Polymer Bulletin 29, 213–217 (1992)

Polymer Bulletin

Determination of the configuration of citraconic anhydride units in copolymers of *p*-methoxystyrene with citraconic anhydride via ^{13}C NMR spectroscopy

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Summary

The configuration of citraconic anhydride units in *p*-methoxystyrene/citraconic anhydride copolymers prepared in methyl ethyl ketone at 50.0±0.1°C and the corresponding copolymer compositions and comonomer unit sequence distributions were determined over a range of comonomer feed mole fractions using ^{13}C NMR spectroscopy. It was found that the ratio of *Z* (zusammen) to *E* (entgegen) configurations of citraconic anhydride units in these copolymers increased with the degree of alternation of the comonomer units, reaching a constant value of approximately 1.72 when the comonomer units were almost completely alternating and the mole fraction of citraconic anhydride units in the copolymers approached 0.50.

Introduction

In recent studies (1),(2) we have reported that in the alternating copolymerisation of maleic anhydride (MA) with *p*-methoxystyrene (*p*-MST) and *p*-chlorostyrene (*p*-CST) respectively, the ratio of *Z* (zusammen) to *E* (entgegen) configurations of MA units in these copolymers increased along with the degree of alternation of the respective comonomer units, reaching a constant value in each case when the comonomer units were almost completely alternating.

In this work, copolymers of *p*-MST were prepared with citraconic anhydride (CA) over a range of comonomer feed mole fractions to determine the configuration of the CA units in these copolymers and hence further investigate any link that may exist between the alternating tendency and stereoregularity of the monomer units in copolymerisation systems in which pairs of monomer units can form 1:1 charge transfer complexes in the comonomer feed. This is in line with the work of Olson, Butler *et al.* (3),(4),(5),(6) which proposes that if such donor-acceptor complexes participate in the polymerisation process, stereoregularity may be introduced into the microstructure of the resulting copolymer.

Experimental

p-MST (Fluka) and CA (Fluka) were determined to have purities of > 99.9% by ^{1}H and ^{13}C NMR and used as supplied. 2,2'-azobisisobutyronitrile (AIBN) (Fluka) was recrystallised from dry methanol. Methyl ethyl ketone (MEK) (Unilab) was dried over $CaCl_2$, distilled and kept over molecular sieves. Petroleum spirit was distilled and dried over sodium. Required amounts of the comonomers ([*p*-MST+CA] = 4.000M), AIBN (0.0305M) and MEK were added to a glass ampoule and sealed under vacuum after freeze-thaw degassing. The polymerisation was carried out by placing the glass ampoule

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in an oil bath at 50.0±0.1°C for a predetermined period. The reaction was terminated and unreacted *p*-MST removed by quickly pouring the reaction mixture into low boiling point (60-80°C) petroleum spirit at room temperature. The copolymer was then dissolved in MEK, reprecipitated in boiling petroleum spirit (b.p. 80-120°C) to remove residual CA and dried *in vacuo* at 50°C for 16 hours. The majority of copolymer samples were prepared to conversions of less than 5 wt %. All copolymers were prepared to conversions of less than 10 wt %.

^{13}C NMR spectra of the copolymers were obtained on approximately 25% w/v solutions in acetone-d_6 using a Bruker AC-300 spectrometer under conditions allowing only the acquisition of quaternary carbon resonances. Acquisitions were made over 16 to 19 hour periods at 35°C using 5 mm o.d. sample tubes. The mole fraction of CA units in each copolymer (F_0) was determined from the relative areas of the carbonyl resonances at 175.8 and 172.2 ppm and the aromatic resonance at 160.3 ppm in the NMR spectra using spectrometer integrals, whilst sequence distribution and *Z/E* ratios were determined using peak areas measured with the *linesim* peak simulation program (7). Fig.1 shows a typical spectrum for a copolymer with $F_0 = 0.474$.

Results and discussion

The quaternary ^{13}C NMR spectra of the *p*-MST/CA copolymers were assigned as in Fig.1, following generally, previously reported assignments for similar copolymers (1),(2),(3). The splitting of the resonance corresponding to the C3 carbons of the citraconic anhydride units shown in Fig.2, was assigned to the *Z* (49.3 ppm) and *E* (50.4 ppm) configurations of these units, following the assignment based on the model compound 2,3-dimethylsuccinic anhydride presented previously (1).

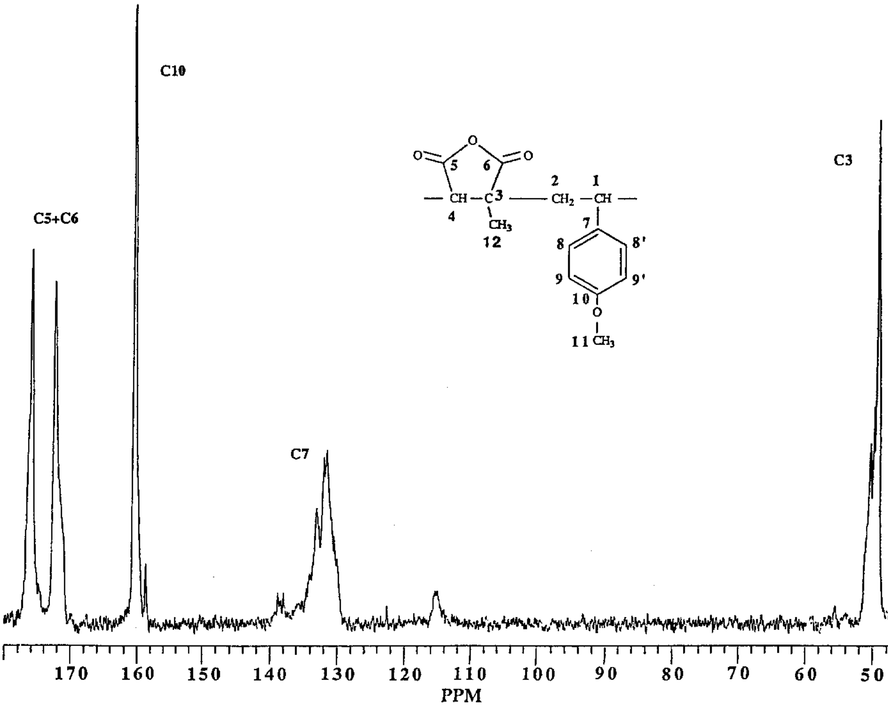

Fig.1. Typical quaternary ^{13}C NMR spectrum of a *p*-MST/CA copolymer ($F_0 = 0.474$)

The resonances in Fig.2 corresponding to the C7 carbons of the *p*-MST units in the copolymers can be assigned (8),(9) to the following *p*-MST centred triad distributions:

010	131 - 135 ppm - alternating
011+110	133 - 138 ppm - semi-alternating
111	138 - 139 ppm - non-alternating

where 0 = CA, 1 = *p*-MST

It should be noted that, unlike the triad resonances reported previously (1),(2) these resonances overlap, introducing a larger error into the determination of sequence distribution for these copolymers. This is particularly true in the case of the 010 and 011 +110 resonances where the overlapping region is approximately 2 ppm in width.

The C7 resonances in Fig.2 show an increasing tendency for the monomer units in these copolymers to alternate as the mole fraction of CA in the feed (f_0) increases. The areas of these triad resonances were measured and the results presented in Fig.3, where it can be seen that over the range $f_0 = 0.05$ to $f_0 = 0.90$ the copolymers change from consisting of approximately 20% alternating triads to 100% alternating triads. Fig.4 correspondingly shows an increase in the mole fraction of CA units in the copolymers from approximately 0.35 to 0.50 over the same range. At the same time the C3 resonances in Fig.2 show an increase in the ratio of *Z* to *E* configurations of CA units in these copolymers. The ratio of *Z* to *E* configurations was determined by measuring the area of each of the peaks in the C3 resonances, and is presented in Fig.5.

It can be seen from Figs.2 & 5 that, although there is a predominance of *Z* configurations in these copolymers over the mole fraction range studied, the *E* content is largest when the tendency of the monomer units to alternate is lowest, i.e. when the mole fraction of CA units in the feed is low, with the

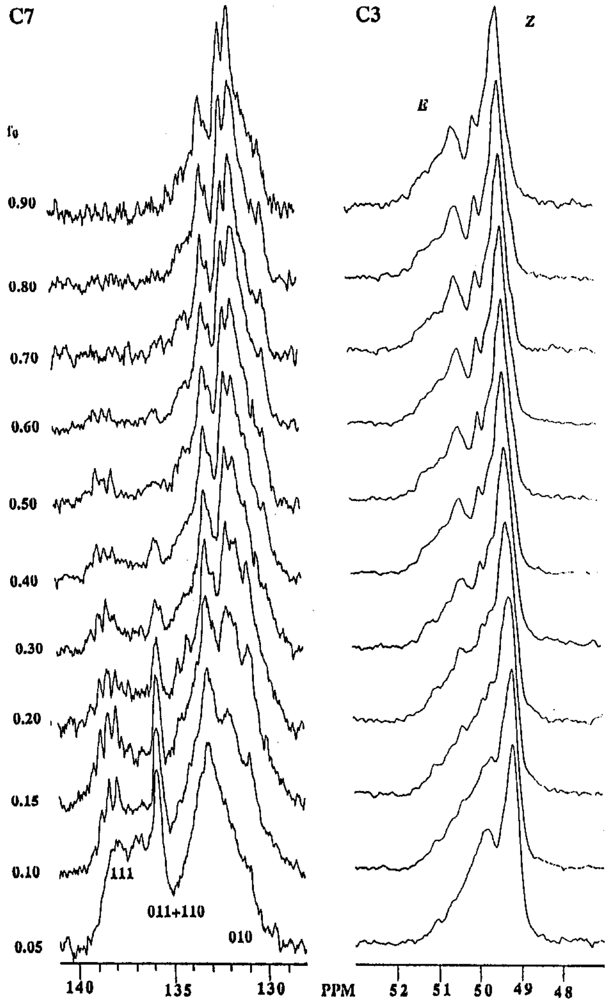

Fig.2. ^{13}C NMR spectra of C3 and C7 carbons of *p*-MST/CA copolymers over the mole fraction range $f_0 = 0.05$ to $f_0 = 0.90$.

Z content progressively increasing with the tendency to alternate. At around $f_0 = 0.60$ the copolymer appears to be almost completely alternating, with the *Z*/*E* ratio reaching a constant value of 1.72±0.04.

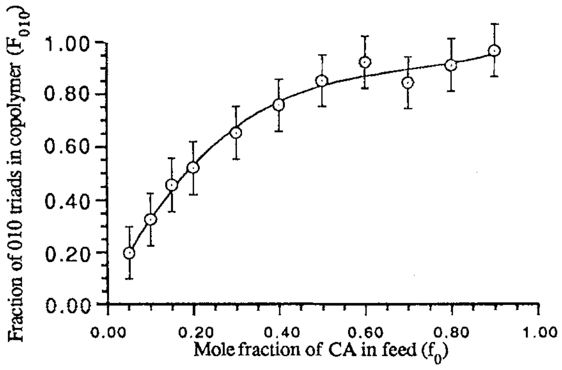

Fig.3. 010 triad fraction plot for *p*-MST/CA copolymers prepared in MEK at 50°C.

Similar results were found for the alternating copolymerisations of *p*-MST with MA (1) and *p*-CST with MA (2) which attained constant *Z*/*E* ratios of 1.33 and 0.73 respectively, when the monomer units were almost completely alternating and the mole fraction of MA in the copolymers approached 0.50.

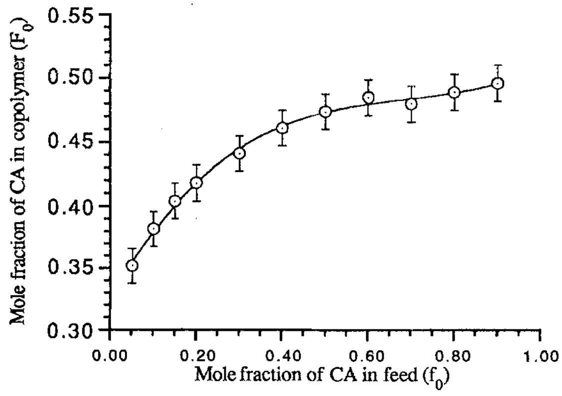

Fig.4. Overall copolymer composition plot for *p*-MST/CA copolymers prepared in MEK at 50°C.

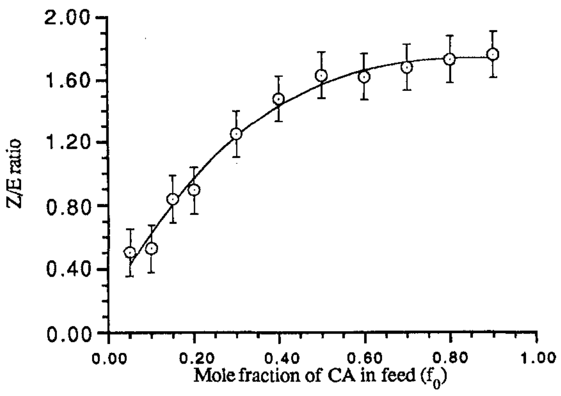

Fig.5. *Z/E* ratio plot for CA units in copolymers of *p*-MST with CA prepared in MEK at 50°C.

The above results therefore further confirm our finding of a link between the alternating tendency and the stereoregularity of the monomer units in these copolymers, which is in line with the suggestions of Olson, Butler *et al.* (4),(5),(6).

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Accepted July 15, 1992 C