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

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Summary

The configuration of citraconic anhydride units in *p*-chlorostyrene/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 semi-alternating copolymers showed an overall tendency to increase with the degree of alternation of the monomer units.

Introduction

In recent work (1),(2),(3) we have determined the configuration of cyclic anhydride units in alternating copolymers of *p*-methoxystyrene (*p*-MST) with maleic anhydride (MA), *p*-chlorostyrene (*p*-CST) with MA and *p*-MST with citraconic anhydride (CA) over a wide range of mole fractions in the comonomer feed. This was done in an effort to establish a link between the stereoregularity of the copolymer microstructure and the alternating tendency of the monomer units in copolymerisation systems in which pairs of comonomer units can form 1:1 charge transfer complexes in the comonomer feed, following the suggestions of Olson, Butler *et al.* (4),(5),(6),(7). In each case it was found that the ratio of *Z* (zusammen) to *E* (entgegen) configurations of the anhydride units in these copolymers increased along with the alternating tendency of the monomer units, reaching constant values when the monomer units were almost completely alternating and the mole fraction of cyclic anhydride units in the copolymers approached 0.50.

In this work, copolymers of *p*-CST were prepared with CA over a range of comonomer feed mole fractions and the configuration of CA units in these copolymers determined in order to establish if a link exists between copolymer microstructure and the alternating tendency of the monomer units in semi-alternating as well as alternating copolymers, where 1:1 charge transfer complexes can form in the comonomer feed.

Experimental

p-CST (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 distiled and dried over sodium. Required amounts of the comonomers ([*p*-CST+CA] = 4.000M), AIBN (0.0305M) and MEK were added to a glass ampoule and sealed under vacuum after freeze-thaw degassing. Polymerisation was carried out by placing the glass ampoule in

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an oil bath at 50.0±0.1°C for a predetermined period. The reaction was terminated and unreacted *p*-CST removed by quickly pouring the reaction mixture into low boiling point (60-80°C) petroleum spirit at room temperature, collecting the product and washing it with the same. The collected copolymer was then further washed with 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 in the absence of NOE. Acquisitions were made over 16 to 19 hour periods at 35°C using 5 mm o.d. tubes. The mole fraction of CA units in each copolymer (F_0) was determined from the relative areas of the carbonyl resonances at 171.5 and 176.0 ppm and the aromatic resonance at approximately 140 ppm (C7) 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 (8). Fig.1 shows a typical spectrum for a copolymer with $F_0 = 0.350$.

Results and discussion

The quaternary ^{13}C NMR spectra of the *p*-CST/CA copolymers were assigned as in Fig.1, following generally, previously reported assignments for similar copolymers (1),(2),(3),(4). The splitting of the resonance corresponding to the C3 carbons of the citraconic anhydride units shown in Fig.2, was assigned to the *Z* (49.2 ppm) and *E* (50.2 ppm) configurations of these units, following the assignments based on the model compound 2,3-dimethylsuccinic anhydride presented previously (1).

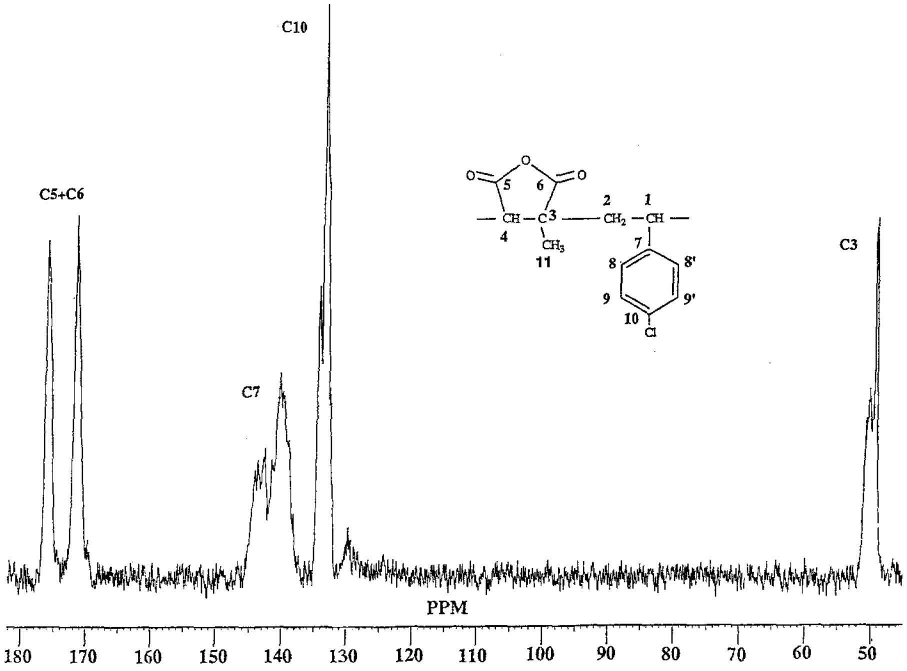

Fig.1 Typical quaternary ^{13}C NMR spectrum of a *p*-CST/CA copolymer ($F_0 = 0.350$)

The resonances in Fig.2 corresponding to the C7 carbons of the *p*-CST units in the copolymers can be assigned (3),(9),(10) to the following *p*-CST centred triad distributions:

010	138 - 140 ppm - alternating
011+110	140 - 143 ppm - semi-alternating
111	143 - 146 ppm - non-alternating

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

As was found for *p*-MST/CA copolymers (3), the overlapping nature of these triad resonances introduces a larger error into the determination of sequence distribution for these copolymers than was involved in our earlier work (1),(2). Again, this is especially true of the 010 and 011+110 resonances which overlap to the greatest degree.

The C7 resonances in Fig.2 show the dramatic change in the alternating tendency of monomer units in the copolymers across the comonomer feed mole fraction range. When the fraction of CA in the feed (f_0) is low, the copolymers are non to semi-alternating, with the tendency of the monomer units to alternate increasing along with f_0. 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 80% non-alternating triads to 70% alternating triads. Fig.4 shows the corresponding increase in the mole fraction of CA units in the copolymers (F_0) from approximately 0.10 to 0.45 across the same range. The C3 resonances in Fig.2 simultaneously show a gradual 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 and 5 that there is a predominance of *Z*

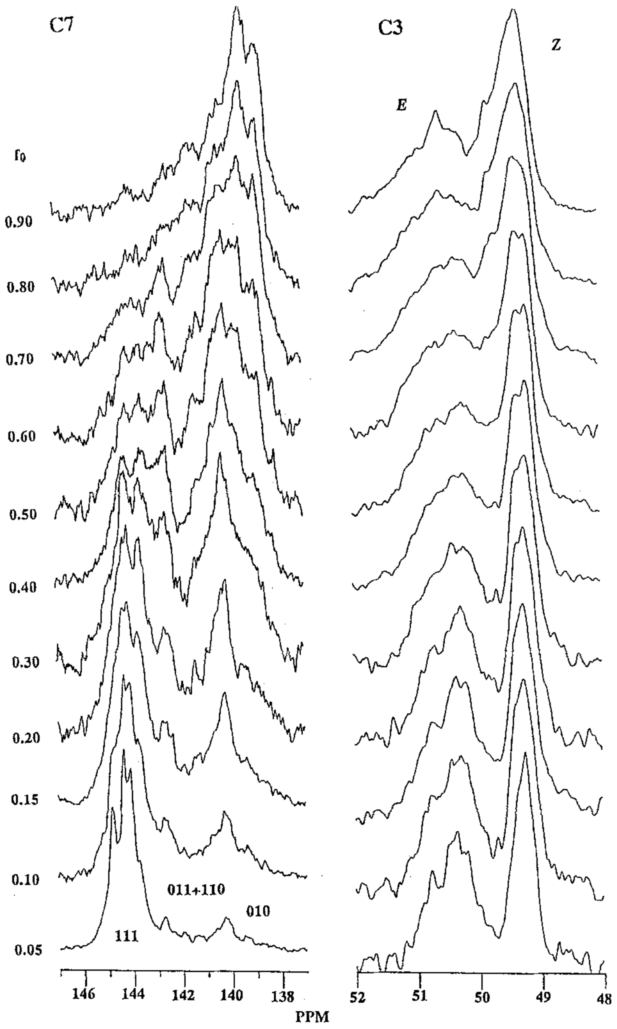

Fig.2 ^{13}C NMR spectra of C3 and C7 carbons of *p*-CST/CA copolymers over the mole fraction range $f_0 = 0.05$ to $f_0 = 0.90$.

configurations in these copolymers over the mole fraction range studied, which increases gradually as the tendency of the monomer units to alternate increases.

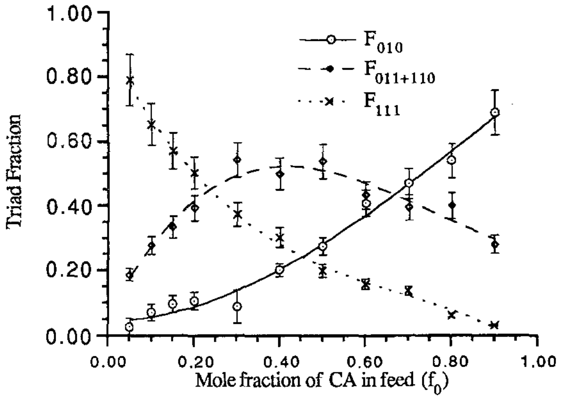

Fig.3 Triad fraction plot for *p*-CST/CA copolymers prepared in MEK at 50°C.

It may also be noted that the greatest changes in the *Z*/*E* ratio occur where the alternating tendency is at a minimum, i.e. when f_0 is low, and where the alternating tendency is at a maximum i.e. when f_0 is high, reaching a maximum value of 1.46±0.15 at $f_0 = 0.90$. In the region $f_0 = 0.20$ to $f_0 = 0.60$ the *Z*/*E* ratio remains almost constant, increasing only marginally.

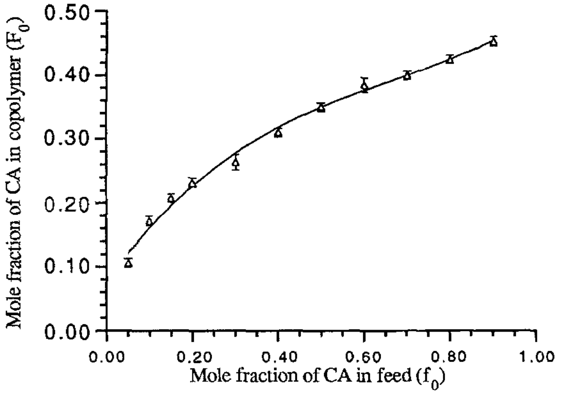

Fig.4 Overall copolymer composition plot for *p*-CST/CA copolymers prepared in MEK at 50°C.

Hence, the stereoregularity of these copolymers increases with the tendency of the monomer units to alternate, which is consistent with our previous work (1),(2),(3) although the precise trend differs in this latest case i.e. neither complete alternation of the monomer units or a constant *Z*/*E* ratio is attained. This is most likely due to the semi-alternating rather than alternating nature of this copolymerisation system.

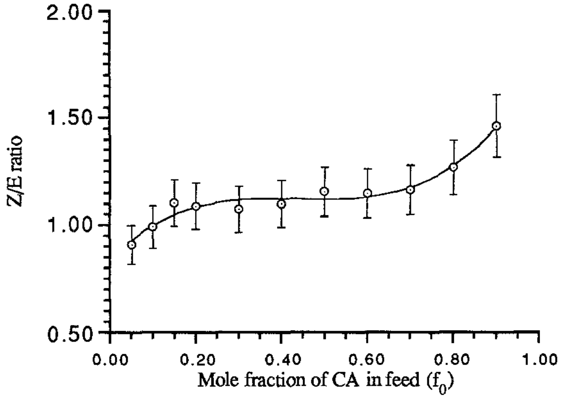

Fig.5 *Z/E* ratio plot for CA units in copolymers of *p*-CST with CA prepared in MEK at 50°C.

The above results therefore appear to support a link between the alternating tendency and stereoregularity of the monomer units in copolymers that can form 1:1 charge transfer complexes in the comonomer feed, which may have implications for the mechanism of copolymerisation in such systems.

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