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Quantitative determination of the content of *cis/trans* configurations of maleic anhydride units in *p*-methoxystyrene-maleic anhydride copolymers by ^{13}C NMR DEPT experiments

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Summary

The configuration of maleic anhydride units in p-methoxystyrene-maleic anhydride copolymers prepared in methyl ethyl ketone at 50°C was studied using ^{13}C NMR DEPT experiments. The ratio of cis (erythro) to trans (threo) configurations was found to increase with the tendency of the monomer units to alternate, remaining almost constant at 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. Also, para substitution on the styrene monomer units was found to greatly improve the resolution of the ^{13}C NMR DEPT spectra for copolymers of p-methoxystyrene and p-chlorostyrene with maleic anhydride as compared with that of styrene-maleic anhydride copolymers.

Introduction

Recently, there has been considerable interest in the study of copolymer sequence distributions and microstructure by ^{13}C NMR spectroscopy as a means of examining the mechanism of copolymerisation systems. O'Donnell, Hill et al. (1),(2) have studied styrene (ST) -maleic anhydride (MA) copolymers using ^{13}C NMR DEPT experiments to determine both sequence distributions and copolymer compositions. Olson, Butler et al. (3),(4),(5),(6) have proposed from their work on the copolymerisation of various N-substituted maleimides with vinyl ethers, that if donor-acceptor complexes participate in the polymerisation process, stereoregularity may be introduced into the microstructure of the copolymer. Applying this to ST-MA copolymers, it is useful then, to determine the quantities of cis and trans configurations of maleic anhydride units in these copolymers.

In this study, ^{13}C DEPT spectra have been obtained for ST- and substituted styrene-MA copolymers in order to identify the NMR signals for the cis and trans configurations of the MA units. Also, the effect of para substitution on styrene in enhancing the resolution of the NMR signals of copolymer backbone carbons will be examined by using p-methoxystyrene (p-MST) and p-chlorostyrene (p-CST) as the comonomers of MA.

Experimental

p-MST (Fluka) and p-CST (Fluka) were determined to have purities of > 99.9% by NMR and used as supplied. ST (Unilab) was distilled before use. 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

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*To whom offprint requests should be sent over sodium. 2,3-dimethylsuccinic anhydride was prepared from 2,3-dimethylsuccinic acid (Aldrich). 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^{0}C for a predetermined period. The reaction was terminated and unreacted styrene removed by quickly pouring the reaction mixture into low boiling point (60-80^{0}C) petroleum spirit at room temperature. The copolymer was then dissolved in MEK, and reprecipitated in boiling petroleum spirit (b.p. 80-120^{0}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 CXP-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 the INVGATE pulse sequence. Acquisitions were made over 16 to 19 hour periods at 35^{0}C using 5 mm o.d. sample tubes.

Results and discussion

^{13}C DEPT experiments were performed, generating methine and methylene sub-spectra for copolymers of p-MST-MA prepared over a wide comonomer feed mole fraction range. The resolution of spectra for copolymers of para substituted styrenes with MA was found to be much better than that obtained for the ST-MA copolymers. Fig.1 shows the comparison of the resolutions of ^{13}C DEPT spectra for ST-MA, p-MST-MA and p-CST-MA copolymers prepared under the same reaction conditions; [monomers] = 1.000M, [AIBN] = 0.0305M in MEK; conversions 5.6%, 5.8% and 6.5%, respectively; mole fraction of MA in feed (X_{MA}) = 0.500.

The quality of the NMR resolution of ST-MA copolymers in Fig.1 is very similar to that reported by O'Donnell et al. (1), who obtained their spectra using a similar 300MHz NMR spectrometer in conjunction with a 10mm probe. It is possible that this improvement in resolution, which enables us to further analyse the fine structure of the spectra, is brought about by the steric effect of the para substituent on the styrene units causing the solution demension of the copolymer to be more spread out than in the case of ST-MA copolymers, resulting in less complicated and hence better resolved NMR signals.

The ^{13}C NMR spectra of the p-MST-MA copolymers were assigned as in Fig.2, following generally the assignment proposed by Butler et al. (6). However, in order to explain the previously unassigned splitting of the resonances in the DEPT sub-spectra for the methylene carbons of the p-methoxystyrene units (C2) and in the sub-spectra for one of the methine carbons of the maleic anhydride units (C3), 2,3-dimethylsuccinic anhydride was prepared as a mixture of cis and trans isomers and used as a model compound to determine the magnitude of the effect of cis/trans configurations of protons on the maleic anhydride units in the copolymer on the chemical shifts for each of these carbons. Fig.3 shows that the effect of cis/trans configurations on the chemical shift of

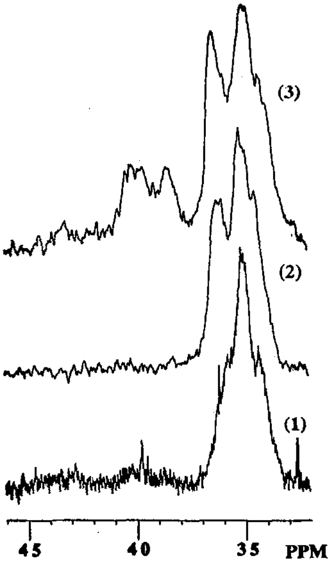

Figure 1. Comparison of the resolutions of ^{13}C NMR DEPT methylene spectra for copolymers of MA with (1) ST, (2) p-MST and (3) p-CST.

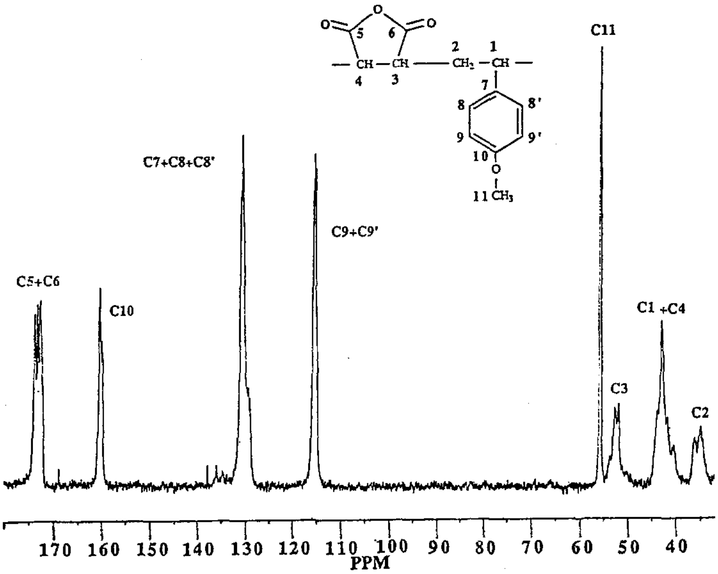

Figure 2. Typical ^{13}C NMR spectrum of a p-methoxystyrene-maleic anhydride copolymer ($X_{MA} = 0.50$).

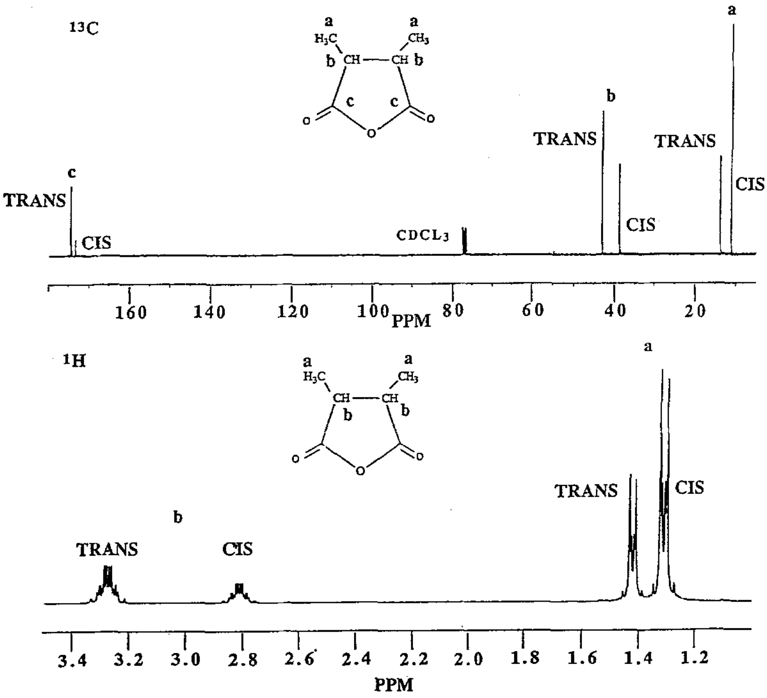

Figure 3. ^{13}C and ^{1}H NMR spectra of 2,3-dimethylsuccinic anhydride (cis and trans forms).

(b) ($\Delta^{13}C$ = -4.2 ppm) was greater than that for (a) ($\Delta^{13}C$ = -2.7 ppm) . Hence it is expected that the peak splitting due to cis/trans configurations of these protons in the copolymer will be larger for C3 than for C2. Thus, in Fig.4, the upfield peak (52.0 ppm) in the methine resonance is assigned to the cis configuration of protons on the maleic anhydride units in the copolymer chain and the downfield peak (52.8 ppm) to the trans configuration . Fig.4 then, shows an increasing cis content across the comonomer feed mole fraction range coupled with increasing alternation of the monomer units. This increase in alternation is shown by the methylene sub-spectra of C2, in which the observed resonances can be assigned to the following triads (1),(2):

MSM	33 - 37 ppm - alternating
MSS+SSM	38 - 42 ppm - partially alternating
SSS	42 - 45 ppm - non-alternating

where M = maleic anhydride, S = p-methoxystyrene

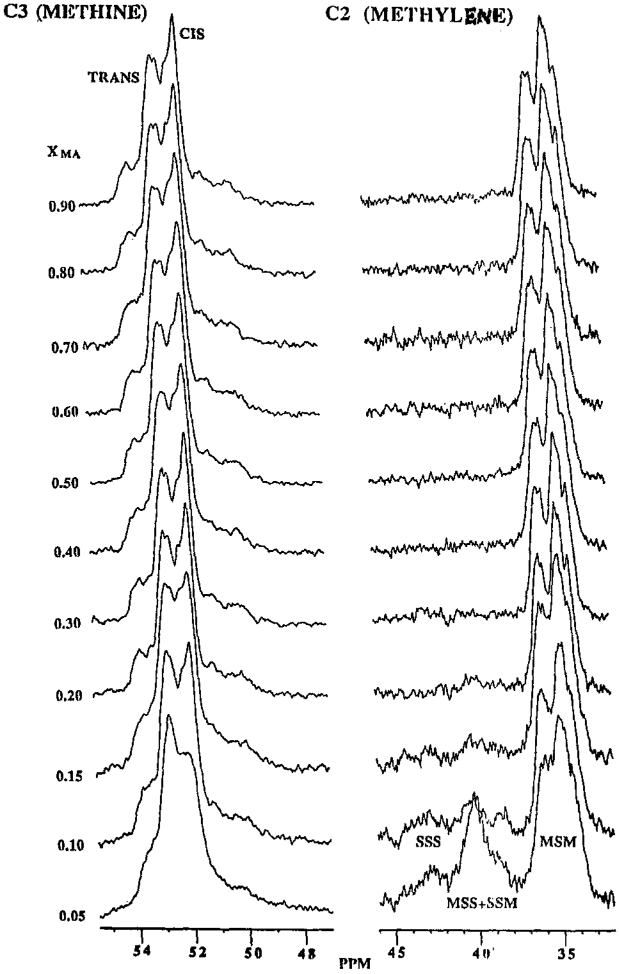

Figure 4. ^{13}C NMR DEPT spectra of the methine (C3) and methylene (C2) carbons of p-MST-MA copolymers over the mole fraction range X_{MA} = 0.05 to X_{MA} = 0.90.

These resonances also show a rapid establishment of alternating sequences as X_{MA} increases.

The areas of the cis and trans components of the methine resonances for C3 in Fig.4 were measured (7) and the results presented in Fig.5. It can be seen then, that for the C3 resonance, the trans content is greatest when the tendency to alternate is lowest, i.e. when X_{MA} is low, with the cis content progressively increasing with the tendency to alternate, i.e. as X_{MA} increases. At around X_{MA} = 0.30, the system appears to be almost completely alternating and the cis/trans ratio levels off at approximately 1.33.

Owing to the much enhanced resolution of para substituted styrene-MA copolymers, the MSM alternating triad resonance for the methylene carbon (C2) shows clear splitting into two main peaks that is possibly due to the tacticity of the p-MST-MA copolymers, with the effect of cis/trans configurations on the maleic anhydride units not being resolved.

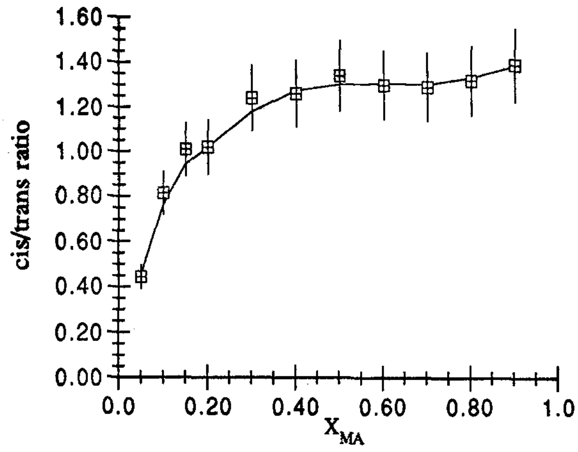

Figure 5. Plot of the ratio of areas of cis and trans components of the methine resonances (C3) for p-MST-MA copolymers vs. X_{MA}.

As X_{MA} increases a change in the splitting of this resonance is observed (Fig.4), with an overall increase in the intensity of the upfield peak at 35.1 ppm relative to the downfield peak at 36.1 ppm with increasing alternating tendency, i.e. as the MSS+SSM and SSS triad resonances disappear. This may indicate a change in tacticity tending towards increased stereoregularity as X_{MA} increases.

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7. Peak areas were measured using the Bruker "linesim" program, version 880601, by P.F. Barron, Bruker (Aust.) Pty. Ltd. (1988).

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