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Structural evidence for a complex participation in the alternating copolymerization of citraconic (α-methylmaleic) anhydride with styrene in *N*,*N*-dimethylformamide

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Summary

The ^{13}C DEPT NMR spectra of semi-alternating copolymers of citraconic (α-methylmaleic) anhydride (CA) and styrene (ST) prepared in a very polar solvent, N,N-dimethyformamide (DMF), with AIBN show that more than 50 % of the linkage configuration at the cyclic CA units is in cis configuration. Since the cis linkage configuration may result when the electron donor-acceptor complex formed between the comonomers is involved in the propagation, it is considered that, in very polar DMF, a participation of the complex is the driving force for the copolymerization.

Introduction

Maleic anhydride (MA) has been known to form alternating copolymers with styrene (ST) (1). There has been attempts to examine copolymerization mechanism by fitting theoretical equations for overall copolymer composition (2) and for triad distribution (3) to the experimental data by non linear least square (NLLS) minimization routine. One difficulty of this method when applied to alternating copolymerization is that, if a copolymerization system undergoes rigidly alternating copolymerization, all the copolymerization models merge together and it is no longer possible to differentiate various copolymerization models. We have reported that, even when the copolymerization is carried out in a very polar solvent such as N,N-dimethylformamide (DMF, the dielectric constant 38.25 at 293.2 K (4)), MA and ST form predominantly alternating copolymers (5) rendering the examination of copolymerization models by this method irrelevant (6).

In a related copolymerization of citraconic anhydride (α-methylmaleic anhydride) (CA) with ST in DMF under the identical polymerization conditions as for the ST-MA copolymerization reported in ref. (5), somewhat less alternating copolymers of CA and ST were obtained. When the NLLS curve fitting of theoretical equations, which were based on copolymerization models, to the monomer unit triad data was applied, those copolymerization models which incorporated some complex participation performed better with so-called *comppen* model (7) showing the most superior fit to the triad data (6); the *comppen* model was a complex participation model, which also took into account of the penultimate unit effect. However, the preference to the models with some complex participation was only marginal because of the alternating nature of the copolymerization and it could not be conclusive by itself. In this report, in order to support the result by the NLLS curve fitting to the triad data reported in ref. (6), structural evidence in the copolymers of CA and ST prepared in DMF is sought by following the suggestion by G.B. Butler (8, 9). The *cis/trans* linkage configuration of

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the cyclic CA units in the copolymers of CA-ST prepared in DMF is determined quantitatively in order to examine the mechanism of alternating copolymerization.

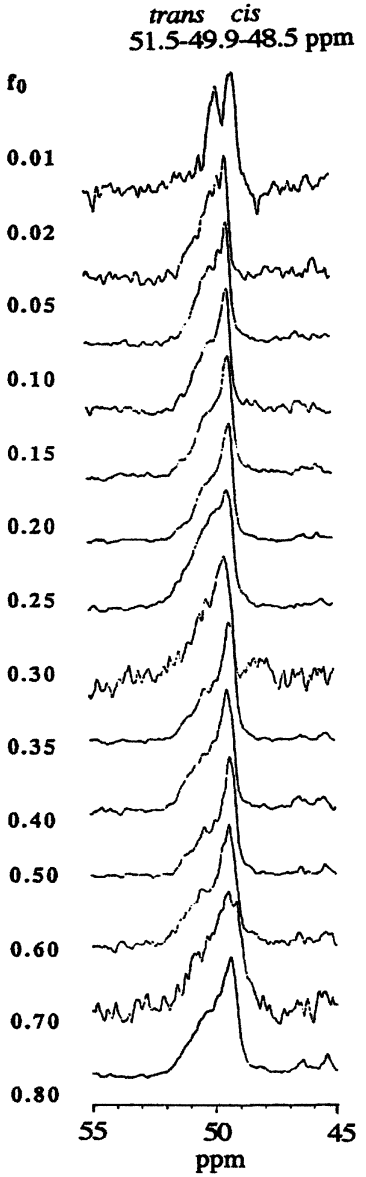


Fig.1 ^{13}C DEPT NMR spectra of α-carbon of CA units in copolymers prepared with feed mole fraction of CA, f_0.

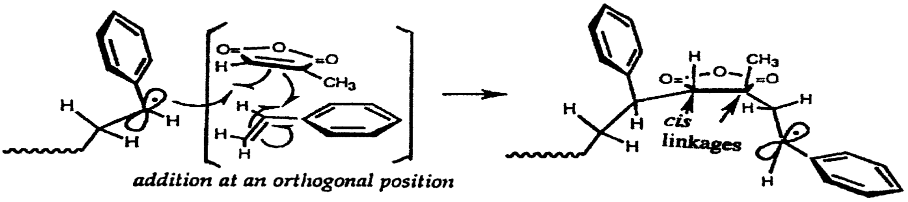
Experimental

The copolymerization conditions were: [AIBN] = $3.05\text{x}10^{-2}$ *M*, in DMF at 50.0±0.1 °C with a total monomer concentration [ST+CA] of 4.00 *M*. Polymerization was carries out in glass tubes which were sealed after freeze-thaw degassing. The conversion was kept to less than 10 % in general and less than 5 % at extreme feed monomer mole ratios. Copolymers were purified by re-precipitating them from the acetone solution in a large amount of high boiling (~110°C) petroleum spirit. The mole ratio of cis and *trans* linkage configurations was determined from the integrated ^{13}C NMR spectra of quaternary α-carbon of CA units in the copolymers (10). An NMR technique *distortionless enhancement by polarization transfer* (DEPT) (11) was employed at 75.46 MHz to isolate target carbon spectra and a peak simulation program *linesim* (12) was used to determine the peak area. The NMR spectra were observed in acetone-d_6 solution in a broad band ^{1}H dual 5 mm probe by a Bruker AC-300 NMR spectrometer with the measurement conditions of: ^{1}H decoupler- and ^{13}C-π/2 pulse times, 9.9 and 4.2 μs, respectively, with a 2-second recycle delay. *J*-modulation time, 3.5 ms, equivalent to J= 142.86 Hz ($\Delta = 0.5/J$ for optimum polarization/sensitivity. 308 K (35 °C). Acquisition period, 15 - 20 hrs.

Results and Discussion

In the ^{13}C DEPT spectra of the α-carbon of the CA units, major peaks observed were at 51.1, 50.5, 50.0 and 49.4 ppm. Following the reported chemical shifts by model compounds (10),the peaks in 51.5 - 49.9 ppm were integrated for the *trans* linkage configuration and the peaks in 49.9 - 48.5 ppm for the cis configuration.

Fig. 1 shows the variation of the peaks of the α-carbon of CA units (unit "0") with respect to the mole fraction of CA in feed mixture, f_0. It is seen that more *cis* configuration is formed when the f_0 is larger. The alternating triad mole fraction of CA-ST-CA triad, F_{010}, where ST units are designated as "1" units and CA as "0", has been reported for the CA-ST copolymers prepared in DMF (6). In DMF solution, the electron donor-acceptor (EDA) complex between CA and ST monomers absorb below 300 nm in uv, with the equilibrium constant reported to be 0.021 M-1 at 23 ° C (6). Since free radicals are not charged, steric hindrance plays a major role in radical reactions. In the copolymerization where only free (non complexed) monomers were involved, the *trans* linkage should be the overwhelming majority at cyclic CA units in the copolymers. However, our data shows that so much as more than 50 % of the linkages at CA units are often in cis configuration. The large proportion of the cis linkage can be explained only when an involvement of the EDA complex in the propagation is considered; when a growing ST radical attacks an EDA complex of CA and ST at an orthogonal or an "edge-on" position of the complex, a concerted reaction within the complex results in a formation of a cis linkage configuration at the CA unit.



When a growing radical attacks the complex on the flat sides of a complex, a *trans* configuration will result, though. It is interesting to see, therefore, if there is any correlation between the mole fraction of the *cis* linkages (F_{cis}) and the mole fraction of the alternating triad sequences (F_{010}) in the copolymers; F_{010} being an indicator for rigid (or complete) alternation as CA does not homopolymerize (13). The correlation is plotted in Fig. 2. If all the alternating triad monomer unit sequences were to be formed exclusively by the reaction of the EDA complex, the plot should be a straight line through the origin in Fig. 2 (14). Since CA is not capable of homopolymerizing, as the mole fraction of CA in the feed increases the copolymer would be formed increasingly by the reaction of the complex and the plot would approach to the straight line. The point on the x-axis where F_{010} = 1 is the situation in which only the rigidly alternating copolymer is formed. The intercept at F_{010} = 1 indicates the maximum extent of the *cis* linkage configuration expected when a complete alternation were achieved in this particular copolymerization under these specific polymerization conditions.

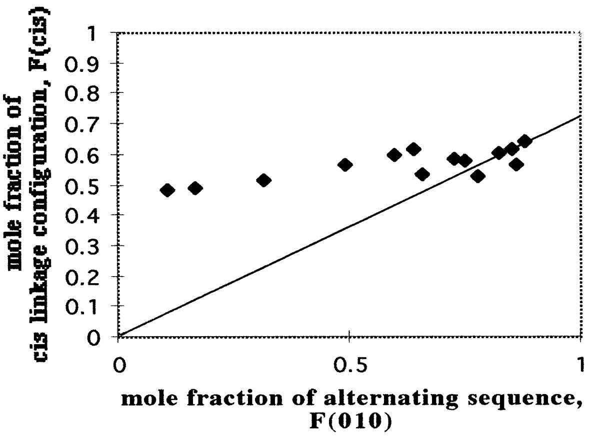


Fig.2. Correlation between the mole fraction of cis linkage configuration at the cyclic CA units F_{cis} and the mole fraction of completely alternating triad F_{010} in copolymer.

This value is estimated in Fig. 2 by an extrapolation to be 0.72; ie., *cis* configuration would be expected to 72 %, and *trans* 28 %. Because ST is capable of homopropagating, the copolymers include some amounts of semi-alternating monomer unit sequences of ST-ST-CA and CA-ST-ST especially when ST monomer concentration in feed is larger, ie. at lower f_0 in feed. The significantly larger amounts of F_{cis} above the straight line when the F_{010} in copolymer is smaller, may indicate that, because of the extremely large polarity of the solvent DMF, the copolymerization can only proceed effectively by the reaction of the EDA complex in forming semi-alternating sequences at lower f_0 in feed; the large solvent polarity of DMF virtually nullifies the lowering of the activation energy, which is due to the polar interaction between a growing radical and a comonomer, in the free monomer additions.

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