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Solvent effects on the copolymerization of *p*-methoxystyrene with maleic anhydride: an investigation into the mechanism of alternating copolymerization

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The comonomer unit sequence distributions and stereoregularity of copolymers of *p*-methoxystyrene (*p*-MST) with maleic anhydride (MA), prepared in $CHCl_3$ at $50 \pm 0.1^\circ C$, have been determined over a wide range of comonomer feed mole fractions using ^{13}C n.m.r. spectroscopy. The results were compared with those obtained from *p*-MST/MA copolymers prepared in methyl ethyl ketone (MEK) at 50°C that have been studied previously. The effects of the solvent on the stereoregularity and alternating tendency of these copolymers, as well as on the extent of comonomer electron donor–acceptor (EDA) complex formation in each system, have been discussed with reference to the mechanism of alternating copolymerization. An explanation for the observed trends is proposed in terms of the role of the EDA complex in alternating copolymerization.

(Keywords: solvent effects; alternating copolymerization; complex participation)

INTRODUCTION

In recent studies of alternating copolymerization systems in which electron donor–acceptor (EDA) complexes are formed between pairs of electron-rich and electron-deficient comonomers, a link has been found to exist between the alternating tendency and the stereoregularity of the comonomer units in a number of systems containing cyclic anhydride units, by using ^{13}C n.m.r. spectroscopy[1-4]. In such cases, the ratio of zusammen (*Z*) to entgegen (*E*) configurations of the anhydride units in these copolymers was found to increase along with the tendency of the comonomer units to alternate, reaching constant values in each case when the copolymers were completely alternating. A comparison of these results[5] revealed that for a series of related copolymers prepared under identical conditions, comonomer systems with greater donor/acceptor strengths, and hence higher values of the equilibrium constant for a 1:1 EDA complex formation, *K*, produced more strongly alternating copolymers with higher overall *Z*/*E* ratios. Hence it was suggested that the above trends are related to the extent of EDA complex formation in each system. Similar results were found by Olson and Butler[6] in their studies of the copolymerization of *N*-substituted maleimides with vinyl ethers. They discovered that the stereochemistry of these predominantly alternating copolymers was markedly dependent on various reaction conditions, including the relative donor and acceptor strengths of the comonomers.

This relationship between the stereochemistry, the alternating tendency of the comonomer units and the value of *K* in these types of copolymerization systems has also been investigated within the same comonomer system, using copolymers of styrene (ST) with maleic anhydride (MA) prepared in two different solvents, but under otherwise identical conditions[7]. The solvents used, methyl ethyl ketone (MEK) and $CHCl_3$, provided significantly different values of *K* due to their widely differing polarities. It was found that, for copolymers prepared in both solvents, the *Z*/*E* ratio of anhydride units again increased along with the tendency of the comonomer units to alternate, reaching a constant value when the copolymers became completely alternating. In addition to this, copolymers prepared in the solvent giving the largest *K* value ($CHCl_3$) were found to be more strongly alternating and have higher *Z*/*E* ratios before complete alternation of the comonomer units occurred, supporting the link between the extent of EDA complex formation and the stereoregularity and alternating tendency in these types of copolymers, as proposed previously[5]. The constant *Z*/*E* ratio attained at complete alternation of the comonomer units, however, was found to be of a comparable value in each solvent. It was therefore also proposed that a single stereoregulatory propagating mechanism is largely responsible for the formation of alternating sequences in this copolymerization system, irrespective of the solvent or the composition of the comonomer feed. Butler and coworkers have suggested[6,8-11] that the presence of a degree of stereoregularity in the microstructure of these types of alternating

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*To whom correspondence should be addressed copolymers may be due to the participation of EDA complexes during propagation. The results of this study, it was proposed, might therefore be considered to be consistent with the participation of EDA complexes in the polymerization process if complex addition were largely responsible for the formation of alternating comonomer sequences in the copolymer chain, and free, as well as complexed, comonomers add to the growing radical chain during propagation to form semi-alternating sequences. This type of mechanism has received support in recent years through the work of Mamedova *et al.*[12-14]. If complex participation was responsible for the above trends, this would necessarily imply that complex addition leads to a high proportion of anhydride units in the *Z* configuration being incorporated into the resulting copolymer. This phenomenon has yet to be satisfactorily explained.

In this work, in order to further investigate the role, if any, of the EDA complex in alternating copolymerization, copolymers of *p*-methoxystyrene (*p*-MST) with MA have been prepared in $CHCl_3$ at 50°C over a range of comonomer feed mole fractions, and the configuration of the MA units in these copolymers determined via ^{13}C n.m.r. spectroscopy, along with the comonomer unit sequence distributions of each copolymer. These results have been compared with those of the *p*-MST/MA copolymers prepared in MEK, but otherwise under identical conditions, reported previously[1], in order to see if the effects of changing solvents observed for ST/MA copolymers[7] could be reproduced when a stronger donor monomer (*p*-MST) was used. The results of this comparison have been interpreted in terms of the relationship between the extent of the 1:1 EDA complex formation in each solvent and the stereoregularity and alternating tendency of the resulting copolymers. An explanation for the observed trends is proposed in terms of the role of the EDA complex in alternating copolymerization.

EXPERIMENTAL

Materials

p-Methoxystyrene (*p*-MST) (Fluka) was determined to have a purity of >99.9% by ^1H and ^{13}C n.m.r. spectroscopy, and was used as supplied. Maleic anhydride (MA) (Unilab) was recrystallized from dry benzene, and 2,2'-azobisisobutyronitrile (AIBN), (Fluka) was recrystallized from dry methanol. Chloroform ($CHCl_3$) was distilled and kept over molecular sieves until needed, while petroleum spirit was distilled and dried over sodium.

Polymerizations

The required amounts of *p*-MST, MA ($[p\text{-MST} + \text{MA}] = 1.000\ \text{mol l}^{-1}$), AIBN ($0.0123\ \text{mol l}^{-1}$) and MEK were added to a glass ampoule to a total volume of 30.00 ml and sealed under vacuum after degassing. Hydroquinone ($<2.7 \times 10^{-3}\ \text{mol l}^{-1}$) was added to inhibit any polymerization taking place before the system became homogeneous at the reaction temperature of 50.0 ± 0.1°C[15]. The reaction was terminated by pouring the reaction mixture into a ten-fold excess of low-boiling-point petroleum spirit (b.p. 60–80°C) at room temperature. The copolymer was then collected and washed thoroughly with further petroleum spirit, after which they were then dissolved in MEK and reprecipitated in boiling petroleum spirit (b.p. 80–120°C) in order to remove any residual MA. After filtration and further washing with boiling petroleum spirit, the collected copolymer was dried *in vacuo* at 50°C for 16 h. All copolymers were prepared to conversions of less than 10% after purification, with those samples prepared at the extremes of the comonomer feed ratios prepared to less than 5%.

Spectroscopy

The ^{13}C n.m.r. spectra were obtained on approximately 10% wt/vol solutions in acetone-d_6 using a Bruker AC-300 spectrometer operating at 75.46 MHz, with a broad brand/^1H dual 5 mm probe. The DEPT pulse sequence was used to obtain methine and methylene sub-spectra of the copolymers. Acquisitions were made over 16 to 19 h periods at 35°C using ^1H and ^{13}C decoupler $\pi/2$ pulse times of 9.9 and 4.2 μs, respectively, and a 2 s recycle time. The J modulation time was set to 3.5 ms, equivalent to $J = 145$ Hz. No detectable differences were observed in experiments performed with an assumed J of 125 Hz. The DEPT sub-spectra were generated from the following combinations of the θ_1, θ_2 and θ_3 experiments, which have final ^1H pulses of $\pi/4$, $\pi/2$ and $3\pi/4$, respectively:

$$\mathrm{CH} = \theta_2 - c(\theta_1 + a\theta_3) \tag{1}$$

$$\mathrm{CH_2} = \theta_1 - a\theta_3 \tag{2}$$

$$\mathrm{CH_3} = \theta_1 + a\theta_3 - b\theta_2 \tag{3}$$

where a, b and c have theoretical values of 1.0, 0.707 and 0, respectively[16]. In practice, due to imperfections in the probe-head tuning and pulse length calibrations, undesired residual peaks often appear in the sub-spectra. Where present, these were removed by adjusting the weighting given to each DEPT experiment in the above equations. In such cases the values of a, b and c used were typically ~1.18, 0.78 and 0.10, respectively.

The areas of resonances in the spectra corresponding to triad sequence distributions were measured using spectrometer integrals. The areas of the resonances corresponding to the Z and E configurations of the anhydride units were measured using the *linesim* peak simulation program[17]. A detailed discussion of the use of *linesim* to determine individual peak areas where peak overlap occurs, is provided elsewhere[5]. No significant increase in the area of these resonances was observed between acquisitions made under these conditions and those made in the presence of a relaxation agent (chromium (III) acetylacetonate), indicating that the nuclei were fully relaxed after a recycle time of 2 s. The composition of each copolymer was determined from the measured sequence distribution data using the following equation[15,18]:

$$\frac{F_1}{F_0} = 1 + \frac{2A_{111} + A_{011+110}}{2A_{010} + A_{011+110}} \tag{4}$$

where 0 = MA, and 1 = styryl unit. In the above, A_{010}, $A_{011+110}$ and A_{111} are the areas of the 010, 011 + 110 and 111 triad sequence distributions, respectively, in the n.m.r. spectra, with F_1 and F_0 the mole fractions of the monomeric units 1 and 0, respectively, in the copolymers. As MA can be considered not to homopropagate under mild conditions[19], only 010, 011 + 110, 111 and 101 triad distributions are possible in these copolymers, i.e. triads involving the homopropagation of MA cannot occur. Hence, as the contributing area of the 101 triads can be accounted for in terms of the two adjoining 1-centred triads, the composition of these copolymers can be expressed solely in terms of the areas of these latter triads.

The pesence of a transitory, contact type *p*-MST/MA EDA (1:1) complex in $CHCl_3$ was confirmed via u.v. spectroscopy, under conditions allowing the application of the Ketelaar equation[20]. The value of the equilibrium constant for complex formation was measured at 2 nm intervals from 336 to 342 nm and its average value in $CHCl_3$ at ambient temperature was determined to be $0.125 \pm 0.005\,l\,mol^{-1}$. The u.v. spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer using 1 cm path length cells.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. methine and methylene DEPT sub-spectra of the *p*-MST/MA copolymers were assigned as in *Figure 1*, following previously reported assignments[1,8,21]. The splitting of the resonance responding to the C3 methine carbons of the MA units shown in *Figure 1* has been assigned to the *Z* (52.0 ppm) and *E* (52.8 ppm) configurations of these units, following the assignments based on the model compound, 2,3-dimethylsuccinic anhydride, presented previously[1].

The ratio of the *Z* to *E* configurations of the MA units in the copolymers was determined over a wide range of mole fractions of MA in the comonomer feed (f_0) by measuring the areas of each of the peaks in the C3 resonance corresponding to each configuration. The results for these copolymers, prepared in $CHCl_3$, were compared to those obtained previously[1] for the *p*-MST/MA copolymers prepared under identical conditions, except for the solvent, which was MEK. The overall composition of the copolymers from each of these systems, expressed as the mole fraction of MA (F_0), is presented in *Table 1* as a function of the mole fraction of MA in the comonomer feed.

The *Z/E* ratios of the copolymers prepared in each solvent are shown in *Figure 2*, where it can be seen that the *Z* content of the copolymers prepared in both solvents is lowest when f_0 is low and increases progressively with f_0. As was found for the ST/MA copolymers studied previously[7], the *Z/E* ratio in both solvents converges to a constant value at high values of f_0. In this present work, the *Z/E* ratios converged to a value of 1.3 ± 0.1 at around $f_0 = 0.30$. Once again, it was also found that before the *Z/E* ratios converge, at $f_0 < 0.30$ in this case, the ratio is higher for copolymers prepared in $CHCl_3$ than for those prepared in MEK.

The alternating tendency of the copolymers prepared in $CHCl_3$ was determined by measuring the fraction of completely alternating *p*-MST-centred triads in these

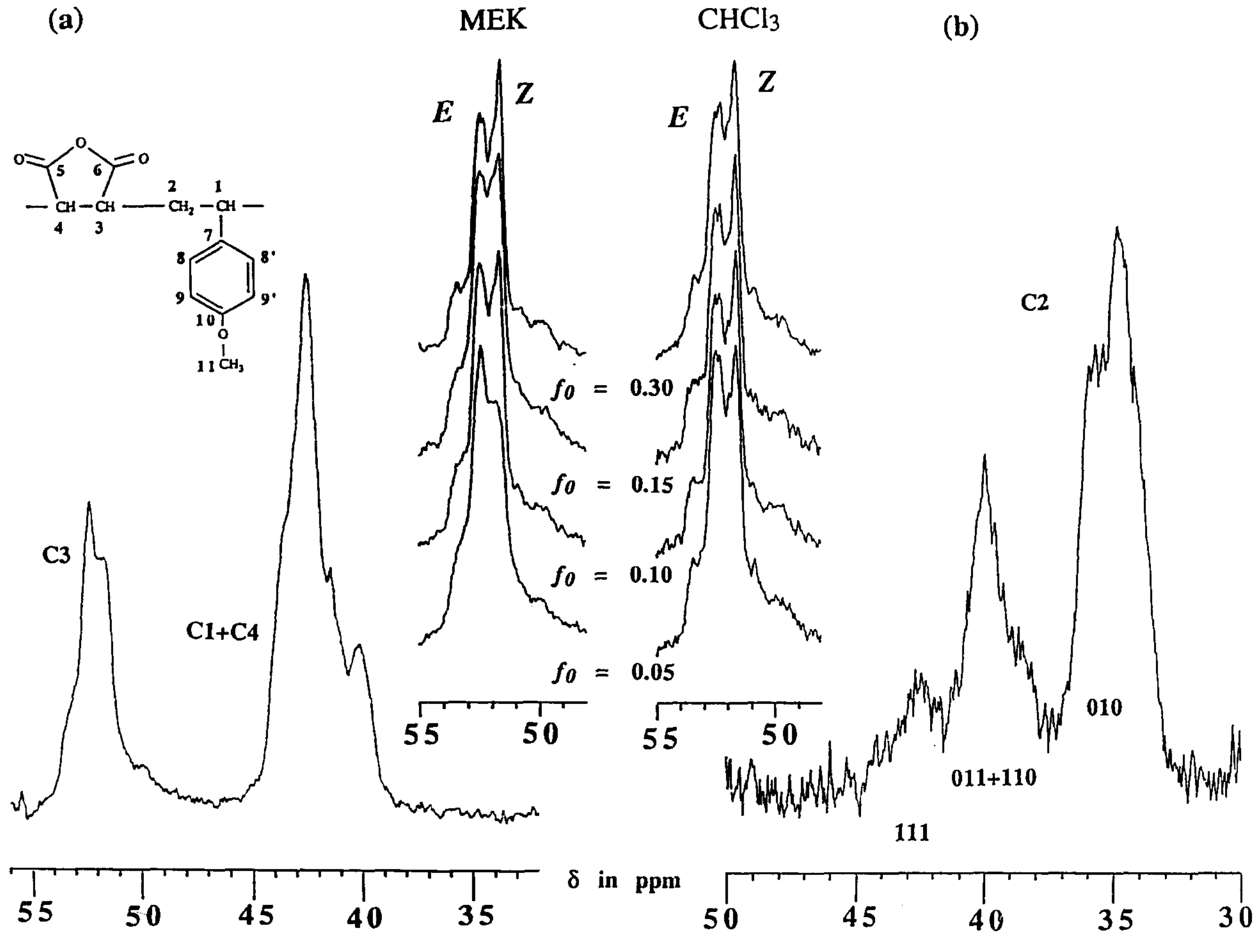


Figure 1 ^{13}C n.m.r. methine (a) and methylene (b) spectra of a typical *p*-MST/MA copolymer (prepared in MEK with $f_0 = 0.05$) showing the assignment of the C2 resonances to *p*-MST-centred triads (*p*-MST = 1; MA = 0). Inset shows the assignment of the C3 resonance to the *Z* and *E* forms of the MA units in these copolymers and the change in the *Z/E* ratio for each solvent

Table 1 Experimental composition data for the copolymerization of *p*-MST with MA in MEK[1,21] and in $CHCl_3$ at 50°C[a]

f_0^b	F_0^c (MEK)	F_0^c ($CHCl_3$)
0.0500	0.427	0.471
0.1000	0.465	0.473
0.1500	0.481	0.487
0.2000	0.493	0.488
0.3000	0.497	0.500
0.4000	0.497	–
0.5000	0.500	0.500
0.6000	0.500	–
0.7000	0.500	0.500
0.8000	0.500	–
0.9000	0.500	0.500

[a] [*p*-MST] + [MA] = 1.000 ± 0.001 mol l^{-1}; [AIBN] = 0.0123 ± 0.0001 mol l^{-1}

[b] Mole fraction of MA in feed (±0.0005)

[c] Mole fraction of MA in copolymer (±0.005)

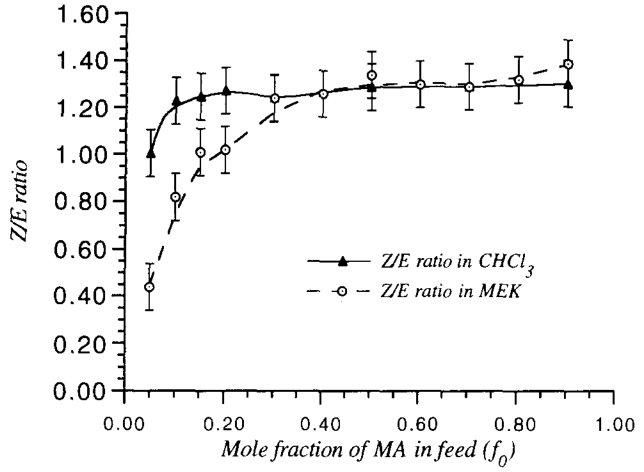


Figure 2 *Z/E* ratio plots obtained for *p*-MST/MA copolymers prepared in MEK and in $CHCl_3$ at a concentration of 1.000 mol l^{-1} and 50°C

copolymers by using the C2 methylene resonances in the ^{13}C n.m.r. spectra, as outlined below:

010	33–37 ppm	alternating triad
011 + 110	37–42 ppm	semi-alternating triad
111	42–47 ppm	non-alternating triad

where 0 = MA and 1 = *p*-MST. These resonances have been characterized following previously reported assignments[1,21]. Again, as MA can be considered not to homopropagate under mild conditions[19], only 010, 011 + 110, 111 and 101 triads are possible in these copolymers, i.e. triads involving the homopropagation of MA cannot occur. As the contributing area of the 101 triads can be accounted for in terms of the two adjoining 1-centred triads, the triad sequence probabilities can be expressed solely in terms of the areas of the 1-centred triads. The fraction of alternating *p*-MST-centred triads, F_{010}, for example, can therefore be expressed as follows:

$$F_{010} = \frac{A_{010}}{A_{010} + A_{011+110} + A_{111}} \qquad (5)$$

Hence, only a completely alternating copolymer will have $F_{010} = 1.0$ at a value of $F_1 = 0.5$, while less alternating copolymers will have $F_{010} < 1.0$ at values of $F_1 > 0.5$.

The fraction of alternating *p*-MST-centred triads in the copolymers prepared in both solvents is shown in *Figure 3*, where it can be seen that in each case there is a strong tendency for the comonomer units to alternate across the range of feed ratios studied. In fact, both systems achieve complete alternation somewhere between $f_0 = 0.20$ and $f_0 = 0.30$. However, the copolymers prepared in $CHCl_3$ are more strongly alternating than those prepared in MEK, where complete alternation has not been attained. By comparing *Figures 2* and *3* it can be seen that for copolymers prepared in both solvents, the *Z/E* ratio becomes constant as the copolymers approach complete alternation at $f_0 \sim 0.30$. This same trend has been consistently observed in alternating copolymerization systems where EDA complexes are known to exist[1–5,7]. The equilibrium constant for 1:1 *p*-MST/MA EDA complex formation, *K*, has been measured in both $CHCl_3$ and MEK in our laboratory via u.v. spectroscopy, with the values being determined as $K = 0.08 \pm 0.02\,l\,mol^{-1}$ in MEK[21] and $K = 0.125 \pm 0.005\,l\,mol^{-1}$ in $CHCl_3$. A comparison of *Figures 2* and *3* also reveals that before the copolymers prepared in each solvent become completely alternating at $f_0 \approx 0.30$, those prepared in the solvent giving the higher *K* value are more strongly alternating and also have higher *Z/E* ratios.

Hence the trends observed in this comparison of *p*-MST/MA copolymers prepared in $CHCl_3$ and MEK are the same as those seen previously for ST/MA copolymers prepared in the same solvents[7]. Once again, the *Z/E* ratios of copolymers prepared in both solvents converge to a constant and comparable value as the copolymers become completely alternating, indicating that a single stereoregulatory mechanism is largely responsible for the formation of alternating sequences in these copolymers, independent of the solvent or the composition of the comonomer feed. In addition, for copolymers where complete alternation has not been attained, the change in alternating tendency and *Z/E* ratio of the copolymers with the change of solvent suggests that more than one mechanism is responsible for the formation of these quasi-alternating copolymers, with the mechanism leading to alternating sequences being favoured by the less polar solvent, $CHCl_3$. If EDA

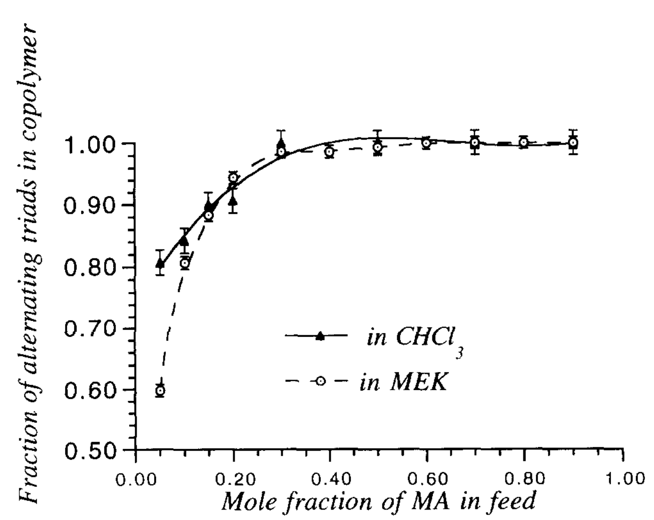


Figure 3 Alternating triad fraction plot for *p*-MST/MA copolymers prepared in MEK and $CHCl_3$ at a concentration of 1.000 mol l^{-1} and 50°C

complexes did add to the growing radical chain during propagation and in so doing, added a degree of stereoregularity to the resulting copolymer, as suggested by Butler and coworkers[6,8-11], the predominant addition of these complexes to form alternating sequences could be expected to result in a convergence of Z/E ratios to a constant value, regardless of the solvent, as the copolymers became completely alternating. Similarly, if addition of the free comonomers 1 and 0, as well as complexed comonomers, occurred during propagation to form semi-alternating sequences in the quasi-alternating copolymers, the use of a less polar solvent which favours complex formation, such as $CHCl_3$, might be expected to result in more strongly alternating copolymers, with higher Z/E ratios, from the same starting composition, than the use of a more polar solvent in which complex formation was not favoured, such as MEK.

If EDA complex participation is largely responsible for the formation of alternating sequences as described above, the stereochemistry of complex addition needs further investigation if the formation of a predominance of Z-MA units in the completely alternating copolymer samples is to be explained when the E form is more thermodynamically favourable[10,22]. In addition, workers studying rigidly alternating copolymers in the past have suggested that complex addition should lead to rigidly stereoregular alternating copolymers, not ones in which a mixture of configurations exist[23-25]. Butler and coworkers[6,9] have proposed a mechanism based on the maximum orbital overlap theory of Mulliken[26], for the formation of *cis*(erythro) succinimide units in copolymers of *N*-substituted maleimides with vinyl ethers, that may provide an explanation for this result. The mechanism, adapted to the present case, is presented in *Scheme 1*. This shows that addition of the growing radical chain to the side of the complex that is *syn* to the styrene unit leads to the addition of an MA unit in the Z configuration (a), while attack from the opposite side (b), yields the E configuration. EDA complex participation following this mechanism can therefore lead to the addition of both Z- and E-MA units to the growing radical chain. As the addition of free comonomers to the chain could normally be expected to result in MA units in the E configuration, EDA complex addition via *Scheme 1* can hence be seen as the main source of Z-MA units in the copolymers.

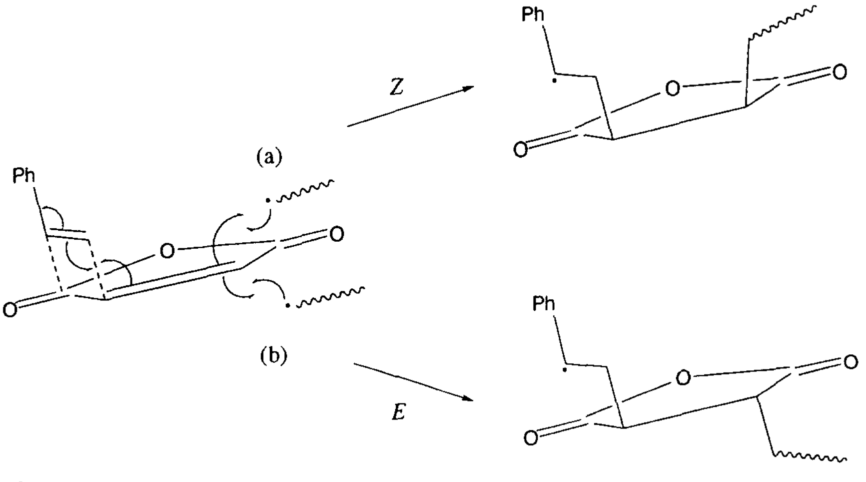
If this were so, where a copolymer was completely alternating and the formation of alternating sequences was largely due to EDA complex addition, the fraction of MA units in that copolymer with the Z configuration (F_Z) would be a measure of the probability of the addition of a single complex yielding a Z-MA unit for that particular system, regardless of the overall sequence distribution of the individual copolymer. For example, as the Z/E ratio for these p-MST/MA copolymers attained a constant value of 1.3 ± 0.1 when the copolymers were completely alternating, regardless of the solvent, the fraction of MA units in the Z configuration in these copolymers with complete alternation is 0.57 ± 0.05. Therefore, complex addition as described by *Scheme 1* would give MA units in the Z configuration approximately 57% of the time where it was the main source of alternating sequences. If this mechanism provides an accurate description of the copolymerization system under study, the fraction of MA units in the Z configuration in a copolymer of any overall sequence distribution in this system should be related to the fraction of alternating triads in that copolymer by the following simple relationship:

$$F_Z = p_Z F_{010} \tag{6}$$

where F_Z is the fraction of MA units with the Z configuration to be found in a given copolymer, F_{010} is the fraction of completely alternating p-MST-centred triads in the copolymer, and hence a measure of the degree of complex addition occurring, and p_Z is the probability of a single complex addition of MA resulting in the Z configuration. For the p-MST/MA copolymerization system under study here, the value of p_Z would therefore be 0.57 ± 0.05.

In order to test the validity of these assumptions, the fraction of MA units in the Z configuration has been predicted by using equation (6) for each of the p-MST/MA copolymers prepared in $CHCl_3$ and MEK, and these data are compared to the experimentally determined data in *Figures 4* and *5*.

Comparison of the experimental and calculated



Scheme 1 Proposed mechanism for the formation of Z- and E-MA units via EDA complex addition, showing attack by the radical chain yielding (a) a Z-MA unit and (b) an E-MA unit

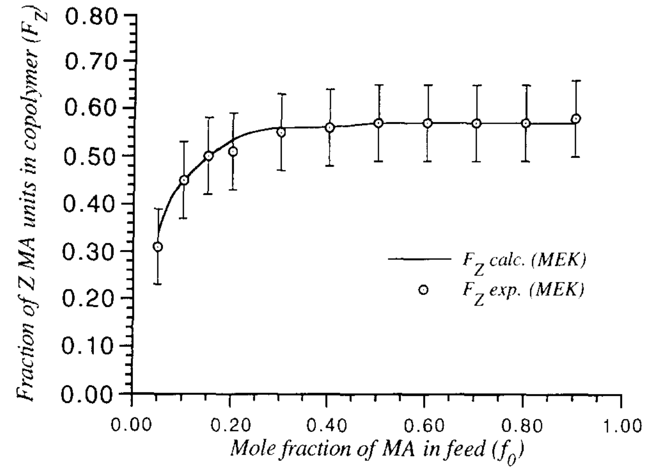


Figure 4 Plot of the fraction of Z-MA units (F_Z) in *p*-MST/MA copolymers prepared in MEK at a concentration of 1.000 mol l^{-1} and 50°C, showing also F_Z as predicted by equation (6) for $p_Z = 0.57 \pm 0.05$

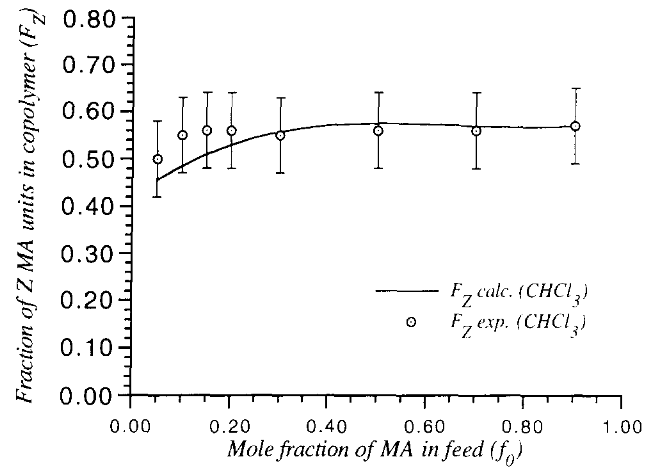


Figure 5 Plot of the fraction of Z-MA units (F_Z) in *p*-MST/MA copolymers prepared in CHCl$_3$ at a concentration of 1.000 mol l^{-1} and 50°C, showing also F_Z as predicted by equation (6) for $p_Z = 0.57 \pm 0.05$

fractions of MA units in the *Z* configuration for the copolymers prepared in MEK displayed in *Figure 4* shows an extremely good agreement between the two sets of data, with the sum of the squares of the differences between the experimental and calculated data (*SS*) being 2.1×10^{-3}. The comparison of calculated and experimental F_Z data for the copolymers prepared in CHCl$_3$, displayed in *Figure 5*, gives a *SS* value of 1.1×10^{-2} and although this is an order of magnitude larger than for the MEK data, it again shows an agreement between the two sets of data that is well within the experimental error ranges. The difference in the goodness of fit to the experimental data in this latter case may be a result of the difficulty in measuring the small changes, relative to the magnitude of the error for each measurement, in the *Z*/*E* ratio of these copolymers with an increasing f_0 value, when compared with the comparatively large changes experienced in the MEK case.

To further investigate the validity of this simple relationship, the fraction of MA units in the *Z* configuration has also been predicted using equation (6) for the ST/MA copolymers, prepared in MEK and CHCl$_3$, studied previously[7], and is compared to the respective experimental data in *Figures 6* and *7*. The overall composition of the copolymers from each of these systems is presented in *Table 2*.

The value of p_Z for these copolymers, obtained from the fraction of MA units in the *Z* configuration at

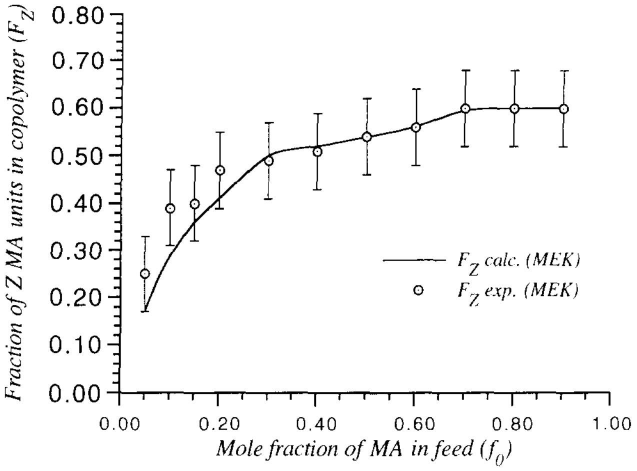


Figure 6 Plot of the fraction of Z-MA units (F_Z) in ST/MA copolymers prepared in MEK at a concentration of 4.000 mol l^{-1} and 50°C, showing also F_Z as predicted by equation (6) for $p_Z = 0.60 \pm 0.05$

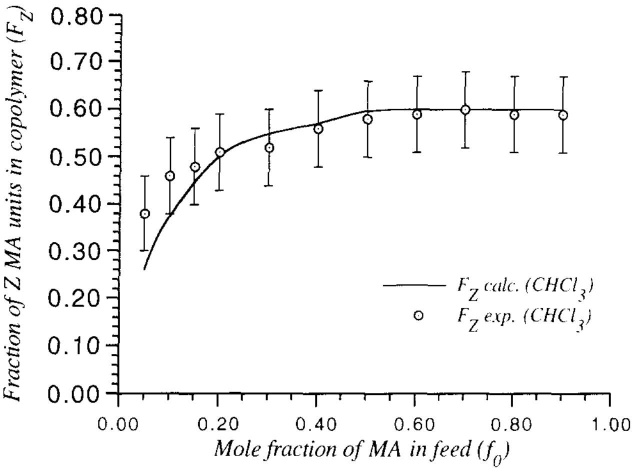


Figure 7 Plot of the fraction of Z-MA units (F_Z) in ST/MA copolymers prepared in CHCl$_3$ at a concentration of 4.000 mol l^{-1} and 50°C, showing also F_Z as predicted by equation (6) for $p_Z = 0.60 \pm 0.05$

Table 2 Experimental composition data for the copolymerization of ST with MA[7] in MEK and in CHCl$_3$ at 50°C[a]

f_0^b	F_0^c (MEK)	F_0^c (CHCl$_3$)
0.0500	0.375	0.407
0.1000	0.415	0.440
0.1500	0.440	0.458
0.2000	0.453	0.479
0.3000	0.477	0.488
0.4000	0.484	0.494
0.5000	0.487	0.500
0.6000	0.492	0.500
0.7000	0.500	0.500
0.8000	0.500	0.500
0.9000	0.500	0.500

[a] [ST] + [MA] = 4.000 ± 0.001 mol l^{-1}; [AIBN] = 0.0305 ± 0.0001 mol l^{-1}
[b] Mole fraction of MA in feed (±0.0005)
[c] Mole fraction of MA in copolymer (±0.015)

$F_{010} = 1.0$, has been determined to be 0.60 ± 0.05. Once again, good agreement is obtained between the experimental and calculated results in each solvent. The *SS* values for the copolymers prepared in MEK and $CHCl_3$ are 2.1×10^{-2} and 2.3×10^{-2}, respectively, with the calculated values of F_Z being within the experimental error ranges in the majority of cases.

It should be noted that while equation (6) will necessarily give an excellent prediction of F_Z when the copolymers are completely alternating (i.e. at $F_{010} = 1.0$), the predictions of F_Z made for copolymers prepared in MEK, in particular, also display good agreement with the experimental data when the copolymers are not completely alternating. Hence, considering the gross assumptions made in deriving this relationship, equation (6) predicts the fraction of MA units with the *Z* configuration in copolymers from each of these copolymerization systems surprisingly well. The success of this equation in predicting F_Z in these systems therefore lends support to complex participation (via *Scheme 1*) as being the single stereoregulatory mechanism largely responsible for the formation of alternating sequences in these *p*-MST/MA and ST/MA copolymers. Similarly supported is the contention that variations in the alternating tendency and stereoregularity of these copolymers with solvent and hence *K* where the copolymers were not completely alternating, are the result of the addition of free and complexed comonomers to the growing radical chain during propagation, thus leading to the formation of semi-alternating sequences in the resulting copolymers. The values of p_Z found for both the *p*-MST/MA and ST/MA copolymerization systems suggest that *Scheme 1*, if applicable, yields Z-MA units approximately 60% of the time.

While the solvent effects on the *p*-MST/MA and ST/MA copolymerization systems reported here do not conclusively prove that EDA complexes participate in alternating copolymerization, plausible explanations for the observed trends have been proposed by assuming that complex participation does occur and by applying strictly defined conditions to this assumption. This does not, however, exclude the possibility of these trends being the result of an independent solvent-related effect on the mechanism of alternating copolymerization.

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