

Monomer unit sequence distribution and linkage configurations at citraconic anhydride units in the copolymers of citraconic anhydride and styrene prepared in carbon tetrachloride

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Summary

The triad monomer unit sequence distribution and the *cis* and *trans* linkage configurations at the cyclic citraconic anhydride units are quantitatively determined for the copolymers of citraconic anhydride (α -methylmaleic anhydride) (CA) and styrene (ST) prepared with AIBN in CCl_4 solutions at 50 °C. Semi-alternating copolymers are obtained for most feed compositions with rigidly alternating copolymers being formed when CA in feed is more than 90 %. Greater than 50 % of the linkages at CA units are found to be in *cis* configuration in semi-alternating copolymers. This may be explained if the donor-acceptor complex formed between CA and ST participates in the copolymerization.

Introduction

A prominent feature in the radically initiated copolymerization of maleic anhydride with styrene (ST), which produces alternating copolymers, is that an electron donor-acceptor (EDA) complex is formed between the comonomers (1). Citraconic anhydride (CA) (α -methylmaleic anhydride) has been reported to form an EDA complex in CHCl_3 with the equilibrium constant of 0.098 M^{-1} at 15 °C (2). In this article, the monomer unit sequence distribution and the *cis/trans* configurations at the cyclic CA units in CA-ST copolymers prepared in CCl_4 solutions are reported. Since CCl_4 has a low dielectric constant of 2.238 at 20 °C (3), it is expected that the concentration of the EDA complex between CA and ST is relatively substantial. If additions of free monomers to a propagating radical is sterically controlled, as is usually the case for free radical addition reactions (4), the *trans* configuration should dominate. On the other hand, a quantitative determination of *cis* and *trans* configurations may provide structural evidence for participation of the EDA complex (5).

Experimental

ST (Ajax) and CA (Fluka) were determined to have purities of >99.8 % by ^1H and ^{13}C NMR spectroscopies and used as supplied. 2,2'-azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol. CCl_4 (Unilab) was distilled and dried over molecular sieves. Petroleum spirit was distilled and dried over sodium. Required amounts of the comonomers ($[\text{CA}+\text{ST}] = 4.000 \text{ M}$), AIBN (0.0305 M) and CCl_4 were added to a glass ampoule and sealed under vacuum after freeze-thaw degassing. Polymerization was carried out by placing the glass ampoule in an oil bath at 50.0 ± 0.1 °C for a predetermined period. The reaction was terminated and unreacted CA and ST removed by quickly pouring the reaction mixture into petroleum spirit at room temperature, collecting the product and washing it with petroleum spirit. 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 20 hours. All copolymers were prepared to conversions of less than

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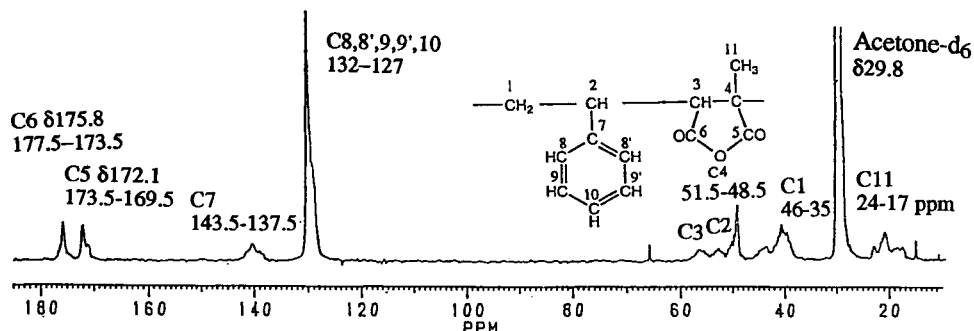


Fig. 1. Typical ^{13}C NMR spectrum of CA-ST alternating copolymer. $[\text{CA}+\text{ST}]=4.000$ M, mole fraction of CA in feed $f_0 = 0.95$, polymerized at 50.0°C , in CCl_4

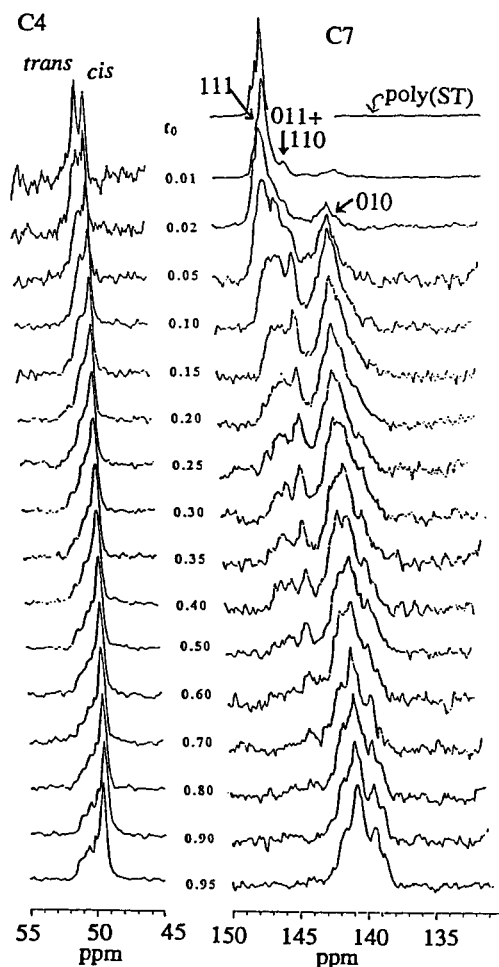


Fig. 2. Quaternary ^{13}C spectra of C4 and C7 carbons of CA(0)/ST(1) copolymers: f_0 = mole fractions of CA in feed monomer mixture

10 wt % with copolymers obtained from extreme ends of feed monomer compositions to less than 5 wt %.

^{13}C NMR spectra of the copolymers were obtained on approximately 20 % w/v solutions in acetone- d_6 in precision NMR tubes using a Bruker AC300 spectrometer; at 75.46 MHz with a broad band ^1H dual 5 mm probe, over 20 hour periods, at 35°C . The ^1H decoupler- and ^{13}C - $\pi/2$ pulse times were set at 9.9 and 4.2 μsec , respectively. The recycle delay was set at 2 sec for the DEPT (distortionless enhancement by polarization transfer) subspectra (6), and at 5 sec for quaternary ^{13}C spectra. The J modulation time was set to be 0.00345 s, which was equivalent to $J = 144.93$ Hz ($\Delta = 0.5/J$ for the optimum polarization/sensitivity ratio). The triad sequence distribution and *cis/trans* ratio were determined using peak areas measured with the *linesim* peak simulation program (7) and were confirmed by the paper-cutting method.

Results and Discussion

The spectrum of a typical alternating CA-ST copolymer is shown in Fig. 1. Absorption peaks are assigned following previously reported assignments for similar copolymers (8). Since CA does not homopolymerize under ordinary conditions (2), the possibility of forming CA(0)-CA(0) sequences is eliminated. The triad sequence distribution is determined from the resonances of C7 quaternary carbon (9) (10).

The splitting of the spectrum of C4 quaternary carbon is assigned to either *cis* or *trans* configurations at the cyclic CA units based on the model compound 2,3-dimethylsuccinic anhydride (11). The variation of the spectra of C4 and C7 carbons with respect to the feed monomer composition are shown in Fig. 2. The triad sequence distribution is shown in Fig. 3 with respect to the feed monomer composition. It is seen that

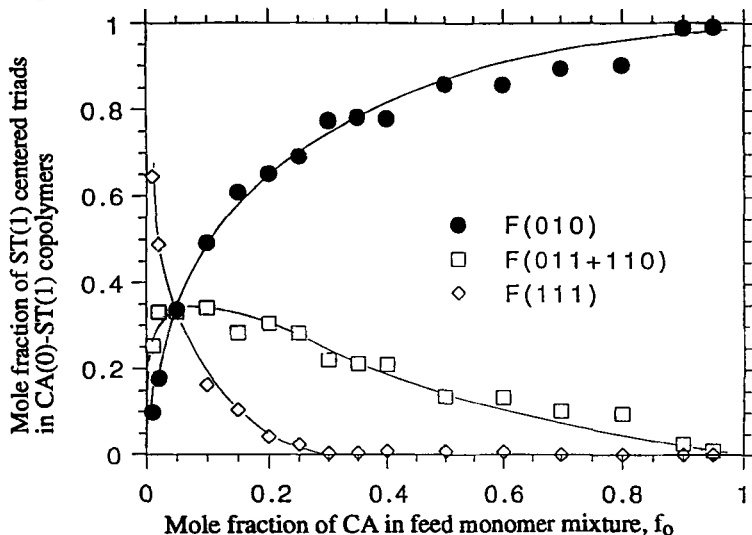


Fig. 3. Triad mole fractions, F(010), F(011+110) and F(111), in the copolymers of CA(0) and ST(1) prepared in CCl_4 at 50 °C

only semi-alternating copolymers are obtained for a wide range of feed monomer composition and that the comonomer units rigidly alternate in the copolymer only when the copolymers are prepared with more than 90 % of CA in the feed. The proportion of the *cis* configuration at the cyclic CA units in the copolymer is shown in Fig. 4 and it

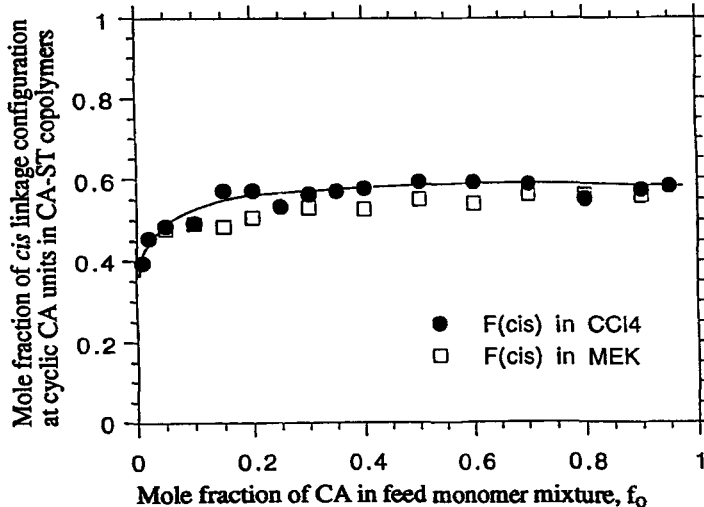


Fig. 4. Proportion of *cis* linkage configuration at cyclic CA units in the copolymers of CA and ST prepared in CCl_4 and in MEK (ref. 12) at 50 °C.

is compared with the proportion of *cis* configuration in the CA-ST copolymers obtained in methyl ethyl ketone (MEK) (12), which is much more polar than CCl₄, with the dielectric constant of 18.56 at 20 °C (3). The proportion of the *cis* configuration increases with the extent of alternation of the comonomer units in the copolymers and the proportion becomes almost constant when semi-alternating copolymers are formed. The proportion of the *cis* linkages is virtually the same for the copolymers obtained in MEK and in CCl₄ although the *cis* proportion may seem to be slightly larger for the copolymers prepared in relatively non-polar CCl₄.

It is remarkable to find that as much as 50 % of the linkages of the cyclic CA units are in *cis* configuration. This is contrary to the concept of free monomer additions to a propagating radical chain because addition of radicals are sensitive to steric hindrance; free monomer additions should give *trans* configuration overwhelmingly. A *cis* linkage, however, can be considered to be the result of an addition of the EDA complex formed between CA and ST monomers; when a propagating ST radical attacks the CA side of an EDA complex at an orthogonal position of the complex, followed by a concerted addition of ST within the complex, it is possible to form a *cis* linkage at a cyclic CA unit (5). The fact that the proportion of the *cis* configuration is not significantly affected by the polarity of the solvents may mean that the same mechanism operates in the copolymerizations in CCl₄ and in MEK in forming alternating and semi-alternating copolymers, and that the mechanism is not affected by the quantity of the donor-accepter complex. Because the complex participation mechanism for the copolymerization does provide an explanation for the large proportion of the *cis* configuration in semi-alternating and alternating copolymers, and because the overall rate of alternating copolymerizations has been reported (13)(14) to be greater than first order with respect to the monomer concentration, which is contrary to the prediction by mechanisms based on free monomer additions but is what is predicted by a complex participation mechanism, it is possible that the EDA complex formed between the comonomers is participating in forming alternating and semi-alternating CA-ST copolymers.

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