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

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Summary

The configuration of maleic anhydride units in *p*-chlorostyrene/maleic anhydride copolymers prepared in methyl ethyl ketone at 50±0.1°C and the corresponding comonomer unit sequence distributions were determined using the ^{13}C DEPT NMR sequence. It was found that the ratio of *cis* (erythro) to *trans* (threo) configurations of maleic anhydride units increased with the degree of alternation of the comonomer units, reaching a constant value of approximately 0.73 when the comonomer units were almost completely alternating.

Introduction

In the study of the mechanism of alternating copolymerisation, the determination of copolymer sequence distributions and microstructure by ^{13}C NMR spectroscopy has become increasingly important. In a recent paper (1) we reported the assignment of peaks at 52.0 ppm and 52.8 ppm in the ^{13}C NMR spectra of *p*-methoxystyrene/maleic anhydride copolymers to the *cis* and *trans* configurations respectively of maleic anhydride units in these strongly alternating copolymers. The ratio of *cis* to *trans* configurations of the maleic anhydride units was determined from these peaks, over a wide range of comonomer feed mole fractions, and was found to increase along with the tendency of the monomer units to alternate, reaching a constant value of approximately 1.33 when the mole fraction of maleic anhydride in the feed was larger than 0.30 and the monomer unit sequence was almost completely alternating.

In this work, copolymers of *p*-chlorostyrene (*p*-CST) were prepared with maleic anhydride (MA) under the same conditions over a range of comonomer feed mole fractions to study the ratio of *cis* to *trans* configurations of maleic anhydride units in these less strongly alternating copolymers.

Experimental

p-CST (Fluka) was determined to have a purity of > 99.9% by ^{1}H and ^{13}C NMR and used as supplied. MA (Unilab) was recrystallised from dry benzene. 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 comonomer, MA ([comonomer+MA] = 1.000M), 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 in an oil bath at 50±0.1°C for a predetermined period. The reaction was terminated and unreacted

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styrene 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, and reprecipitated in boiling petroleum spirit (b.p. 80-120°C) to remove residual MA. 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. The DEPT pulse sequence was used to obtain methine and methylene sub-spectra, whilst complete carbon spectra of the copolymers were obtained using inverse-gated heteronuclear decoupling (INVGATE sequence). Acquisitions were made over 16 to 19 hour periods at 35°C using 5 mm o.d. sample tubes. Peak areas were measured using the *linesim* peak simulation program (2).

Results and discussion

The ^{13}C NMR spectra of the *p*-CST/MA copolymers were assigned as in Fig.1, following generally, previous reported assignments for similar copolymers (1),(3). The splitting of the resonance in the DEPT sub-spectra corresponding to the C3 methine carbons of the maleic anhydride units (Fig.2) was assigned to the *cis* (51.2 ppm) and *trans* (52.3 ppm) configurations of these units, following the assignment based on the model compound 2,3-dimethylsuccinic anhydride presented previously (1). The resonances in the DEPT sub-spectra for the C2 methylene carbons of the *p*-CST units in the copolymers (Fig.2) can be assigned (1),(4),(5) to the following *p*-CST centred triad distributions:

010 33 - 37 ppm - alternating
011+110 38 - 42 ppm - semi-alternating
111 42 - 45 ppm - non-alternating

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

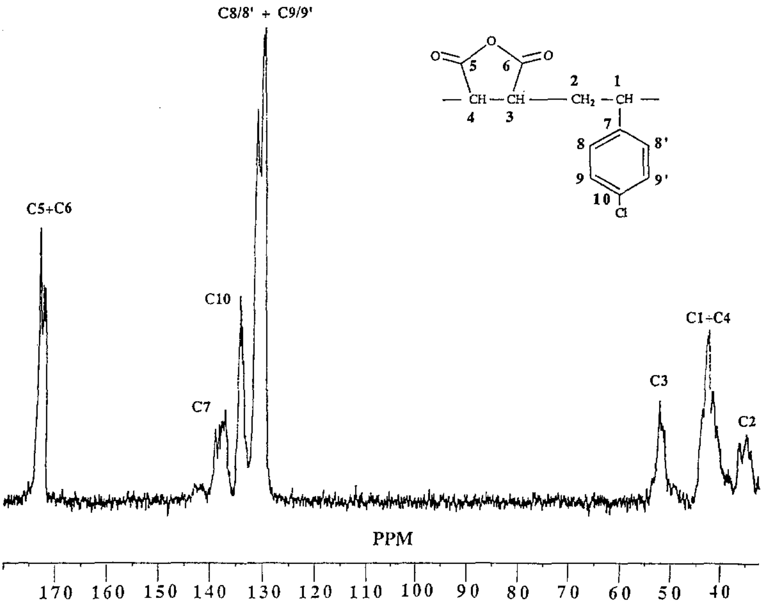

Fig. 1. Typical ^{13}C NMR spectrum of a *p*-CST/MA copolymer ($f_0 = 0.50$)

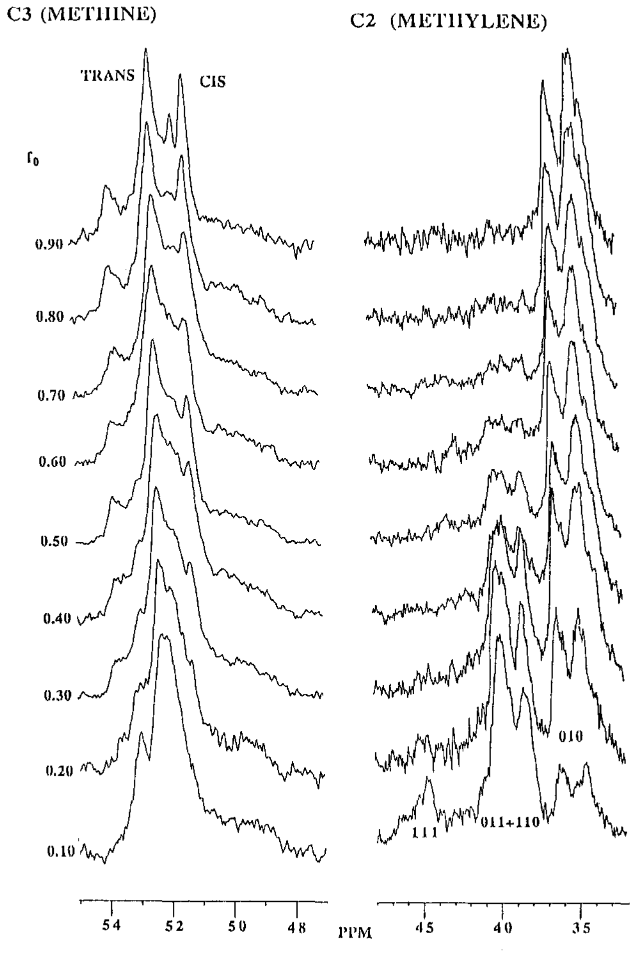

Fig.2. ^{13}C DEPT NMR spectra of methine (C3) and methylene (C2) carbons of *p*-CST/MA copolymers over the mole fraction range $f_0 = 0.10$ to $f_0 = 0.90$.

These methylene resonances show an increasing tendency for the monomer units to alternate as the fraction of MA in the feed (f_0) increases. The areas of these triad resonances were measured and the results are presented in Fig.3, where it can be seen that over the range $f_0 = 0.10$ to $f_0 = 0.90$ the copolymers change from consisting of approximately 20% alternating triads to 100% alternating triads. At the same time the ratio of *cis* to *trans* configurations of maleic anhydride units in the copolymers is seen to increase from the splitting of the C3 methine resonance in Fig.2. The ratio of *cis* to *trans* configurations was determined by measuring the area of each of the peaks in the C3 resonances, and is presented in Fig.4.

It can be seen then, that for the C3 resonance, the *trans* content is greatest when the tendency of the monomer units to alternate is lowest, i.e. when f_0 is low, with the *cis* content progressively increasing along with the tendency to alternate. At around $f_0 = 0.80$ the copolymer appears to be almost completely alternating and the *cis*/*trans* ratio reaches a constant value of approximately 0.73.

These results are consistent with those found for copolymers of *p*-methoxystyrene with MA, which exhibit a stronger tendency to alternate and have a higher overall *cis*/*trans* ratio which also reaches a constant value when the comonomer units are almost completely alternating, indicating a link between the alternating tendency and the resulting stereoregularity of the monomer units in these copolymers. This is in line with the suggestions of Olson, Butler *et al.* (6),(7),(8) which propose that the stereochemistry of monomer units in a copolymer may be influenced by the nature of the copolymerisation.

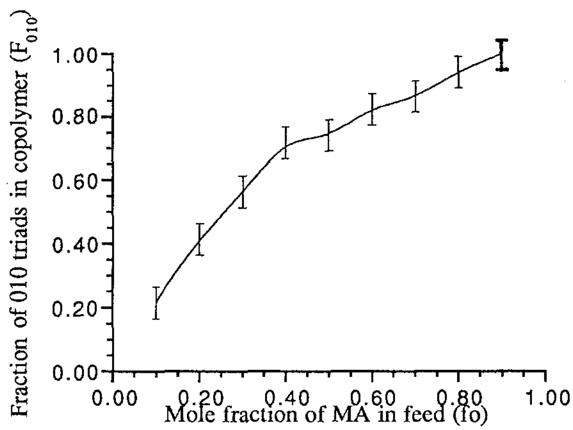

Fig.3. 010 triad fraction plot for *p*-CST/MA copolymers prepared in MEK at 50°C

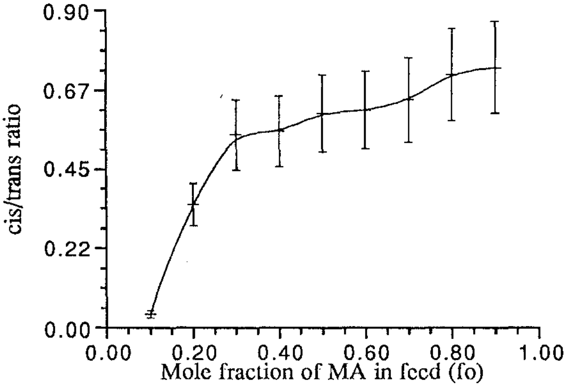

Fig.4. *cis/trans* ratio plot for C3 methine carbons in copolymers of *p*-CST with MA

References

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