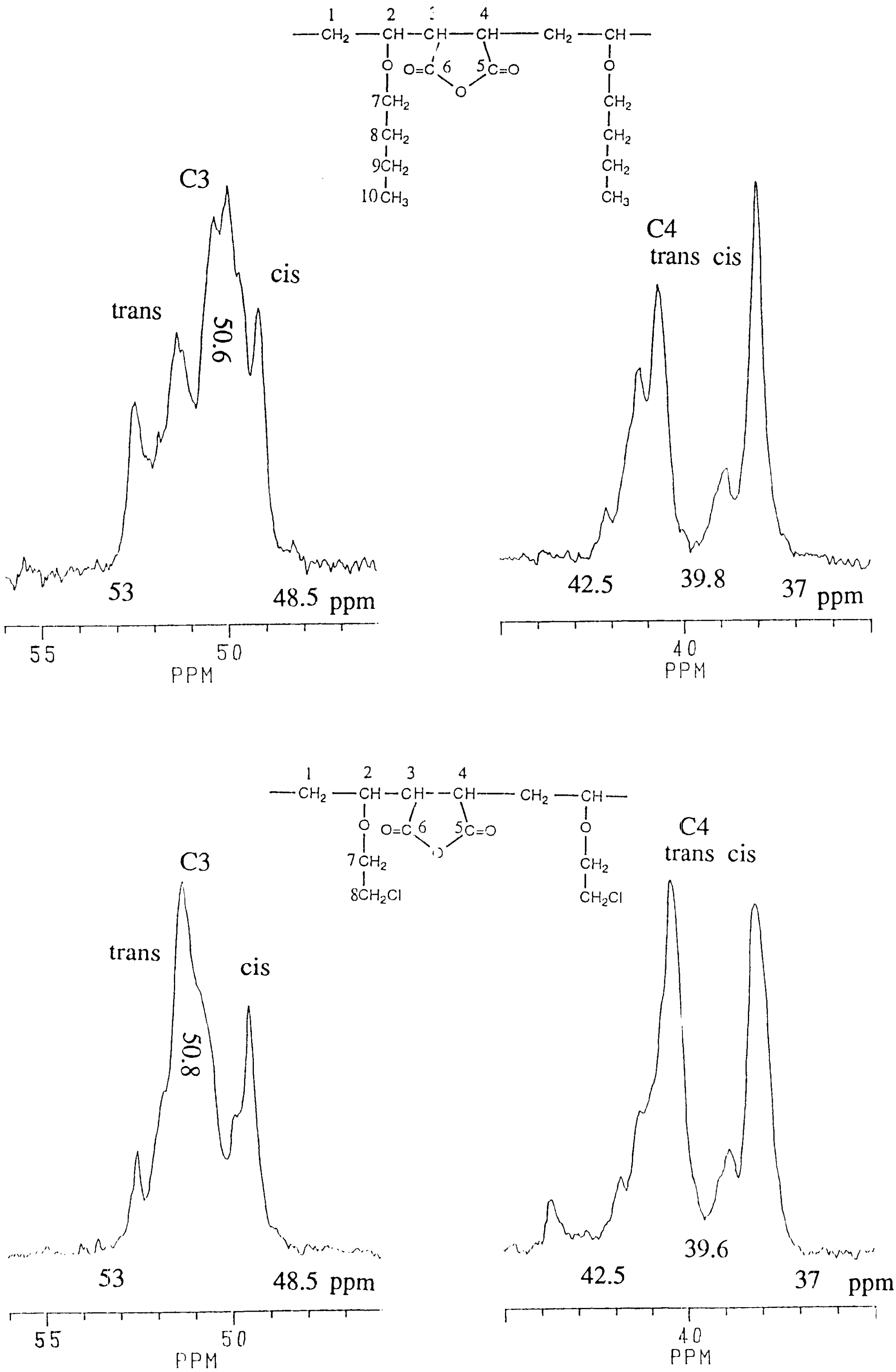
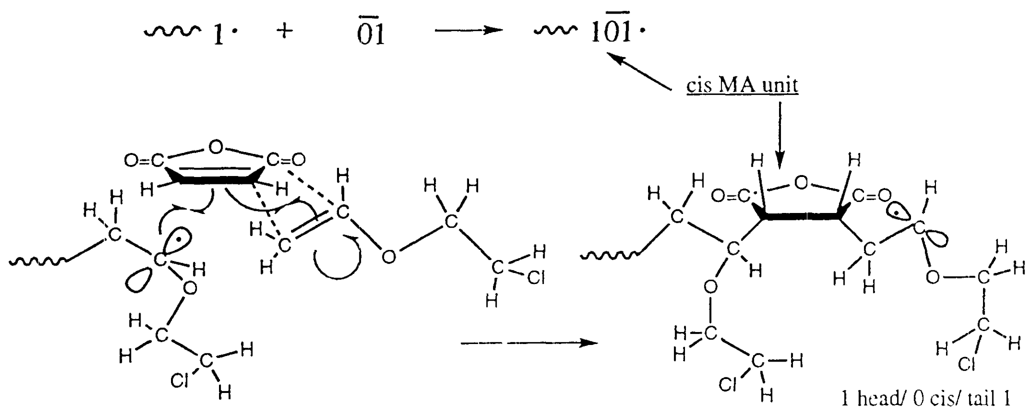


Fig.4.3.3 DEPT ^{13}C NMR subspectra of methine(CH) C3 and C4 of MA(0)- CEV(1) and MA(0)-BVE(1) copolymer.

complexes may be less likely for MA-vinyl ether complexes as compared with the complex of MA and ST. This may explain the smaller F_{cis} in the alternating MA-CEV copolymers and the MA-BVE copolymers compared to the F_{cis} in MA-ST copolymers.

Scheme 9 : The most likely propagating reactions leading to the *cis* linkage configuration at the cyclic MA units in MA-2-chloroethyl vinyl ether copolymer.



5. Conclusion

The copolymer of styrene (ST or 1) and maleic anhydride (MA or 0) would be more thermodynamically stable in less hindered *trans* linkage configuration at the cyclic MA units than in the *cis* linkage configuration. Kinetically, a free monomer or a comonomer complex when adding to a propagating polymer radical will approach the *trans* position of the radical to the polymer chain with smaller activation energy rather than the higher activation energy approach to the *cis* position of the radical. This will form the less sterically hindered *trans* linkage configurations at the MA units in the copolymer. In this experiment, the copolymers of ST with MA and of ST with CA were found to form more *cis* linkages than *trans* linkages at the MA or CA units. A mechanism in which a propagating ST polymer radical attacks at the orthogonal position and/or at an edge-on position followed by a concerted addition of the ST molecule to its MA partner within the complex, is the most likely explanation for the alternating copolymerisation of ST with MA or ST with CA. The non linear least squares (NLLS) curve fitting and the test functions on the triad sequence distribution data indicate the participation of the comonomer complexes. The high content of the *cis* linkage configuration at the anhydride cyclic units in the copolymers strongly supports this complex addition propagation mechanism. The content of the *cis* linkages of the several other related alternating copolymers such as the copolymers of MA with *trans*-stilbene, α-methylstyrene or allylbenzene, the copolymers of ST with MA derivatives such as bromomaleic anhydride or dichloromaleic anhydride and the copolymers of MA with vinyl ether such as 2-chloroethyl vinyl ether or n-butyl vinyl ether indicate the similar complex addition propagation mechanism.

The evidence for a participation of the EDA complex in the alternating copolymerisation studied here is summarised below.

Copolymers of MA-ST are found to be rigidly alternating copolymers when prepared with the MA mole fraction in feed (f_0) is greater than 0.20 in CCl_4 and when f_0 is greater than 0.40 in DMF due to the higher concentration of MA-ST comonomer complex in nearly non polar CCl_4 compared to the concentration of MA-ST complex in highly polar DMF. The NLLS curve fitting to the experimental alternating triad mole fractions and the examination by the test functions on the triad distribution data imply that the complex participation model is the most applicable model for the MA-ST copolymerisation carried out in both CCl_4 and DMF.

The CA copolymerised with ST only sluggishly and formed the rigidly alternating copolymers only when the mole fraction of CA in feed f_0 was extremely high close to 0.90-0.95 in CCl_4 . Most copolymers of CA and ST were only semi alternating copolymers. The copolymers of ST and CA were slightly more alternating when prepared in CCl_4 compared with those prepared in DMF. The difference in solvent effect was found to be much less pronounced for the ST-CA copolymerisation system than for the ST-MA copolymerisation system, probably due to the smaller extent of complexation for ST and CA (the smaller K value than for ST and MA). The complex participation model, the complex dissociation model and the comppen model were fitted better to the experimental data than the terminal model and the penultimate unit effect model were. The complex participation model appeared to be slightly more applicable than other models for the CA-ST copolymerisation in CCl_4 than in DMF according to the test functions.

The mole fraction of the *cis* linkage configuration at the cyclic MA units (F_{cis})in the MA-ST copolymers increased along with the MA mole fraction in feed (f_0) when f_0 was less than 0.30 and then it appeared to reach a constant when f_0 was greater than 0.30. An average value of F_{cis} =0.57±0.07 was determined for the f_0 range of 0.20-0.90. The effect of the solvent polarities on the constant value of F_{cis} was negligible between the copolymers prepared in CCl_4 and those prepared in DMF. Ten alternating MA-ST copolymers prepared in ten different solvents of the different polarities ranging from CCl_4 with the dielectric constant ε=2.24 to DMF with ε=36.7 showed a reasonably constant value of F_{cis}=0.58±0.07 regardless the solvent.

The mole fraction of the *cis* linkage configuration at the cyclic CA units in the CA-ST copolymers (F_{cis}) seemed to be not affected by the solvent polarities of either CCl_4 or DMF. F_{cis} increased along with CA mole fraction in feed (f_0) when the f_0 in feed was smaller than 0.15 and then seemed to approach to a constant value when the f_0 was greater than 0.15. An average value of F_{cis}=0.58±0.06 was determined for the f_0 range of 0.15-0.95.

More than half of the linkages at the cyclic MA units or CA units in MA-ST copolymers or CA-ST copolymers, respectively, were found to be in the *cis* configuration . One most likely mechanism leading to the large amount of the *cis* linkages is that a propagating ST radical attacks the MA(0) or CA(0) side of a MA-ST or CA-ST complex (01) at an orthogonal position and/or at an edge-on position followed by a concerted addition of the ST molecule to its MA partner within the complex .

The effect of the solvent polarities appeared to be dominated by the chemical properties of the comonomers in the alternating copolymerisation of MA and ST and of CA and ST.

The values of F_{cis} of several related copolymers supported the above described mechanism in which the complex addition was indicated by the large amount of the *cis* linkage configurations (F_{cis}=0.57 and F_{cis}=0.58 for MA-ST copolymers and CA-ST copolymer, respectively). The copolymer of MA and *trans*-stilbene had a similar F_{cis} of 0.565 implying that they were formed by a similar mechanism. The value of F_{cis} =0.465 of MA-α-methylstyrene copolymer and a little larger value of F_{cis}=0.73-0.75 in the MA-allylbenzene copolymer could be explained by the difference in the steric hindrance in the complex addition . The copolymer of ST and MA, and the copolymers of ST and various derivatives of MA (i.e., citraconic anhydride (CA), bromomaleic anhydride (BMA), dichloromaleic anhydride (DCMA)) showed the very comparable F_{cis} value of around 0.54-0.59 which indicated very similar propagating mechanisms of the inserting additions of a propagating radical in between the comonomer complexes in the copolymerisations of these monomers. For the alternating copolymer of ST-maleimide the F_{cis} value was determined to be 0.305. For the copolymer of MA and chloroethyl vinyl ether and that of MA and n-butyl vinyl ether the F_{cis} values were determined to be 0.44 ± 0.04 and 0.46 ± 0.04, respectively.