Chapter 1. Introduction

Background

Since copolymers provide more interesting chemical and physical properties with respect to the homopolymers due to their combination of two or more monomers, they attract polymer chemists to investigate the mechanism of their formation.

One system where the copolymerisation mechanism is not fully understood is the alternating radical copolymerisation of maleic anhydride (MA or 0) and styrene (ST or 1). ST is readily homopolymerised to form poly(styrene), whilst MA monomer is universally recognised not to be homopolymerised[1]. A most likely explanation for the low tendency of homopolymerisation of MA is due to the electron deficient nature of the carbon-carbon double bond in MA [2]. In other word, MA is recognised to be as a powerful electron acceptor [3], which tends to copolymerise with an electron donor monomer easily. In the MA-ST copolymerisation system, when a growing polymer ending with a MA reacts with a ST monomer or a growing polymer ending with a ST radical reacts with a MA monomer, the resulting copolymer chain will be alternating (~~01010101~~). Because ST polymerises with itself, several ST units may attach to each other before a ST ending polymer radical cross-propagates with a MA monomer. This process results in semi-alternating (~~1101011~~) and non-alternating (~~1111~~) copolymer sequences. Other examples of alternating copolymerisation include the systems of MA with *trans*-stilbene(STI), MA with a substituted styrene (such as *p*-methoxystyrene or *p*-chlorostyrene), MA with α-methylstyrene (MST), MA with allylbenzene(AB), ST with derivatives of MA such as citraconic anhydride (CA), bromomaleic anhydride (BMA), dichloromaleic anhydride (DCMA) and difluoromaleic anhydride .

The MA-ST copolymerisation system has been the most thoroughly investigated [4] copolymerisation system. Mayo and Lewis [5] proposed what is now called the terminal model in order to explain the overall copolymer composition. Alfred et al. [6] and Merz et al.[7] then proposed the penultimate unit effect model as an alternative model. They

assumed that the penultimate unit in the growing chain had a significant influence on the reaction with an incoming monomer. Barb [8] applied the effect of the penultimate unit of a copolymer radical for describing the copolymerisation mechanism . Barlett and Nozaki [2] proposed an involvement of a 1:1 donor-acceptor complex in the mechanism of such alternating copolymerisation system as the system of MA with ST. Seiner and Litt [9] derived an equation for the overall copolymer composition of copolymers by taking into account of a participation of comonomer donor-acceptor complexes into the copolymerisation process. Tsuchida et al.[10,11] proposed that the complex of MA and ST participated in the propagation reactions in non or less polar solvents in the copolymerisation of MA with ST. They [10] also suggested that repulsive interaction between MA chain-end radical and MA in complex was possible cause for the dissociation of the complex during the propagation. Dodgson and Ebdon [12,13] studied the effects of solvents with widely varied dielectric constants on the resulting MA-ST copolymers which were prepared in bulk and in solutions. They concluded that the penultimate effect was favoured over a complex-participation in describing the copolymerisation mechanism. Hill, O'Donnell and Sullivan [14] applied both the penultimate and the complex-participation models when studying the triad sequence distribution of MA-ST copolymer prepared in bulk copolymerisation at 60°C. The sequence distribution in the copolymer were studied by the Distortionless Enhancement by Polarisation Transfer (DEPT) [13]C Nuclear Magnetic Resonance (NMR) spectroscopy[15]. Brown et al.[16] found that the complex participation model was best fit for the triad sequence data in the copolymerisation of p-methoxystyrene and MA, while both the penultimate and the complex participation models seemed to describe the copolymerisation of p-chlorostyrene with MA equally well.

In an effort to incorporate the penultimate unit effect in the complex participation model, Brown et al. [17] combined these two models in a new model called the "comppen model".

Studying "pulsed laser copolymerisation" of styrene and maleic anhydride, Sanayei, O'Driscoll and Klumperman [18] concluded that the penultimate unit effect model best described the copolymerisation.

Seymour and Garner [19,20] have studied the temperature effects on the copolymerisation of MA with ST, MST, vinyl acetate and acrylonitrile. They suggested that below 80°C the complex of MA with ST and with MST played a dominant roll resulting in alternating copolymers, while above this temperature, because the concentration of the complex became negligible, copolymerisation occurred only via the free monomer resulting in random copolymers.

Tsuchida et al. [11] reported the overall rate of the copolymerisation of ST and MA at 70°C to be much greater in less polar solvents (CCl$_4$ or benzene), the rate becoming a maximum value at the equal comonomer concentrations of ST and MA in feed although the copolymerisation rate of ST and MA in polar solvent (acetone or tetrahydrofuran (THF)) monotonously increased with increasing MA composition in feed.

Javni, Fles and Vukovic[21], by using Shirota's [22,23] method, studied the initial overall rate of the copolymerisation of MA with MST in butanone (MEK) and in benzene. They analysed the overall rate of the copolymerisation as a sum of the propagation rate due to the free monomer addition and the propagation rate due to the addition of the charge transfer complex formed between the comonomers. They reported that the propagation rate due to the addition of the charge transfer complex contributed to a major extent to the overall propagation rate in a non polar solvent such as benzene. The propagating rate due to the addition of the comonomer complex tended to dominate the propagating rate due to the free monomer addition more prominently when the total comonomer concentration in feed mixture is larger. A similar result has been reported for the copolymerisation of ST with MA when the total comonomer concentration in feed is 0.5-2.0M in MEK[24].

Vukovic et al.[25,26] have reported that the overall rate of alternating copolymerisation of ST with MA was definitely larger than first order with respect to the total monomer concentration. That is consistent with the participation of a 1:1 electron donor-acceptor (EDA) complex in the propagation step, while the penultimate unit effect

model based on the free monomer additions should give a first order dependency of the rate on the total monomer concentration.

In addition to the kinetic method, the investigation of copolymerisation mechanism has been largely based on the non lineai least squares (NLLS) model fitting analysis, which had been developed by Hill and O'Donnell on the overall copolymer composition data and on the comonomer unit sequence distribution data [14,27,28,29]. However, when this analysis is applied to alternating and semi alternating copolymerisation systems any difference among the copolymerisation models disappears, the monomer unit sequence being rigidly alternating in perfectly alternating copolymers.

Butler and his co-workers suggested that there must be a structural evidence in the resulting MA-ST copolymers if a monome -monomer complex actually participated in the copolymerisation[30,31].

Olson and Butler [32-35] found that the stereochemistry of the copolymers formed by various N-substituted maleimides and several vinyl ethers, was markedly dependent on the copolymerisation conditions. According to the theory by Muliken[36] the maximum stabilisation of a charge-transfer complex is to be expected if a complex adopts a conformation in which there is a maximum overlap between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molercular orbital (LUMO) of the acceptor molecule. It is therefore conceivable that if a complex adds to a radical chain end in a concerted manner (as opposed to a stepwise addition of the monomers), then a certain amount of siereo regularity may be introduced into the copolymer chain and the stereoregularity may be related to the extent of the complex participation in the propagation reactions[30].

Because the EDA complexation is primarily a polar association of two very polarised monomers, the polarity of the solvent affects the equilibrium constant of the complexation (K); in a more polar solvent the magnitude of the K is smaller.

$$\text{Donor (D)} + \text{Acceptor (A)} \underset{}{\overset{K}{\rightleftharpoons}} \text{Complex (D-A)}$$
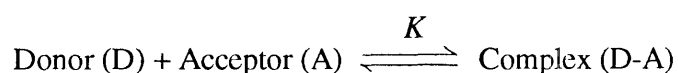
Because the complexation process is slightly exothermic, the magnitude of the K becomes smaller at a higher temperature.

Considering the Mulliken theory Butler et al.[35] proposed a mechanism, which involved with an attack by a polymer radical on the side of the monomer complex that is *syn* to the vinyl ether component of the complex to rationalise the stereochemical features of N-substituted maleimide- 2-chloroethyl vinyl ether (CEV) copolymers. From the study of the stabilisation energy of the MA-ST complexation, the authors showed [31] that the Diels-Alder geometry was more stable than the geometry of the [2+2] cyclo addition and that the geometry of the 1:1 adduct formed by an *endo* approach in the Diels-Alder geometry mode was more stable than that of an *exo* approach. The authors also proposed that, the link between the alternation of the monomer units and the stereo regularity in the copolymers would imply an important aspect for the propagating mechanism of the copolymerisation [30,31,35].

The copolymerisation of the citraconic (or α-methylmaleic) anhydride (CA) and ST was studied in $CHCl_3$ [37] and in MEK [38,39]. The complex participation model was shown to best describe the copolymerisation of ST with CA in MEK [38,39].

Purpose of this project

In order to examine the mechanism of a typical alternating copolymerisation system of ST with MA, the copolymerisation of ST with MA and the copolymerisation of ST and CA are studied in this thesis for the monomer unit triad sequence distribution and the linkage configurations at the cyclic anhydride units in the copolymers . Nearly non polar carbon tetrachloride (CCl_4) and the highly polar N,N-dimethylformamide (DMF) were used as the solvents for the copolymerisation of MA with ST and that of CA with ST to study the solvent effects on the alternating tendency and on the formation of the *cis/trans* linkage configurations at the cyclic anhydride units in the copolymers.

The applicability of five models, the terminal model, the penultimate unit effect model, the complex participation model, the complex dissociation model and the comppen model, to the triad sequence distribution data is examined for the copolymerisation of MA with ST and that of CA with ST. As suggested by Butler et al.[30,31] the stereo regularity in

amount of the *cis/trans* linkage configurations at the cyclic anhydride units is quantitatively determined. The microstructure of the copolymers is determined by ^{13}C NMR spectroscopy. The triad fractions are determined by the methylene DEPT ^{13}C NMR sub spectra of the CH_2 carbon in MA-ST copolymers following the reported method[15,40-43]. The methine DEPT ^{13}C NMR sub spectra of the CH carbon of MA units in MA-ST copolymers are used to determined the relative amounts of *cis/trans* linkage configurations at the cyclic MA units [41,42,44]. In CA-ST copolymers the quaternary ^{13}C NMR spectra of the aromatic "next to chain" carbon of ST units [39,45-48] and the quaternary "chain" carbon of MA units [38,41,44,46,47] are used to determine the ST centred triad fractions and the mole fractions of the *cis/trans* linkage configurations at the cyclic CA units, respectively.

The mole fraction of the *cis* linkage configuration at the cyclic anhydride acceptor monomer units is also determined for several other related copolymers in order to confirm the results found in the copolymers of MA-ST and CA-ST comonomer systems.

Chapter 2. Theory

Radical copolymerisation is considered to consist of initiation, propagation and termination reactions, of which only the propagation reactions influence the composition of the resulting copolymer and the distribution of monomer units within the copolymer chain[49,50] because it is the propagation step in which the polymer is formed. The rates of initiation and termination are assumed to become equal in a short time (*steady state assumption*), so that a constant radical concentration is quickly achieved[51]. This assumption is used to derive the differential forms of *composition equations*. Because the initial reaction conditions are used in the derivation of the equations, these equations are only applied for very *low conversions*. Furthermore, based on the likelyhood of a series of given propagation reactions (a kinetic-probabilistic basis), *transition probabilities* can be expressed in term of the reactivity ratios and the instantanous concentration of reacting components. The probability of selecting a monomer unit to enter a polymer chain can also be derived. From these relationships the *triad fraction equations* are formulated to describe the *sequence distribution* of monomer units within the copolymer chain.

Theoretical interpretations of copolymerisation mechanism have been often derived from different kinetic descriptions of the elementary propagating reactions. Five copolymerisation models have been worked out for the equations for the overall copolymer composition and for the triad mole fraction. These equations of the terminal model (model 1), penultimate unit effect model (model 2), complex participation model (model 3) and complex dissociation model (model 4) are summarised[48]. The derivation of the comppen model (model 5), a combination of the penultimate unit effect model and the complex participation model has been reported[17].
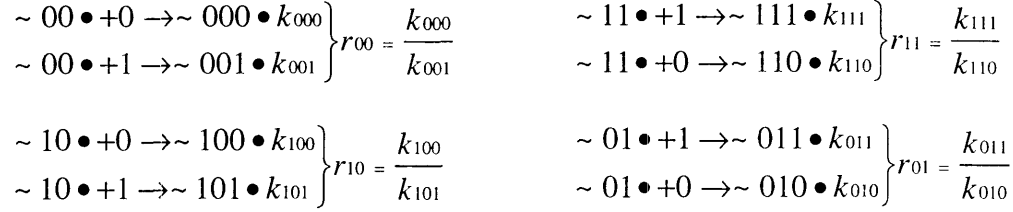
Scheme 1 presents the proposed propagating reaction and the definitions of the reactivity ratios of all five above mentioned models. The equations for the overall copolymer composition and the triad fraction according to these five models are presented in scheme 2. If one monomer, e.g., monomer 0 does not homopolymerise, some

<u>Scheme 1</u>: The propagating reactions and definitions of the reactivity ratios of the terminal-, penultimate unit effect-, complex participation-, complex dissociation- and comppen- copolymerisation models. 0 and 1 are the comonomers.
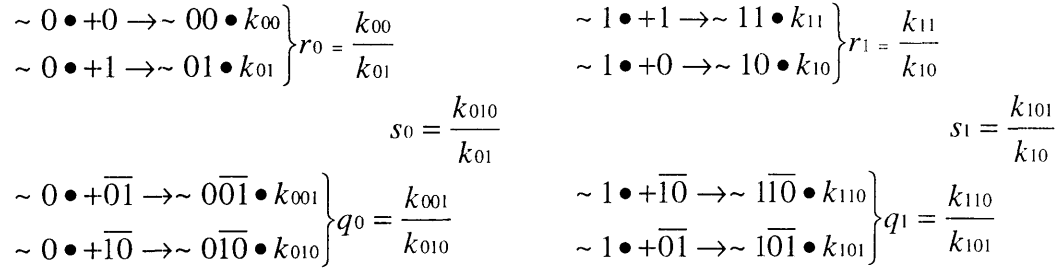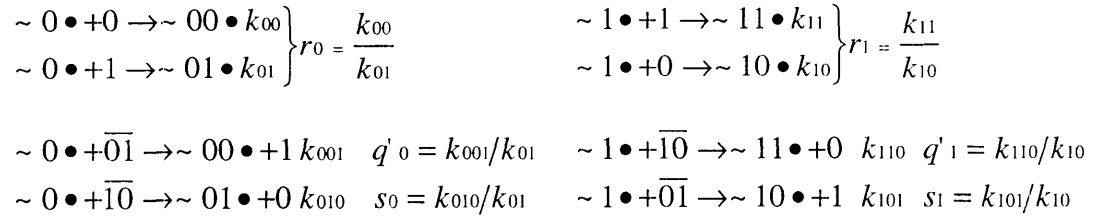
1. Terminal Model

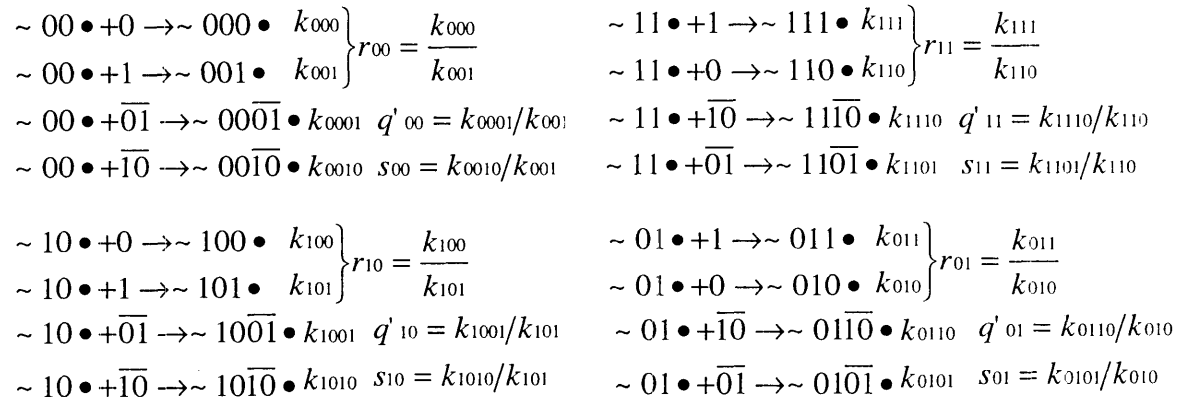$$\left.\begin{array}{l} \sim 0\bullet+0 \rightarrow \sim 00\bullet k_{00} \\ \sim 0\bullet+1 \rightarrow \sim 01\bullet k_{01} \end{array}\right\}r_0 = \frac{k_{00}}{k_{01}} \qquad \left.\begin{array}{l} \sim 1\bullet+1 \rightarrow \sim 11\bullet k_{11} \\ \sim 1\bullet+0 \rightarrow \sim 10\bullet k_{10} \end{array}\right\}r_1 = \frac{k_{11}}{k_{10}}$$

2. Penultimate Unit Effect Model

$$\left.\begin{array}{l} \sim 00\bullet+0 \rightarrow \sim 000\bullet k_{000} \\ \sim 00\bullet+1 \rightarrow \sim 001\bullet k_{001} \end{array}\right\}r_{00} = \frac{k_{000}}{k_{001}} \qquad \left.\begin{array}{l} \sim 11\bullet+1 \rightarrow \sim 111\bullet k_{111} \\ \sim 11\bullet+0 \rightarrow \sim 110\bullet k_{110} \end{array}\right\}r_{11} = \frac{k_{111}}{k_{110}}$$

$$\left.\begin{array}{l} \sim 10\bullet+0 \rightarrow \sim 100\bullet k_{100} \\ \sim 10\bullet+1 \rightarrow \sim 101\bullet k_{101} \end{array}\right\}r_{10} = \frac{k_{100}}{k_{101}} \qquad \left.\begin{array}{l} \sim 01\bullet+1 \rightarrow \sim 011\bullet k_{011} \\ \sim 01\bullet+0 \rightarrow \sim 010\bullet k_{010} \end{array}\right\}r_{01} = \frac{k_{011}}{k_{010}}$$

3. Complex Participation Model

$$\left.\begin{array}{l} \sim 0\bullet+0 \rightarrow \sim 00\bullet k_{00} \\ \sim 0\bullet+1 \rightarrow \sim 01\bullet k_{01} \end{array}\right\}r_0 = \frac{k_{00}}{k_{01}} \qquad \left.\begin{array}{l} \sim 1\bullet+1 \rightarrow \sim 11\bullet k_{11} \\ \sim 1\bullet+0 \rightarrow \sim 10\bullet k_{10} \end{array}\right\}r_1 = \frac{k_{11}}{k_{10}}$$

$$s_0 = \frac{k_{010}}{k_{01}} \qquad\qquad s_1 = \frac{k_{101}}{k_{10}}$$

$$\left.\begin{array}{l} \sim 0\bullet+\overline{01} \rightarrow \sim 0\overline{01}\bullet k_{001} \\ \sim 0\bullet+\overline{10} \rightarrow \sim 0\overline{10}\bullet k_{010} \end{array}\right\}q_0 = \frac{k_{001}}{k_{010}} \qquad \left.\begin{array}{l} \sim 1\bullet+\overline{10} \rightarrow \sim 1\overline{10}\bullet k_{110} \\ \sim 1\bullet+\overline{01} \rightarrow \sim 1\overline{01}\bullet k_{101} \end{array}\right\}q_1 = \frac{k_{110}}{k_{101}}$$

4. Complex Dissociation Model

$$\left.\begin{array}{l} \sim 0\bullet+0 \rightarrow \sim 00\bullet k_{00} \\ \sim 0\bullet+1 \rightarrow \sim 01\bullet k_{01} \end{array}\right\}r_0 = \frac{k_{00}}{k_{01}} \qquad \left.\begin{array}{l} \sim 1\bullet+1 \rightarrow \sim 11\bullet k_{11} \\ \sim 1\bullet+0 \rightarrow \sim 10\bullet k_{10} \end{array}\right\}r_1 = \frac{k_{11}}{k_{10}}$$

$$\sim 0\bullet+\overline{01} \rightarrow \sim 00\bullet+1\, k_{001} \quad q'_0 = k_{001}/k_{01} \qquad \sim 1\bullet+\overline{10} \rightarrow \sim 11\bullet+0\; k_{110}\quad q'_1 = k_{110}/k_{10}$$

$$\sim 0\bullet+\overline{10} \rightarrow \sim 01\bullet+0\, k_{010} \quad s_0 = k_{010}/k_{01} \qquad \sim 1\bullet+\overline{01} \rightarrow \sim 10\bullet+1\; k_{101}\quad s_1 = k_{101}/k_{10}$$

5. Comppen Model

$$\left.\begin{array}{l} \sim 00\bullet+0 \rightarrow \sim 000\bullet\ k_{000} \\ \sim 00\bullet+1 \rightarrow \sim 001\bullet\ k_{001} \end{array}\right\}r_{00} = \frac{k_{000}}{k_{001}} \qquad \left.\begin{array}{l} \sim 11\bullet+1 \rightarrow \sim 111\bullet\ k_{111} \\ \sim 11\bullet+0 \rightarrow \sim 110\bullet\ k_{110} \end{array}\right\}r_{11} = \frac{k_{111}}{k_{110}}$$

$$\sim 00\bullet+\overline{01} \rightarrow \sim 00\overline{01}\bullet k_{0001} \quad q'_{00} = k_{0001}/k_{001} \qquad \sim 11\bullet+\overline{10} \rightarrow \sim 11\overline{10}\bullet k_{1110}\quad q'_{11} = k_{1110}/k_{110}$$

$$\sim 00\bullet+\overline{10} \rightarrow \sim 00\overline{10}\bullet k_{0010} \quad s_{00} = k_{0010}/k_{001} \qquad \sim 11\bullet+\overline{01} \rightarrow \sim 11\overline{01}\bullet k_{1101}\quad s_{11} = k_{1101}/k_{110}$$

$$\left.\begin{array}{l} \sim 10\bullet+0 \rightarrow \sim 100\bullet\ k_{100} \\ \sim 10\bullet+1 \rightarrow \sim 101\bullet\ k_{101} \end{array}\right\}r_{10} = \frac{k_{100}}{k_{101}} \qquad \left.\begin{array}{l} \sim 01\bullet+1 \rightarrow \sim 011\bullet\ k_{011} \\ \sim 01\bullet+0 \rightarrow \sim 010\bullet\ k_{010} \end{array}\right\}r_{01} = \frac{k_{011}}{k_{010}}$$

$$\sim 10\bullet+\overline{01} \rightarrow \sim 10\overline{01}\bullet k_{1001} \quad q'_{10} = k_{1001}/k_{101} \qquad \sim 01\bullet+\overline{10} \rightarrow \sim 01\overline{10}\bullet k_{0110}\quad q'_{01} = k_{0110}/k_{010}$$

$$\sim 10\bullet+\overline{10} \rightarrow \sim 10\overline{10}\bullet k_{1010} \quad s_{10} = k_{1010}/k_{101} \qquad \sim 01\bullet+\overline{01} \rightarrow \sim 01\overline{01}\bullet k_{0101}\quad s_{01} = k_{0101}/k_{010}$$

<u>Scheme 2:</u> The equations for the overall copolymer composition and the triad sequence distribution according to the five copolymerisation models; terminal-, penultimate unit effect-, complex participation-, complex dissociation- and comppen models.

$$X_0 = \frac{[0]}{[1]} \approx \frac{[0]_0}{[1]_0} = \frac{f_0}{f_1}$$

molar ratio of 0- to 1-unit in <u>monomer mixture</u> at any instant, assumed to be equal the initial molar ratio of 0- to 1-unit in monomer feed mixture

$$Y_0 = \frac{d[0]}{d[1]} \approx \frac{F_0}{F_1}$$

molar ratio of 0- to 1-unit in <u>copolymer</u> formed at any instant is assumed to be equal the molar ratio of 0- to 1-unit in copolymer

$$X_1 = \frac{[1]}{[0]} \approx \frac{[1]_0}{[0]_0} = \frac{f_1}{f_0}$$

molar ratio of 1- to 0-unit in <u>monomer mixture</u> at any instant, assumed to be equal the initial molar ratio of 1- to 0-unit in monomer feed mixture

$$Y_1 = \frac{d[1]}{d[0]} \approx \frac{F_1}{F_0}$$

molar ratio of 1- to 0-unit in <u>copolymer</u> formed at any instant is assumed to be equal the molar ratio of 1- to 0-unit in copolymer

f_0, f_1 = Mole fraction of monomer 0 and monomer1 in <u>feed mixture</u>, $f_0+f_1=1$.

F_0, F_1 = Mole fraction of monomer 0 and monomer1 in <u>copolymer</u>, $F_0+F_1=1$.

Composition Equation

$F_0+F_1=1$

Triad distribution Equation

$F_{010}+F_{(011+110)}+F_{111} = 1$

1. Terminal Model

$$\frac{F_1}{F_0} = \frac{1+r_1.X_1}{1+r_0.X_0} \quad (1)$$

$$F_{010} = \frac{1}{(1+r_1.X_1)^2} \quad (2)$$

$$F_{(011+110)} = \frac{2.r_1.X_1}{(1+r_1.X_1)^2} \quad (3)$$

$$F_{111} = \frac{(r_1.X_1)^2}{(1+r_1.X_1)^2} \quad (4)$$

2.Penultimate Unit Effect Model

$$\frac{F_1}{F_0} = \frac{1+r_{01}.X_1.\dfrac{1+r_{11}.X_1}{1+r_{01}.X_1}}{1+r_{10}.X_0.\dfrac{1+r_{00}.X_0}{1+r_{10}.X_0}} \quad (5)$$

$$F_{010} = \frac{1}{1+2.r_{01}.X_1+r_{01}.r_{11}.X_1^2} = \frac{1}{D2} \quad (6)$$

$$F_{(011+110)} = \frac{2.r_{01}.X_1}{D2} \quad (7)$$

$$F_{111} = \frac{r_{01}.r_{11}.X_1^2}{D2} \quad (8)$$

3.Complex Participation Model

$$\frac{F_1}{F_0} = \frac{(1-P_{00}).(P_{10}+P_{110})+(1-P_{10}).(P_{01}+P_{001})}{(1-P_{11}).(P_{01}+P_{001})+(1-P_{01}).(P_{10}+P_{110})} \quad (9)$$

$$F_{010} = \frac{p_1(1^1).(1-P_{11})^2}{p_1(1^1).(1-P_{11})^2 + p_1(1^2).(2-P_{11})} = \frac{p_1(1^1).(1-P_{11})^2}{D3} \quad (10)$$

$$F_{(011+110)} = \frac{2.p_1(1^2).(1-P_{11})}{D3} \quad (11)$$

$$F_{111} = \frac{p_1(1^2).P_{11}}{D3} \quad (12)$$

Individual transition probabilities:

$P_{00} = \quad r_0.[0] /\Sigma 0$

$P_{01} = \quad [1] /\Sigma 0$

$P_{001} = q_0.s_0.[01] /\Sigma 0$

$P_{010} = \quad s_0.[01] /\Sigma 0$

$\Sigma 0 = r_0.[0]+[1]+(q_0+1).s_0.[01]$

$P_{00}+P_{01}+P_{001}+P_{010} = 1$

$P_{11} = \quad r_1.[1] /\Sigma 1$

$P_{10} = \quad [0] /\Sigma 1$

$P_{110} = q_1.s_1.[01] /\Sigma 1$

$P_{101} = \quad s_1.[01] /\Sigma 1$

$\Sigma 1 = r_1.[1]+[0]+(q_1+1).s_1.[01]$

$P_{11}+P_{10}+P_{110}+P_{101} = 1$

Probability of selecting a sequence of n units 1 :

$$p_1(1^1) = \frac{p_0}{P_{10}+P_{110}}.\left[(1-P_{11}).(P_{01}+P_{001}).(P_{10}+P_{101})+P_{010}.(P_{10}+P_{110})\right] \quad \text{for n=1} \quad (13)$$

$$p_1(1^n) = \frac{p_0.P_{11}^{(n-2)}}{P_{10}+P_{110}}.\left\{(1-P_{11}).(P_{01}+P_{001}).[P_{11}.(P_{10}+P_{101})+P_{110}]\right\} \quad \text{for n>1} \quad (14)$$

4.Complex Dissociation Model

$$\frac{F_1}{F_0} = \frac{p_1}{p_0} = \frac{P_{01}+P_{010}}{P_{10}+P_{101}} \quad (15)$$

$$= \frac{([1]+s_0.[01]).[r_1.[1]+[0]+(q'_1+s_1).[01]]}{([0]+s_1.[01]).[r_0.[0]+[1]+(q'_0+s_0).[01]]}$$

$$F_{010} = (P_{10}+P_{101})^2 \quad (16)$$

$$F_{(011+110)} = 2.(P_{11}+P_{110}).(P_{10}+P_{101}) \quad (17)$$

$$F_{111} = (P_{11}+P_{110})^2 \quad (18)$$

Individual transition probabilities for the state space of events:

$P_{00} = \quad r_0.[0] /\Sigma 0$

$P_{01} = \quad [1] /\Sigma 0$

$P_{001} = q'_0.[01] /\Sigma 0$

$P_{010} \quad s_0.[01] /\Sigma 0$

$\Sigma 0 = r_0.[0]+[1]+(q'_0+s_0).[01]$

$P_{00}+P_{01}+P_{001}+P_{010} = 1$

$P_{11} = \quad r_1.[1] /\Sigma 1$

$P_{10} = \quad [0] /\Sigma 1$

$P_{110} = q'_1.[01] /\Sigma 1$

$P_{101} = \quad s_1.[01] /\Sigma 1$

$\Sigma 1 = r_1.[1]+[0]+(q'_1+s_1).[01]$

$P_{11}+P_{10}+P_{110}+P_{101} = 1$

5.Comppen Model

$$\frac{F_1}{F_0} = 1 + \frac{p_1(1^3) + p_1(1^2)}{p_1(1^1) + p_1(1^2)} \quad (19)$$

$$F_{010} = \frac{p_1(1^1)}{p_1(1^1) + 2.p_1(1^2) + p_1(1^3)} = \frac{p_1(1^1)}{D5} \quad (20)$$

$$F_{(011 + 10)} = \frac{2.p_1(1^2)}{D5} \quad (21)$$

$$F_{111} = \frac{p_1(1^3)}{D5} \quad (22)$$

Probability of selecting a sequence of n units 1 :

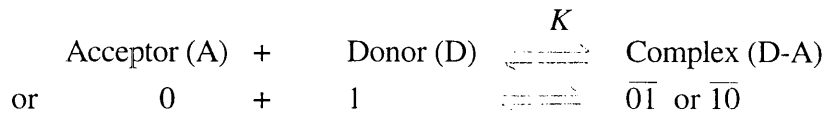$$p_1(1^1) = p_0.\{(P_{010} + P_{0101}) + [(P_{101} + P_{001}) + \alpha] + P_{1010} + P_{0010}\} \quad \text{for n=1} \quad (23)$$

$$p_1(1^n) = p_0.P_{111}{}^{n-2}.(P_{110} + P_{1101} + \frac{P_{0110}}{P_{011}}).P_{011}.(P_{101} + P_{001} + \alpha) \quad \text{for n>1} \quad (24)$$

$$\alpha = \frac{p_{01}}{p_0} = P_{1001} + P_{0001} + \frac{P_{1001} + P_{0001} + P_{101} + P_{001}}{P_{0110} + P_{1110} + P_{010} + P_{110}}.(P_{1101} + P_{1010}) \quad (25)$$

Individual transition probabilities for the state space of events:

$P_{000} = r_{00}.[0] / \Sigma 00$ $P_{111} = r_{11}.[1] / \Sigma 11$

$P_{001} = [1] / \Sigma 00$ $P_{110} = [0] / \Sigma 11$

$P_{0001} = q'_{00}.[01] / \Sigma 00$ $P_{1110} = q'_{11}.[01] / \Sigma 11$

$P_{0010} \quad s_{00}.[01] / \Sigma 00$ $P_{1101} = s_{11}.[01] / \Sigma 11$

$\Sigma 00 = r_{00}.[0] + [1] + (q'_{00} + s_{00}).[01]$ $\Sigma 11 = r_{11}.[1] + [0] + (q'_{11} + s_{11}).[01]$

$P_{100} = r_{10}.[0] / \Sigma 10$ $P_{011} = r_{01}.[1] / \Sigma 01$

$P_{101} = [1] / \Sigma 10$ $P_{010} = [0] / \Sigma 01$

$P_{1001} = q'_{10}.[01] / \Sigma 10$ $P_{0110} = q'_{01}.[01] / \Sigma 01$

$P_{1010} \quad s_{10}.[01] / \Sigma 10$ $P_{0101} = s_{01}.[01] / \Sigma 01$

$\Sigma 10 = r_{10}.[0] + [1] + (q'_{10} + s_{10}).[01]$ $\Sigma 01 = r_{01}.[1] + [0] + (q'_{01} + s_{01}).[01]$

The equilibrium constant of comonomer complexation (K):

$$\text{Acceptor (A)} \quad + \quad \text{Donor (D)} \quad \overset{K}{\rightleftharpoons} \quad \text{Complex (D-A)}$$

$$\text{or} \quad 0 \quad + \quad 1 \quad \rightleftharpoons \quad \overline{01} \text{ or } \overline{10}$$

$$K = \frac{[\overline{01}]}{[0].[1]} = \frac{[\overline{01}]}{([0]_0 - [\overline{01}]).([1]_0 - [\overline{01}])} \quad \text{or} \quad [\overline{01}]^2 - ([0]_0 + [1]_0 + \frac{1}{K}).[\overline{01}] + [0]_0.[1]_0 = 0$$

The complex concentration is calculated without any assumption (Seiner and Litt [9]):

$$[\overline{01}] = \frac{1}{2}\left[([0]_0 + [1]_0 + \frac{1}{K}) - \sqrt{([0]_0 + [1]_0 + \frac{1}{K})^2 - 4.[0]_0.[1]_0} \right] \quad (27)$$

reactivity ratios may be fixed to be zero These fixed values can be used for the initial estimates of the reactivity ratios for the non-linear least squares (NLLS) curve fitting of the theoretical equations to the experimental data . Scheme 3 (Appendix, Section 7.4) sumarises these restrictions.

The terminal model, proposed independently by Alfred and Goldfinger [6] and Mayo and Lewis [5], was the first to account for the different reactivities of two monomer involved in a copolymerisation. The reaction scheme consists of four propagation reactions with a rate constants (k) for each reaction. Two reactivity ratios (r) are defined as the ratio of the rate constant of the homopropagation and the rate constant of the crosspropagation of a polymer radical ending with monomer unit 0 or 1 (~0· and ~1·). The composition equation of this model is listed in scheme 2.

Merz, Alfred and Goldfinger[7] proposed the penultimate unit effect model, which took into account the effect of penultimate units of the growing chains on their reactivity with incoming monomers. Eight propagation reactions with eight rate constants (k) are considered in this model. Four reactivity ratios (r) are defined in a similar way to the terminal model, as the relative rate of the homo- to that of the cross-propagation for growing radical chains ending with ~00·, ~01·, ~11· or ~10· units. The composition equation was deduced.

Using probability theory, Ito and Yamashita [52] deduced the triad sequence distribution equations for the terminal and the penultimate unit effect model.

Cais, Farmer, Hill and O'Donnell [53] cescribed the complex participation model on the kinetic probabilistic basic. The comonomer complex addition was considered in the propagating reaction scheme. Eight propagation reactions with eight rate constants (k) were presented parallel with the eight individual transition probabilities (P). Six reactivity ratios (r) and the equilibrium constant (K)of the comonomer complexation composed the parameter set of this copolymerisation model. The composition and the triad fraction equations were derived without any restrictions.

Similarly, Hill., O'Donnell and O'Sullivan [29] designed the complex dissociation model. When a polymer radical attacks a comonomer complex , only one monomer of the complex added to the growing radical and the other monomer dissociated away. The parameter set included six reactivity ratios (r) and the equilibrium constant (K) of the comonomer complexation. The overall copolymer composition and the triad sequence distribution were derived from the eight individual transition probabilities (P).

Brown and Fujimori [17] combined the penultimate unit effect model and the complex participation model in one model which was named "comppen" model. It contained sixteen propagating reactions and sixteen individual transition probabilities (P). Twelve reactivity ratios and the equilibrium constant of the comonomer complexation composed the parameter set.

Kinetic description of a copolymer system can be quantified with the copolymerisation parameters, i.e., the reactivity ratios. To determine the copolymerisation parameters, a data set, which shows the correlation between the molar ratios of two monomers in comonomer feed mixtures (X_0, X_1) and those of comonomer units in the corresponding resulting copolymers (Y_0, Y_1), should be prepared. The conversion should be kept low (less than 5%) to ensure the uniformity of copolymer composition and to validate the derivation of the composition equation by assuming that the instantaneous monomer concentration ([0], [1]) are equal the initial monomer concentration ([0]$_0$, [1]$_0$).

In the following paragraphs, several methods for the determination of the reactivity ratios from the overall copolymer composition data according to the terminal model are briefly reviewed.

The intersection method proposed by Mayo-Lewis[5] based on the following equation:

$$r_1 = \frac{X_0^2}{Y_0}.r_0 + X_0.(\frac{1}{Y_0} - 1) \quad (27)$$

which is derived by applying the steady state assumption for the basic differential copolymerisation composition equation :

$$\frac{d[0]}{d[1]} = \frac{[0]}{[1]}.\frac{r_0 \cdot [0] + [1]}{r_1 \cdot [1] + [0]} \quad (28)$$

For each experimental data of (X_0, Y_0) , a straight line is plotted with the slope of Y_0^2/X_0 and the intercept of $X_0.[(1/Y_0)-1]$. A series of experimental data will provide a series of the straight lines, which cross each other to make an intersection. The ordinate and the abscissa of the centre point of this intersection give the best values of r_0 and r_1 with the radius over this intersection as the experimental uncertainties.

In the linearization method, Fineman and Ross [54] (1950) constructed a straight line by the following equation;

$$\frac{f_0.(1-2.F_0)}{(1-f_0).F_0} = r_1 - \frac{f_0^2.(1-F_0)}{(1-f_0)^2.F_0}.r_0 \quad \text{or} \quad X_0.(\frac{1}{Y_0}-1) = r_1 - \frac{X_0^2}{Y_0}.r_0 \quad (29)$$

The equation of Yezrielev et al.[55] (1969) has the form:

$$\frac{Y_0}{\sqrt{X_0}}.r_0 - \frac{\sqrt{X_0}}{Y_0}.r_1 + \frac{1}{\sqrt{Y_0}} - \sqrt{Y_0} = 0 \quad (30)$$

for which a unique solution exists for both normal and inverted data.

Joshi [56] (1973) use this equation for NLLS fitting run by a computer program to calculate the reactivity ratios.

Kelen and Tudos [57] introduced a graphically evaluable linear equation in the form of :

$$\frac{X_0.(Y_0-1)}{\alpha + \frac{X_0^2}{Y_0}} = (r_0.+\frac{r_1}{\alpha}).\frac{\frac{X_0^2}{Y_0}}{\alpha + \frac{X_0^2}{Y_0}} - \frac{r_1}{\alpha} \quad (31) \quad \alpha^2 = \left[\frac{X_0^2}{Y_0}\right]\text{max}.\left[\frac{X_0^2}{Y_0}\right]\text{min}$$

where α = arbitrary constant ($\alpha > 0$). The reactivity ratios r_0 and r_1 were determined from the intercept and the slope of the plot. The value of α is to chosen so as to minimise the experimental error.

For the penultimate model, Barb [8] used a linearised form of the composition equation simplified for the case when one monomer, e.g., monomer 0 does not homopropagate, so k_{000} and k_{100} were set to be zero and therefore r_{00} and r_{10} were zero. The composition equation was then reduced to be :

$$Y_1 = \frac{F_1}{F_0} = 1 + \frac{r_{01}.X_1.(1+r_{11}.X_1)}{1+r_{01}.X_1} \quad (32)$$

which was rearranged to give a linear equation $\quad r_{11} = \frac{Y_1-2}{X_1} + \frac{Y_1-1}{X_1^2}.\frac{1}{r_{01}} \quad (33)$

The reactivity ratios r_{11} and r_{01} were then obtained by an intersection or a linearization method.

Karad and Schneider[58] calculated the reactivity ratios for the complex participation model using the composition equation derived by Seiner and Litt[9] with some restrictions (i.e., $k_{00}=k_{001}=0$ when monomer 0 does not homopolymerize)

$$\frac{F_1}{F_0} - 1 = \frac{r_{10} \cdot \frac{[1]}{[0]} + \frac{r_{10} \cdot [\overline{01}]}{r_{110} \cdot [0]}}{1 + \frac{r_{10} \cdot [\overline{01}]}{r_{1(01)} \cdot [0]} + r_3 \cdot \frac{[\overline{01}]}{[1]} \cdot \left(1 + \frac{r_{10} \cdot [\overline{01}]}{r_{110} \cdot [0]}\right)} \quad (34)$$

where $r_{10}=k_{11}/ k_{10}$, $r_{110}=k_{11}/ k_{110}$, $r_{101}=k_{11}/ k_{101}$, $r_{1(01)}=k_{11}/ (k_{110} + k_{101})$, $r_3=k_{010}/ k_{01}$. When the concentration of monomer 1 is much greater than the concentration of the comonomer complex ($[1]>>[01]$). This equation was reduced to a linear equation :

$$\frac{F_1}{F_0} - 1 = Y_1 - 1 = \frac{r_{1(01)}}{r_{110}} + r_{1(01)} \cdot \left(\frac{[1]}{[\overline{01}]} - \frac{(Y_1 - 1) \cdot [0]}{r_{10} \cdot [\overline{01}]}\right) \quad (35)$$

The reactivity ratio r_{10} was assigned the value of r_1 of the classical terminal model. The reactivity ratios r_{110}, r_{101}, $r_{1(01)}$ were determined from the slope and the intercept of the equation (35). At last, the reactivity ratio r_3 can be calculated by the equation (34).

Similarly, the authors [58] also derived the composition equation for the complex dissociation model in this special case where monomer 0 does not homopolymerize :

$$Y_1 - 1 = \frac{F_1}{F_0} - 1 = \frac{r_{10} \cdot \frac{[1]}{[0]} + \frac{r_{10} \cdot [\overline{01}]}{r_{110} \cdot [0]}}{1 + \frac{r_{10} \cdot [\overline{01}]}{r_{101} \cdot [0]}} \quad (36)$$

where $k_{00}=k_{001}=0$ due to the non-homopolymerisation of the monomer 0, $r_{10}=k_{11}/ k_{10}$, $r_{110}=k_{11}/ k_{110}$, $r_{101}=k_{11}/ k_{101}$. The equation (36) can be then rearanged to the following linear equation:

$$Y_1 - 1 = \frac{r_{101}}{r_{110}} + r_{101} \cdot \left(\frac{[1]}{[\overline{01}]} + \frac{(Y_1 - 1) \cdot [0]}{r_{10} \cdot [\overline{01}]}\right) \quad (37)$$

With the use of the computer, the most convenient method of obtaining the best values of copolymerisation parameters from the available experimental information is the

direct search method[4,53]. This method was developed for the direct curve fitting using non linear least square (NLLS) minimising techniques. This method is proved to be very helpful, especially for the complex participation model and complex dissociation model, which have seven parameters, six reactivity ratios and an equilibrium constant of the complex formation, involved in their copolymer equations, where the linearisation does not seem to tolerate the various reaction conditions to yield satisfactory results.

Marquardt's algorithm [59,60] (also called "optimisation" routine) in conjunction with NLLS procedures, which is available for seeking the minimum sum of the squares (SS) of the differences between experimental and calculated data, was used when Pittman and Rounsefell[61] constructed three Fortran(IV) Programs for the "charge-transfer-copolymerisation", which was later called the complex participation model , to yield the "best value" for each of the six reactivity ratios and equilibrium constant. They emphasised the importance of selecting optimum experimental design and a non linear solution.

Using the direct search method developed by Chandler [62], Cais et al.[53] designed a computer program used for the complex participation model and later for the complex dissociation model. They adopted the Seiner-Litt [9] and the Pittman -Rousefell [61] treatments of the complex participation model. Their equations were expressed in term of transition probabilities to calculate the "best estimates" for the reactivity ratios and the equilibrium constant for complex formation.

Hill et al.[4,14] noticed that the triad monomer unit sequence distribution in copolymers (F_{triad}) is more sensitive in distinguishing between various copolymerisation models than the overall copolymer composition. But since the experimental data of sufficient accuracy for the sequence distributions are frequently difficult to obtain, they suggested that reactivity ratios should be estimated by fitting the overall copolymer composition (F_0) data. On this proposal they calculated the reactivity ratios for the copolymerisation of ST and MA at 60°C in bulk [14]. They also mentioned that calculated

and experimental data can then provide a means of judging the applicability of copolymerisation models [4,14]. Later however, they reported that the reactivity ratios were determined with higher precision from the triad fractions than from the copolymer composition when they studied the copolymerisation of ST and acrylonitrile at 60°C in bulk[27].

The output data of the terminal model and the penultimate model seem to be quite reliable since the number of parameters are 2 and 4, respectively, and by selecting reasonable experimental conditions, the NLLS procedure would converge to a sharp minimum in the hypersurface containing the parameter sets [14,28]. But even by good initial estimates for input data it revealed that multiple broad minima on hypersurface may often occur when working with more than 2 parameters, especially in the case of complex models , which involved with seven parameters. "The minimum of hypersurface is well defined and sharp in the direction of all parameters except s_0, where the minimum , though clearly defined, is relatively shallow ' [53].

The result of the NLLS curve fitting may be evaluated by the sum of squares (SS) value and the standard error (S_y) value which are defined as follows

$$SS = \Sigma \ (Y_{exp.} - Y_{calc.})^2 \qquad [63, p.242]$$

where $Y_{exp.}$ = experimental data
             $Y_{calc.}$ = calculated values

The standard error (S_y) can be calculated from the SS value.

$$S_y \ = \sqrt{\frac{SS}{n-p}} \qquad [63, p.247]$$

where   n = number of observations or number of data points
             p = degree of freedom or number of variable parameters.

The so called "test functions **a** and **b**" calculated from the triad fraction data were first used by Hill et al.[14]. Scheme 4 summarises the definition of the test functions **a** and

b and their variation patterns for distinguishing the four models: terminal-, penultimate unit effect-, complex participation- and complex dissociation models[14,15,39,48,64,65].

Scheme 4 : Test functions **a** and **b** for testing the applicability of the copolymerisation models.

$$\mathbf{a} = \frac{[0]}{[1]} \bullet \frac{2F_{111}}{F_{(011+110)}}$$

$\mathbf{a}$(max) when F_{111}(max) and $F_{(011+110)}$ (min)

$\mathbf{a}$(min) when F_{111}(min) and $F_{(011+110)}$ (max)

$$\mathbf{b} = \frac{[0]}{[1]} \bullet \frac{F_{(011+110)}}{F_{010}}$$

$\mathbf{b}$(max) when $F_{(011+110)}$(max) and F_{010} (min)

$\mathbf{b}$(min) when $F_{(011+110)}$(min) and F_{010} (max)

Steady state assumption allows: $\quad \dfrac{[0]}{[1]} = \dfrac{[0]_0}{[1]_0} = \dfrac{f_0}{1 - f_0}$

Extreme points: when $F_{111}=0$ $\mathbf{a} = 0$

$\qquad\qquad\qquad F_{(011+110)}=0$ $\mathbf{a} = +\infty$ and $\mathbf{b} = 0$

Restriction of the triad data

$F_{010} + F_{(011+110)} + F_{111} = 1$ $0 \le F_{\text{triad}} \le 1$

$f_0 \qquad\qquad = 0 \ - \ (1)$ (When monomer 0 does not homopolymerize,

$F_{010} \qquad\quad = 0 \ - \ 1\text{-} \ (0)$ $0 \le f_0 < 1$ for polymer to exist)

$F_{(011+110)} \quad = 0 \ - \ \text{max} \ - \ 0$

$F_{111} \qquad\quad = 1 \ - \ 0$

1. Terminal Model	$a = b = r_1$
2. Penultimate Unit Effect Model	$a \ne b$, $\quad a = r_{11}$, $\quad b = r_{01}$
3. Complex Participation Model	$a \ne b$, $\quad$ **a** and **b** may vary with F_0
4. Complex Dissociation Model	$a = b$, $\quad$ **a** and **b** may vary with F_0

The relation between the copolymer composition (F_0, F_1) and the fraction of the dyad sequences (F_{dyad}) and the triad sequnces (F_{triad}) can be viewed in scheme 5.

<u>Scheme 5:</u> Relation between the overall copolymer composition (F_0 and F_1) and the dyad and triad sequence distribution (F_{dyad} and F_{triad})

- supposed all monomers result only 1 polymer with infinite chain length
- because Maleic anhydride does not homopropagate, in Maleic anhydride (0)- Styrene (1) copolymer there are no 00 sequences

4 Dyads   00, 01, 10, 11

Sum of dyad fractions:

$F_{(01+10)} + F_{11} = 1 \qquad (F_{00} = 0)$

<u>Sum of composition fractions:</u>

$\underline{F_0 + F_1 = 1}$

$$\frac{F_1}{F_0} = \frac{F_{11} + F_{(01+10)}}{F_{(01+10)}} = \frac{1}{F_{(01+10)}} \qquad \text{or} \qquad \frac{F_0}{F_1} = F_{(01+10)}$$

$$F_0 = \frac{1}{1 + \dfrac{F_1}{F_0}} = 1 \bigg/ (1 + \frac{1}{F_{(01+10)}})$$

$$F_0 = \frac{F_{(01+10)}}{1 + F_{(01+10)}} \qquad \text{and} \qquad F_1 = \frac{1}{1 + F_{(01+10)}}$$

8 Triads	<u>1- centred triads</u>	<u>0- centred triads</u>	
alternating sequence	**010**	**101**	
semi-alternating sequence	**011**	**100**	(not exit)
	110	**001**	"
non-alternating sequence	**111**	**000**	"

Sum of 1- (or 0-) centred

triad fractions: $F_{010} + F_{(011+110)} + F_{111} = 1$ while $F_{101} = 1$ because $F_{(100+001)} = F_{000} = 0$

$$\frac{F_1}{F_0} = \frac{1}{F_{010} + \dfrac{F_{(011+110)}}{2}} \qquad \text{or} \qquad \frac{F_0}{F_1} = F_{010} + \frac{F_{(011+110)}}{2}$$

in 010 triads:
every <u>one</u> 1-unit is together
with <u>one</u> 0-unit

in 011 and 110 triads:
every <u>two</u> 1-units is together
with <u>one</u> 0-unit

This relation is deduced to the following equation

$$\frac{F_1}{F_0} = \frac{2}{2F_{010} + F_{(011+110)}} \qquad \text{or} \qquad \frac{F_1}{F_0} = 1 + \frac{2F_{111} + F_{(011+110)}}{2F_{010} + F_{(011+110)}} \qquad [14,15]$$

$$F_0 = \frac{1}{1 + \dfrac{F_1}{F_0}} = 1 \bigg/ (1 + \frac{2}{2F_{010} + F_{(011+110)}}) \qquad F_1 = \frac{1}{1 + \dfrac{F_0}{F_1}} = \frac{1}{1 + F_{010} + \dfrac{F_{(011+110)}}{2}}$$

Chapter 3. Experimental

3.1. Reagents and solvents

Styrene (ST), (Ajax) proved its purity of $\geq 99.5\%$ by ^{1}H NMR spectroscopy and was used as supplied.

Maleic anhydride (MA), (Ajax) was recrystallised from dried benzene (by sodium wires).

Citraconic anhydride (CA), (Fluka), assay 99% was used as supplied.

2,2'-azobisisobutyronitrile (AIBN), (Riedel-de Haen) was recrystallised from methanol.

N,N-dimethylformamide (DMF), (Fluka), assay ~99%(GC) was dried over molecular sieve Type A4 (Ajax) [66].

Carbon tetrachloride (CCl_4) was distilled and kept over molecular sieve.

Diethyl ether (anhydrous) (DEE), (BHD) was dried over Na wires.

Low boiling point (bp. 60-80°C) and high boiling point (bp. 80-110°C) petroleum spirit were dried over Na wires.

Acetone was distilled and kept over molecular sieves.

Bromomaleic anhydride (BMA), (Aldrich), 97%, was used as supplied.

Dichloromaleic anhydride (DCMA), (Aldrich), 97%, was used as supplied.

Maleimide (MI), (Aldrich), 99%, was used as supplied.

Other solvents are used as supplied.

3.2. Radical copolymerisation

All polymerisations were carried out in CCl_4 and in DMF with a total monomer concentration of 4.000 ± 0.001 mol/l, an initiator (AIBN) concentration of 0.0305 ± 0.0001 mol/l at the temperature of 50.0 ± 0.1°C. MA, AIBN, a small amount of hydroquinone ($<3\times10^{-3}$ mol/l) which was to inhibit the polymerisation before the reaction mixture was

ready for polymerisation [14] and, ST were weighed and placed in a glass ampoule. The solvent (either CCl4 or DMF) was then added to make up a total volume of 10.00±0.05 ml. The ampoule was sealed under vacuum after repeated freeze-degas-thaw procedures. The polymerisation was carried out in an oil thermostat. The ampoule was shaken well throughout the reaction. The conversion was kept to be less than 10% in general and less than 5% when the monomer mole fraction of MA or CA in feed was smaller than 0.2 or when it was larger than 0.8. The copolymers prepared in CCl4 were precipitated in petroleum spirit (bp.60-80°C), dissolved in a small amount of acetone and reprecipitated in boiling petroleum spirit (bp.80-110°C). The copolymers prepared in DMF were precipitated and reprecipitated from acetone solution in a large amount of DEE. The copolymer was then dried in desiccator under vacuum at room temperature for about 20 hrs .

All copolymerisations of ST with CA were carried out in a similar way in which the precipitated copolymers were washed thoroughly in boiling petroleum spirit or in DEE.

The plot of the conversion vs. reaction time ($t_{reaction}$) was used to estimate the possible $t_{reaction}$ needed to keep the conversion of the copolymer low.

Tab.7.2.1 and Tab.7.2.2 (Appendix, Section 7.2) list the preparation conditions for the copolymerisations of ST with MA and those of ST with CA, respectively.

The preparation conditions of the ten MA-ST copolymers polymerized in ten different solvents with the dielectric constants ranging from 2.24 to 36.7 and the preparation conditions for the three copolymers, BMA-ST, DCMA-ST and MI-ST are listed in Tab.7.2.3 and Tab.7.2.4 (Appendix, Section 7.2), respectively.

The following copolymer samples were supplied :

Copolymer	Solvent for preparation	Polymerisation temperature	Mole fraction of MA in feed mixture
MA- *trans*-stilbene (STI)	MEK	60°C	0.6
MA- α methylstyrene (MST)	MEK	50°C	0.6
MA- allyl benzene (AB)	MEK	60°C	0.5 and 0.6
MA- chloroethyl vinyl ether (CEV)	MEK	50°C	0.5 and 0.9

MA- n-butyl vinyl ether (BVE)   MEK   50°C   0.4

AIBN is used as initiator. The conversion of these copolymers were less than 5%.

3.3. ^{13}C NMR spectroscopy

Solutions of copolymers in acetone-d_6 (except the polymers listed below) were prepared to the concentration of 0.08-0.23 w/w (g copolymer/ g acetone) in precision NMR tubes.

Polymer	Solvent used for the NMR sample
Polystyrene	$CDCl_3$
MA-STI copolymer	$CDCl_3$
MI-ST copolymer	$DMSOd_6$
CA-ST copolymer samples with f_0 =0.01	$CDCl_3$

A Bruker AC-300 NMR spectrometer was used for running DEPT (Distortionless Enhancement by Polarisation Transfer) ^{13}C NMR experiments [67] at 75.46 MHz with a broad band ^1H dual 5 mm probe, over 15 to 20 hr periods at 308 K (35°C). The ^1H decoupler- and ^{13}C- $\pi/2$ pulse times were set at 9.9 and 4.2 μsec respectively. The recycle delay (T_1) was set to 4 sec, 2 sec and 5 sec for ^{13}C , DEPT ^{13}C and Quaternary ^{13}C NMR acquisitions, respectively. The J modulation time (Δ) was set to 0.0035 sec, equivalent to J =142.86 Hz (Δ =0.5/J for the optimum polarisation and/or sensitivity) for the DEPT experiments. The J modulation time (Δ) was set to 0.00345 sec (J=144.93 Hz) for the Quaternary experiments. The DEPT FID acquired spectra were exponential fourier transformed and generated by linear combination for the DEPT sub-spectra.

DEPT sub spectra	Types of Carbons (methine, methylene and methyl)
D1 <= $\Theta1$ = $\pi/4$	$CH + CH_2 + CH_3$
D2 <= $\Theta2$ = $\pi/2$	CH imperfection of CH_2 carbons
D3 <= $\Theta3$ = $3\pi/4$	$CH - CH_2 + CH_3$

$\Theta 1$, $\Theta 2$, $\Theta 3$ are the FID (Free Induction Decay) spectra which were exponential fourier transformed to D1, D2, D3 spectra, respectively.

D4 = D1 + a.D3 $(CH + CH_2 + CH_3)+ a.(CH - CH_2 + CH_3)= CH+CH_3$

D5 = D2 - c.D4 $CH \quad\quad\quad - c.(CH \quad\quad + CH_3)= CH$

D6 = D1 - a.D3 $(CH + CH_2 - CH_3)- a.(CH - CH_2 + CH_3) = CH_2$

D7 = D4 - b.D4 $(CH \quad\quad + CH_3)- b. CH \quad\quad\quad = CH_3$

Factor	Theoretical value	Typical values used
a	1.0	1.0 - 1.1
b	0.707 or $2^{-0.5}$	0.68 - 0.78
c	0	< 0.1

Linesim [68] peak simulation program was then run for the spectra of the corresponding carbons for determining the mole fractions of the ST(1) centred triads (F_{010}, $F_{(011+110)}$, F_{111}) , where the 0 and the 1 signified the anhydride monomer unit and the ST monomer unit in the copolymers, and the mole fraction of *cis* linkage configuration at cyclic units in copolymers (F_{cis}). The paper cutting method was used to confirm the integration data.

3.4. Determination of the equilibrium constant of the comonomer complexation by UV spectroscopy.

The UV spectroscopy measurement for the determination of the equilibrium constant (K in l/mol) of the complexation between ST and the acceptor monomers (MA or CA) was carried out on Cary 1E Varian UV-Visible spectrophotometer using a quartz cell with 1cm path length at room temperature (23°C).

The Ketelaar equation[69] was used to determine the value of the K

$$\frac{1}{\varepsilon_{ca} - \varepsilon_a} = \frac{1}{(\varepsilon_c - \varepsilon_a)\cdot K} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_c - \varepsilon_a} \quad\quad K= \text{intercept/ slope}$$

(ε_{ca}, ε_c, ε_a are the molar extinction coefficients of the complex and the

acceptor, the complex alone and the acceptor alone, respectively)

$[D]_0$= initial donor concentration in mol/l

Since the maximum absorption (λ_{max}) of these complexes were covered by the huge absorptions of the donor molecules, it was not possible to use the λ_{max}'s for the determination of the K. Absorptivity of the complex was measured at a few wavelengths closer to the λ_{max} and the K was determined as the average values of the K's observed at these waveleghths.

The details of UV measurments and the calculation for the K were summarised in the Appendix, Section 7.1.
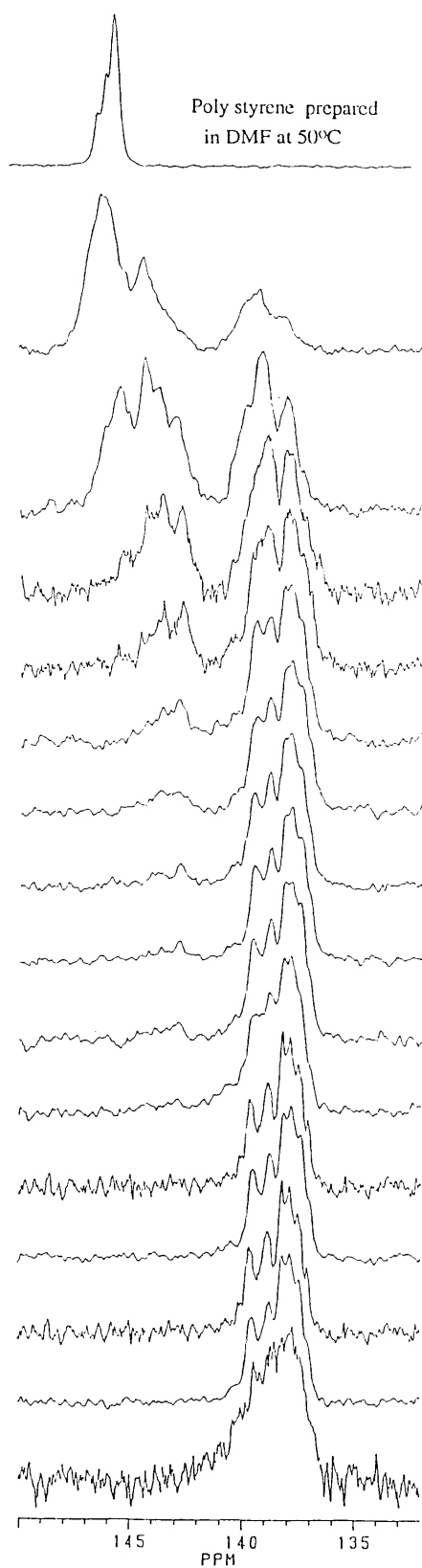
3.5. The resonance of the aromatic quaternary " next to chain " carbon in the determination of the triad sequence distribution.

The same MA-ST copolymer samples prepared in DMF at 50°C were run for the quaternary ^{13}C NMR experiment for the spectra of the aromatic quaternary "next to chain" C7 carbon of ST units. The resonance of the C7 carbon has been reported to be sensitive to the monomer unit sequence distribution [45,7]. The variation of three ST(1) centred triad sub-peaks can be observed along the MA mole fraction in feed (f_0) of between 0.00 and 0.90 (Fig.3.5.1) by both DEPT ^{13}C NMR CH_2 sub-spectra of the chain carbon C1 and the quaternary ^{13}C NMR spectra of the aromatic "next to chain" C7 carbon .

The peak assignment for the triads by C1 carbon was according to Barron et al [15]. The peak assignment for the triads by C7 carbon was determined based on the triad variation along with the MA mole fraction in feed (f_0) and which has been determined by the resonance peaks of C1 carbon. When f_0=0.0 poly(styrene) is formed, only non-alternating (111) sub-peak should appear. When f_0 is larger than 0.4 the copolymer becomes fully alternating, i.e., only the resonance for the alternating triad (010) should

Quaternary C7

111   011+110   010
148 - 145 --- 141.5 ----- 136.5ppm

CH₂ Subspectra of C1

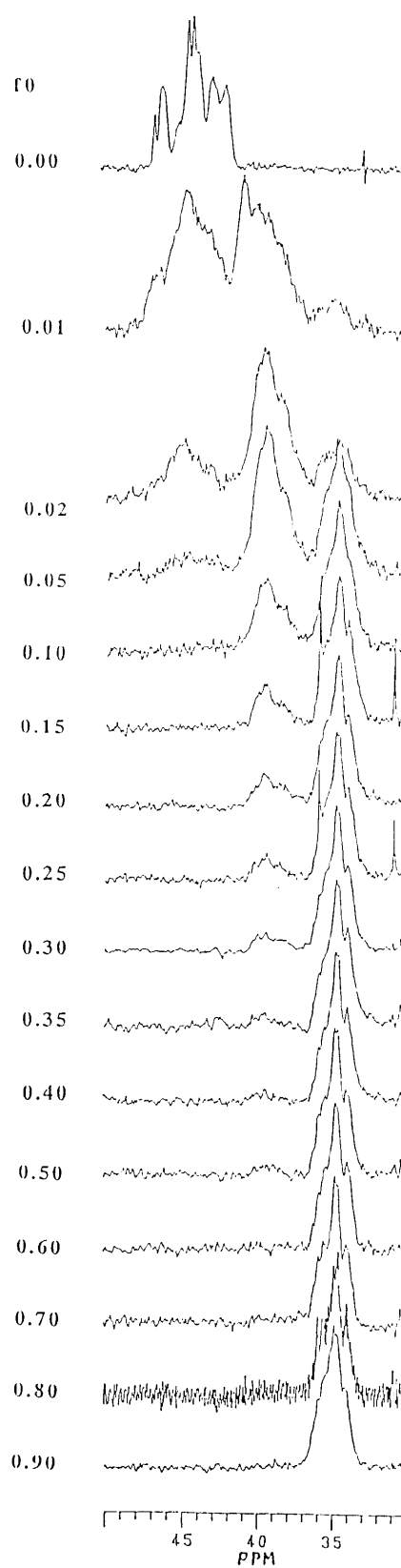111   011+110   010
47 ----- 42 ----- 37 ----- 33ppm

Poly styrene prepared
in DMF at 50°C

f0

0.00

0.01

0.02

0.05

0.10

0.15

0.20

0.25

0.30

0.35

0.40

0.50

0.60

0.70

0.80

0.90

145   140   135
PPM

45   40   35
PPM

Fig. 3.5.1   DEPT ¹³C NMR methylene (CH₂) subspectra of C1 and Quaternary
¹³C NMR spectra of C7. [MA+ST]=4M/ DMF/ 50°C. f0=0.00-0.90.

appear. When f_0 is between 0.1 and 0.4, the copolymer contains only semi-alternating and alternating triad sequences, i.e., the non-alternating (111) triad peak disappears. The resonace of C7 carbon appears in a shorter range (147.5ppm-136.5ppm=11ppm) than in the range for carbon C1 (47ppm-33ppm = 14ppm). In the spectra of C7 carbon the non alternating and the semi alternating triad peaks overlap by around 1ppm at the most when the MA composition in feed is very small, f_0=0.01-0.02 ; while they quite clearly separated in the C1 spectra. The qualitative determination or the chemical shift assignments for three ST(1) centred triad sub-peaks in the spectra of C7 carbon is confirmed by the consistence of the appearances of the three triad sub-peaks from both spectra of C1 and C7.

The quaternary ^{13}C NMR spectra of the aromatic quaternary C7 carbon of the aromatic donor unit (1) in the MA(0)-ST(1)copolymer, the MA(0)- *trans*-stilbene(STI or 1) copolymer, the MA(0)- α-methylstyrene(MST or 1) copolymer and MA(0)-allylbenzene(AB or 1) copolymer are shown in Fig.3.5.2. The spectrum of the C7 carbon of polystyrene is also shown to compare the chemical shift of the non-alternating(111) ST triad. In MA-ST copolymer the sub-peak of the alternating (010) triad appears separately upfield at 140.5-136.5 ppm while the non alternating (111) (or ST sequence) triad and the semi alternating (011+110) triads are overlapped each other by around 1ppm in the range of 146-145ppm.

The MA-STI copolymer, which is completely alternating, gives only the subpeak for the alternating triad at 138-132ppm, which splits at 135ppm due to *trans/cis* linkage configurations. The poly(phenylmethylene) or non alternating triad would be expected to resonanze downfield at around 160-150ppm.

The peak of the alternating (010) triads of MA(0)-MST(1) copolymer appears at 142.5-139ppm while the C7 resonace of poly(α-methylstyrene) appears at around 152-148ppm[71, p333] and that of the semi alternating (011+110) triad would be expected at around (148) 145.5-142.5ppm.

The resonance of the C7 of poly(allylbenzene)[71] and the MA-AB copolymers appears in a similar chemical shift areas of 142-139ppm for the triad sequences.
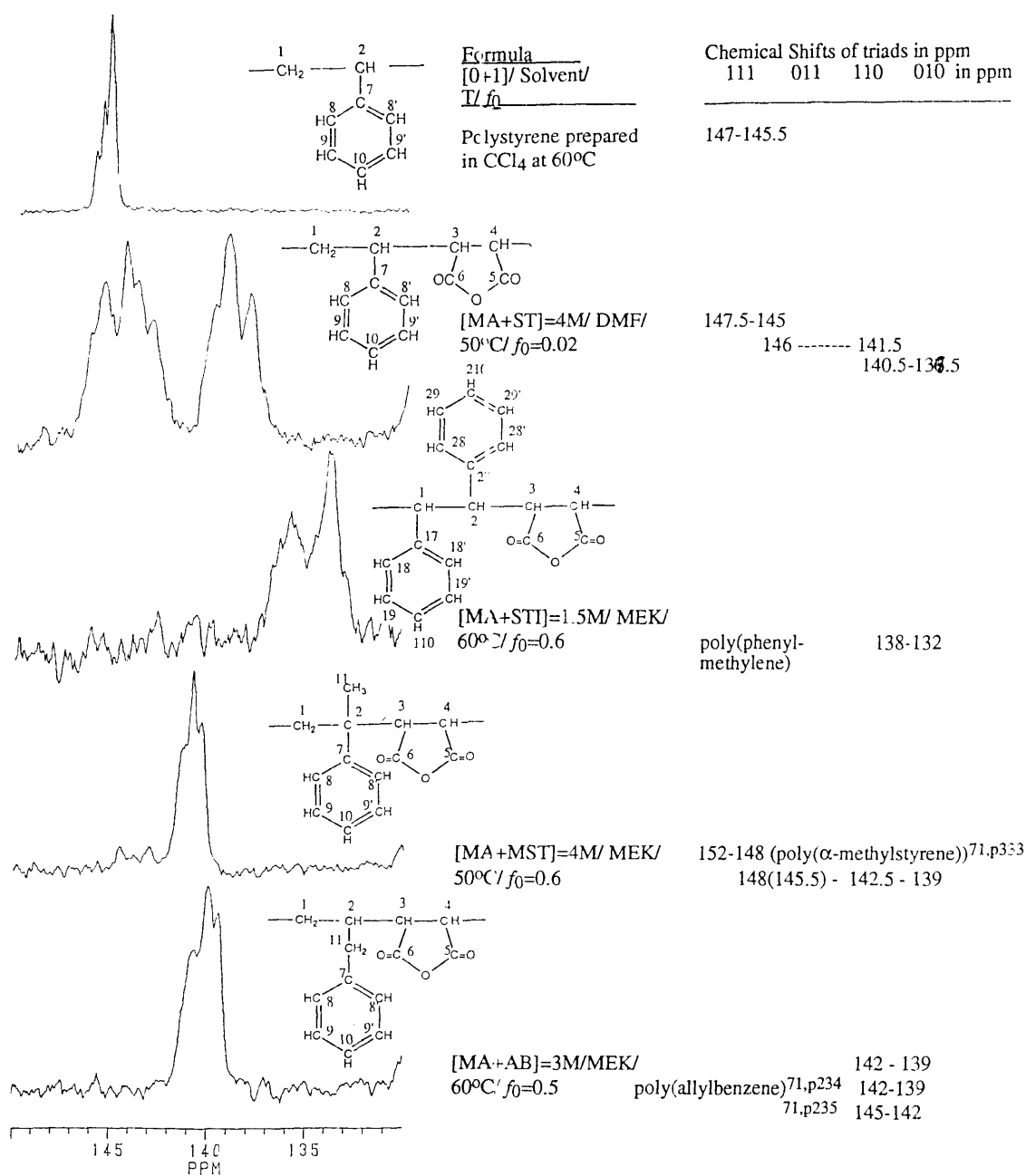
Fig.3.5.2 Quaternary ^{13}C NMR spectra of aromatic quaternary carbon (C7) of

MA(0)-ST(1), MA(0)-STI(1), MA(0)-MST(1) and MA(0)-AB(1) copolymers.

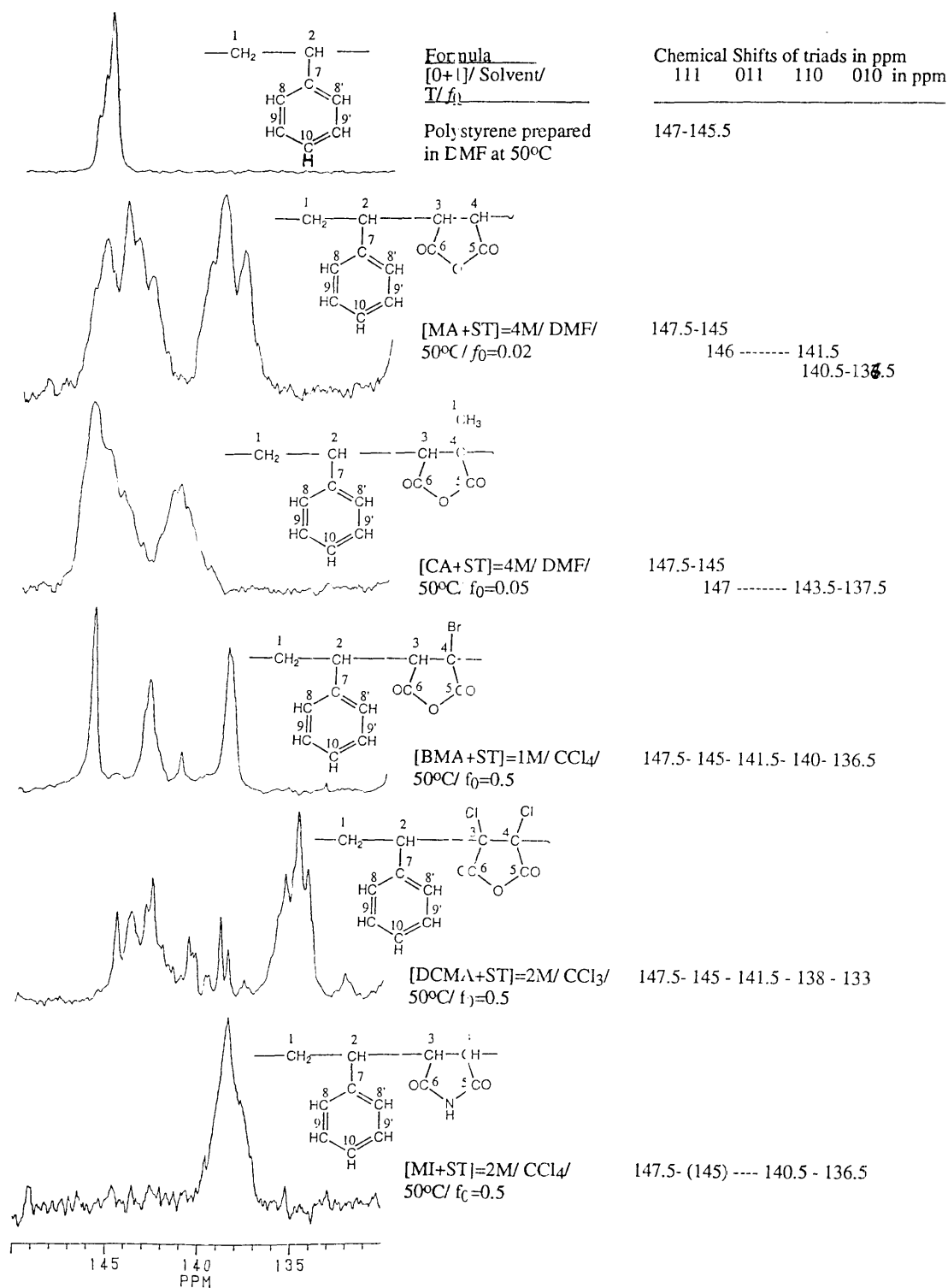| Formula [0+1]/ Solvent/ T/f0	Chemical Shifts of triads in ppm 111 011 110 010 in ppm
Poly styrene prepared in DMF at 50°C	147-145.5
[MA+ST]=4M/ DMF/ 50°C/ f_0=0.02	147.5-145 146 ------- 141.5 140.5-136.5
[CA+ST]=4M/ DMF/ 50°C f_0=0.05	147.5-145 147 ------- 143.5-137.5
[BMA+ST]=1M/ CCl4/ 50°C/ f_0=0.5	147.5- 145- 141.5- 140- 136.5
[DCMA+ST]=2M/ CCl3/ 50°C/ f_0=0.5	147.5- 145 - 141.5 - 138 - 133
[MI+ST]=2M/ CCl4/ 50°C/ f_c=0.5	147.5- (145) ---- 140.5 - 136.5

145   140   135
PPM

Fig.3.5.3 Quaternary ^{13}C NMR spectra of aromatic quaternary "next to chain" carbon (C7) of styrene (ST) unit in MA(0)-ST(1), CA(0)-ST(1), BMA(0)-ST(1), DCMA(0)-ST(1) and MI(0)-ST(1).

In other words, the triad sub-peaks appear overlapping each others because the carbon C7 of allylbenzene unit in the polymer and in the copolymer is not the "next to chain" carbon as in the other three copolymers mentioned above.

Fig.3.5.3 shows the spectra of the C7 aromatic quaternary "next to chain" carbon of the ST(1) units in the MA(0)-ST(1) copolymer, the CA(0)-ST(1) copolymer, BMA(0)-ST(1) copolymer, DCMA(0)-ST(1) copolymer and MI(0)-ST(1) copolymer. The chemical shifts for their triad sub-peaks are also indicated in the figure.

Since the deshielding effect on the resonance of the C7 carbon by the CA unit is weaker than that by the MA unit, the C7 peak of CA-ST copolymer shrinks downfields resulting a large overlapping between the triad sub-peaks. The extent of the overlapping is estimated to be around up to 2ppm at 147-145ppm between non alternating triad sub-peak and the semi-alternating triad sub-peaks.

The existence of the α-bromine atom in the BMA units sharpens the triad sub-peaks of C7 carbon so that the four sub-peaks corresponding to the four kinds of triads, 111, 011, 110 and 010, are clearly observed.

The two chlorine atoms of DCMA units may strengthen the deshielding effect on the spectrum of C7 carbon so that C7 spectrum of DCMA-ST copolymer spreads more upfields as compared to the spectra of C7 carbon in the MA-ST copolymers. The four triad (111, 011, 110 and 010) sub-peaks appear in multiplets which may correspond to the conformation of the copolymer chain.

The spectrum of the C7 carbon of the MI-ST copolymers seems to appear in a very similar manner as for the spectra of the C7 carbon of the MA-ST copolymers, in which the alternating(010) triad sub-peak appears at around 140.5-136.5ppm.

In general, by comparing the chemical shifts of the carbon of the homopolymer, poly(styrene) in this case, which has only non alternating (111) triads and the chemical shifts of the same carbon in the copolymer a clear assignment for triad sub-peaks could be made.