Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ha, Nuygen H. and Fujimori, Kiyohisa(1997) 'Determination of Monomer Unit Sequence Distribution and Linkage Configuration of Copolymers of Styrene and Citraconic Anhydride, and Possibility of a Participation of Electron Donor-Acceptor Complex in the Copolymerization', Journal of Macromolecular Science, Part A, 34: 9, 1593 — 1604

To link to this Article: DOI: 10.1080/10601329708010029

URL: http://dx.doi.org/10.1080/10601329708010029

J.M.S.—PURE APPL. CHEM., A34(9), pp. 1593–1604 (1997)

DETERMINATION OF MONOMER UNIT SEQUENCE DISTRIBUTION AND LINKAGE CONFIGURATION OF COPOLYMERS OF STYRENE AND CITRACONIC ANHYDRIDE, AND POSSIBILITY OF A PARTICIPATION OF ELECTRON DONOR-ACCEPTOR COMPLEX IN THE COPOLYMERIZATION

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ABSTRACT

The copolymerization system of styrene (ST) and citraconic (α-methymaleic) anhydride (CA) was found to form semi-alternating copolymers when polymerized with a total monomer concentration of 4 mol/L in CCl_4 at 50°C, with alternating copolymers being formed only when the CA mole fraction in feed was greater than 0.9. More than 50% of the linkage configurations at the cyclic CA units in the copolymers were found to be in *cis* configuration. This, together with the following observations, is consistent with a participation of the electron donor-acceptor (EDA) complex formed between ST and CA: (a) the complex participation model fits best, although only marginally, to the experimental triad mole fraction of alternating sequences; (b) the alternating monomer unit sequences and the *cis* linkage configuration at the cyclic CA units are more efficiently formed in non polar CCl_4 solutions than in polar methy ethyl ketone. The equilibrium constant for the EDA complexation of ST and CA in CCl_4 at 23°C is determined to be 0.142 ± 0.015 L/mol.

INTRODUCTION

Styrene (ST) and maleic anhydride are a classical comonomer pair which forms alternating copolymers with radical initiators [1]. Citraconic anhydride (α–methylmaleic anhydride) (CA) and ST have been reported to form alternating copolymers in chloroform solutions, in which the equilibrium constant for the formation of the electron donor-acceptor (EDA) complex between ST and CA has been determined to be 0.098 L/mol at 15°C [2]. Recently, a model discrimination study showed that the copolymerization of ST with maleic anhydride in methyl ethyl ketone (MEK) was best described by the penultimate unit effect model [3], with the concept of the bootstrap effect [4] being demonstrated to be useful in explaining solvent effects [5]. The possibility of a participation of the EDA complex formed between the comonomers in alternating copolymerizations has been proposed [6], but there is still no clear-cut conclusion for or against a participation of the complex in alternating copolymerizations. Because both the overall composition and monomer unit sequence distribution become constant in rigidly alternating copolymers, being strictly 1:1, all copolymerization models merge together when applied to a rigidly alternating copolymerization. It has been suggested that finding structural evidence may be useful in examining any participation of the EDA complex in alternating copolymerization [7]. In this report, the monomer unit triad sequence distribution and the relative amounts of *cis/trans* linkage configurations at the cyclic CA units in the copolymers of ST and CA, which are prepared in carbon tetrachloride, are determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy and the mechanism of the propagation step in the alternating copolymerization is discussed. It is hoped that the concentration of the EDA complex of ST and CA is substantial in non polar CCl_4 solutions.

EXPERIMENTAL

2,2'-Azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol. ST (Ajax) and CA (Fluka) were determined to have purities of >99.8% by ^{1}H and ^{13}C NMR spectroscopies and used as supplied. CCl_4 (Unilab) and acetone was distilled and kept over molecular sieves of Type A4 (Ajax). Petroleum spirit was distilled and kept over sodium wire.

A total monomer concentration of 4.000 mol/L and an AIBN concentration of 0.0305 mol/L were used throughout this study. Polymerization was carried out at 50.0 ± 0.1°C in an oil thermostat in sealed glass ampoules; required amounts of ST, CA and AIBN and a trace amount ($<3\mathrm{x}10^{-3}$ mol/L) of hydroquinone to inhibit any polymerization before the reaction mixture was ready for the polymerization [8], were weighed and placed in a glass ampoule. CCl_4 was added to make a total volume of 10.00 mL. The ampoule was then sealed under vacuum after repeated freeze-degas-thaw processes. The conversion was kept to be less than 10% generally and less than 5% when the mole fraction of CA in feed monomer mixture was less than 0.2 or more than 0.8. The polymerization was stopped by precipitating the copolymer in a large amount of petroleum spirit. Copolymers were collected and dissolved in acetone before being reprecipitated in petroleum spirit. The copolymers were then thoroughly washed in boiling petroleum spirit (80- 110 °C). Copolymers were dried under vacuum at room temperature for more than 20 hours.

^{13}C and quaternary ^{13}C NMR spectra were obtained on an approximately 20% w/v solution in acetone-d_6 (Fluka) in precision NMR tubes using a Bruker AC300 spectrometer at 75.46 MHz with a broad band ^1H dual 5 mm probe, over 15 - 20 hour periods at 35°C, with the set recycle delay of 4 s for ^{13}C spectra and 5 s for quaternary ^{13}C spectra. The ^1H decoupler- and ^{13}C-$\pi/2$ pulse times were set at 9.9 and 4.2 μs, respectively. For quaternary ^{13}C NMR experiments, the J modulation time (Δ) was set to be 0.00345 s, which was equivalent to $J = 144.93$ Hz ($\Delta = 0.5/J$ for the optimum polarization and/or sensitivity). The relative amounts of monomer unit triads and the *cis/trans* linkage configurations were determined from the peak areas of quaternary ^{13}C NMR spectra by using *Linesim* peak simulation program [9], and confirmed by the paper-cutting method.

A Varian Cary 1E uv-visible spectrophotometer was used for the determination of the equilibrium constants of EDA complexation between ST and CA.

RESULTS AND DISCUSSION

St and CA form an EDA complex, which absorbs below 330 nm in CCl_4. The equilibrium constant, K in L/mol, of the 1:1 EDA complexation was determined in CCl_4 solutions at 23°C according to the Ketelaar equation [10] by using excess ST as the donor.

$$1/(\varepsilon^{a} - \varepsilon^{A}) = [1/\{K(\varepsilon^{AD} - \varepsilon^{A})\}](1/[D]_{o}) + 1/(\varepsilon^{AD} - \varepsilon^{A}) \qquad (1)$$

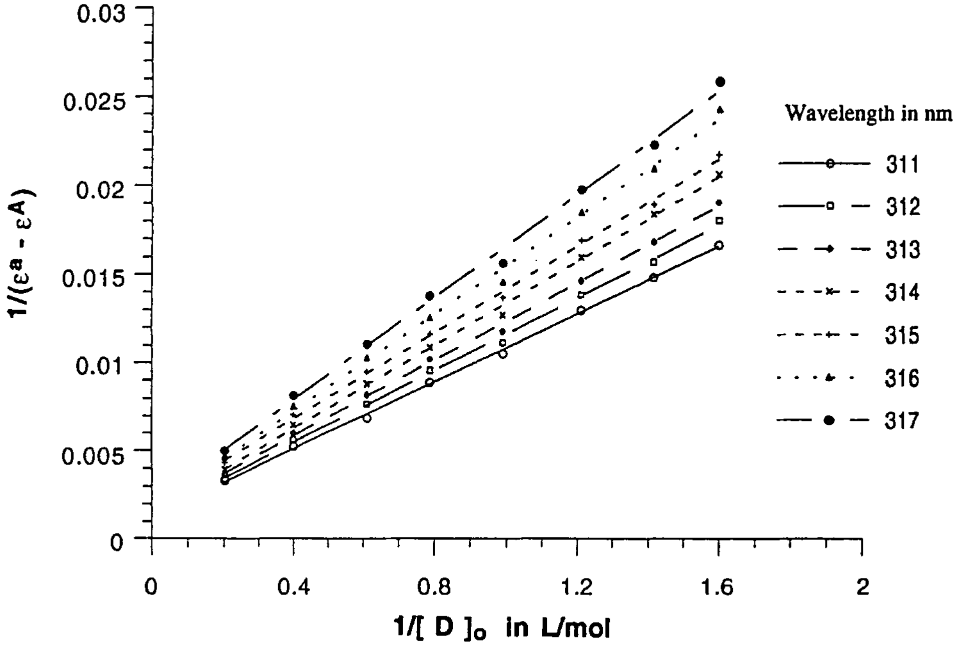

Figure 1. Ketelaar plots for the determination of the equilibrium constant, *K* in L/mol, of the EDA complexation at 23°C between ST and CA in carbon tetrachloride.

where, ε^A and ε^{AD} are the molar extinction coefficients of the acceptor and the EDA complex respectively, $[D]_0$ is the overall concentration of the donor in mol/L and ε^a is an apparent molar extinction coefficient defined as $\varepsilon^a = A'/[A]_0$, where A' is the absorptivity due to the complex and the acceptor, and $[A]_0$ is the overall concentration of the acceptor in mol/L. The Ketelaar plots are shown in Figure 1 for the determination of *K* in CCl_4. The average values of *K* were determined to be 0.142 ± 0.015 L/mol.

Figure 2 shows a ^{13}C NMR spectrum of a typical alternating copolymer of ST and CA. The spectra of the quaternary carbon atoms, C7 in the phenyl group and C4 in the CA unit of the copolymers, were used for the quantitative analysis of the triad monomer unit sequence distribution and the *cis/trans* linkage configurations at the cyclic CA units in the copolymers, respectively. The variation, with respect to the monomer compositions in feed, of the spectra of the quaternary C7 carbon and C4 carbon in the copolymers is shown in Figure 3. Because CA does not homopropagate under ordinary conditions [2], the possibility of forming CA(0)-CA(0)

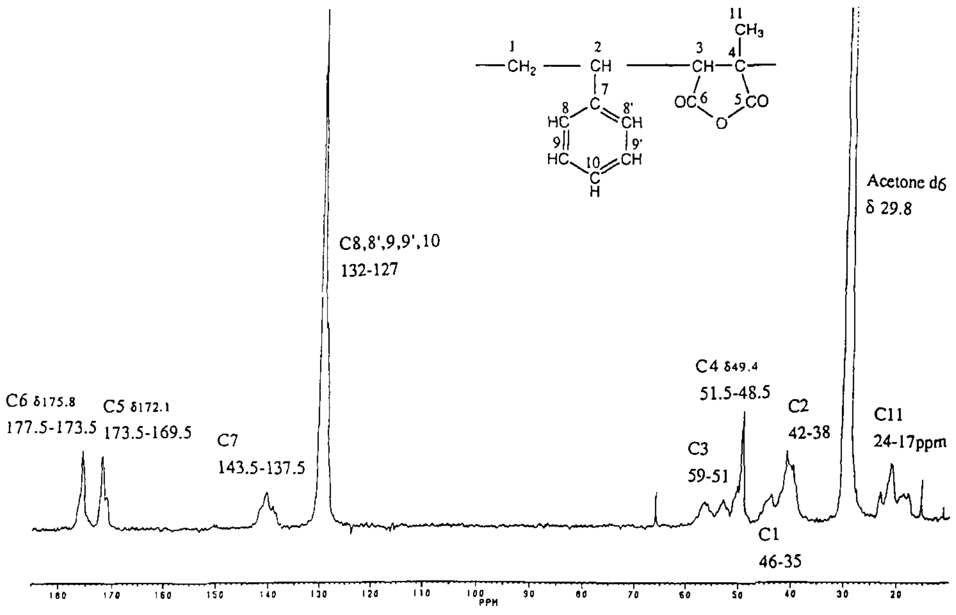

Figure 2. Typical ^{13}C NMR spectrum (taken in acetone-d_6) of a ST-CA alternating copolymer [ST + CA] = 4.000 mol/L; Mole fraction of CA in feed = 0.95; Polymerized at 50.0°C in CCl_4.

sequence is eliminated and the ST(1) centered triads are used for determining the triad distribution. The resonance peaks in the spectra are assigned to the triad sequences of ST(1) units and CA(0) units as follows, based on the previously reported assignments for similar copolymers [11] and the spectrum of poly(styrene) prepared in CCl_4..

alternating sequence of 010	143.5 - 137.5 ppm
semi-alternating sequences of 011 and 110	146.5 - 143.5 ppm
non-alternating sequence of 111	148.0 - 146.5 ppm

The results are in Table 1 together with the overall copolymer composition of CA(0) units, F_0, which is calculated from the triad data according to the following equation [12].

$$F_1/F_0 = 1 + (2F_{111} + F_{(011+110)})/(2F_{010} + F_{(011+110)}) \qquad (2)$$

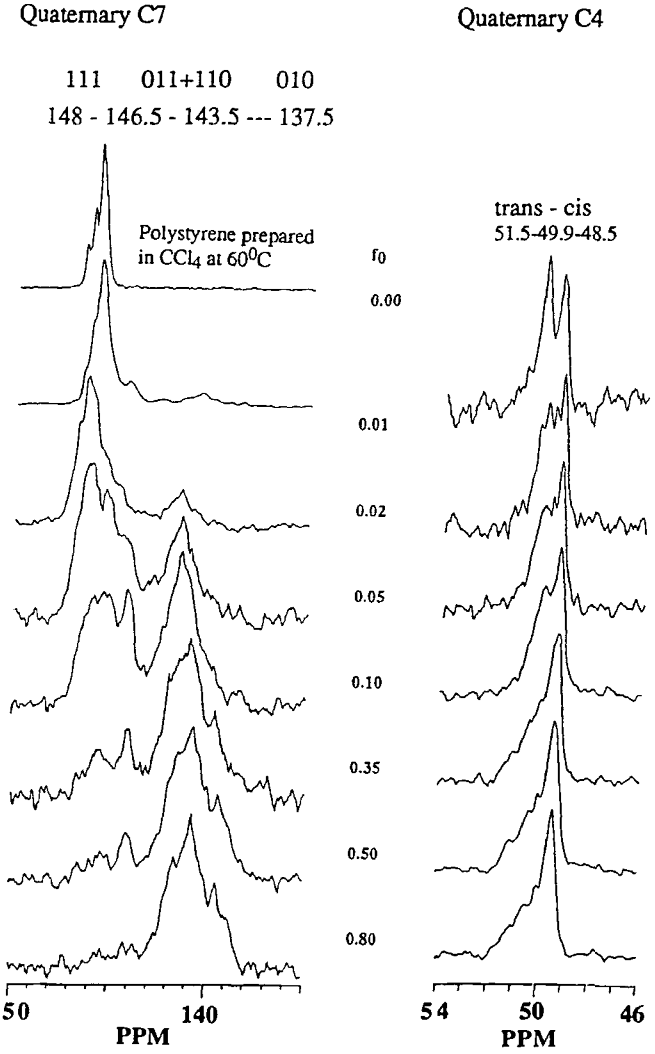

Figure 3. Variation of quaternary C7 and C4 spectra with respect to the mole fraction of CA in feed monomer mixture f_0 for the copolymers prepared in CCl_4.

where F_1 and F_0 are mole fractions of ST(1) units and CA(0) units in copolymers and $F_1 + F_0 = 1$. It is seen in Table 1 that the copolymerization system of ST and CA does not give rigidly alternating copolymers, which occur relatively more easily for the system of ST and maleic anhydride [13]. Copolymers of ST and CA approach to be alternating copolymers when prepared with the mole fraction of CA in feed being more than 0.9. It was also noticed that the rate of the copolymerization

TABLE.1 Mole Fractions of Triad Sequences and the Overall Mole Fraction of CA(0) Units (F_0) in the Copolymers of ST and CA Prepared in CCl_4 at 50 °C.

f_0	F_{010}	$F_{(011+110)}$	F_{111}	F_0
0.01	0.100	0.253	0.646	0.185
0.02	0.178	0.332	0.490	0.256
0.05	0.338	0.331	0.331	0.335
0.10	0.494	0.342	0.164	0.399
0.15	0.611	0.283	0.106	0.429
0.20	0.654	0.305	0.042	0.446
0.25	0.694	0.283	0.024	0.455
0.30	0.777	0.221	0.003	0.470
0.35	0.784	0.212	0.004	0.471
0.40	0.781	0.210	0.008	0.470
0.50	0.860	0.136	0.008	0.481
0.60	0.859	0.134	0.007	0.481
0.70	0.896	0.103	0.000	0.487
0.80	0.903	0.097	0.000	0.488
0.90	0.988	0.025	0.000	0.500
0.95	0.991	0.009	0.000	0.499

*[ST + CA] = 4.000 mol/L, [AIBN] = 0.0305 mol/L f_0: mole fraction of CA in the monomer mixture in feedF_{010}, $F_{(011+110)}$ and F_{111}: mole fractions of 010, (011 and 110), and 111 triads in copolymer, respectively

of ST with CA was very much slower than that of the copolymerization of ST with maleic anhydride in identical conditions. It is considered that this copolymerization system of ST and CA is difficult to form rigidly alternating copolymers and copolymerizes only sluggishly because of the effect of the methyl group in CA; the methyl group of the tertiary CA radical stabilizes the CA radical and may hinder an approach of a monomer. Or, if the complex is actually participating, the methyl group may reduce the reactivity of the EDA complex toward a growing radical.

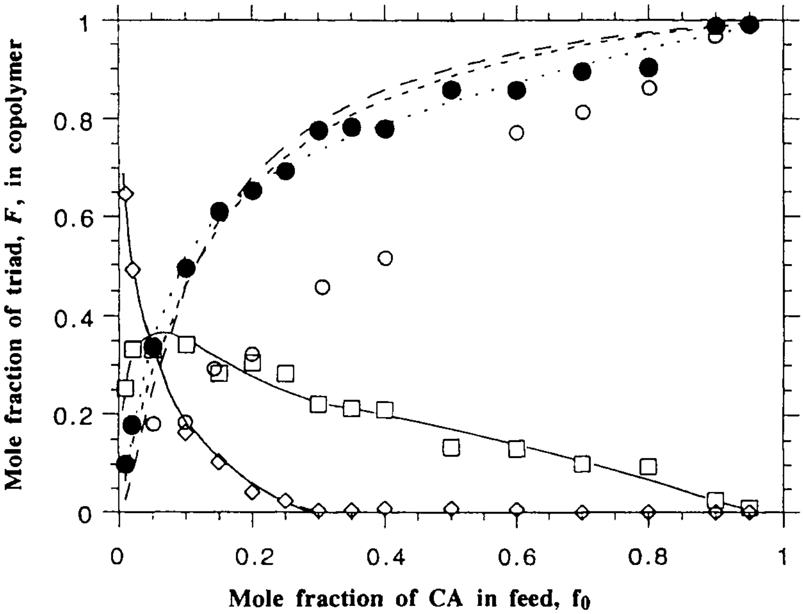

Figure 4. Mole fractions of alternating triads F_{010} (●), semi-alternating triads $F_{(011+110)}$ (□), and non alternating triads F_{111} (◇) with respect to the mole fraction of CA in feed f_0, and the NLLS curve fitting of copolymerization models to experimental F_{010} values for the copolymers of ST and CA prepared in CCl_4 at 50°C. (○): Experimental F_{010} values for ST-CA copolymers prepared in DMF at 50°C [16].

: the best fit curve for F_{010} by the terminal model

: the best fit curve for F_{010} by the penultimate unit effect model

: the best fit curve for F_{010} by the complex participation model

In Figure 4, the triad distributions are shown with respect to the feed monomer composition. The equations for the alternating triad fraction (F_{010}) based on the terminal model [14], the penultimate unit effect model [14] and the complex participation model [8, 15] were applied to the experimental alternating triad fraction data through the non-linear least square (NLLS) minimization routine in order to find the best fit copolymerization model to the experimental data. The following equations for the alternating triad were used.

The terminal model [14]:

$$F_{010} = 1/(1 + r_1 X_1)^2 \qquad (3)$$

TABLE 2. The Sum of Squares (SS) and the Standard Error (SY) in the NLLS Regression Analyses of Copolymerization Models on the Experimental Alternating Triad Fraction F_{010} in the Copolymers of ST and CA*

Copolymerization model	SS	SY
Terminal model	5.3×10^{-2}	5.9×10^{-2}
Penultimate model	2.3×10^{-2}	4.1×10^{-2}
Complex participation model	7.6×10^{-3}	2.5×10^{-2}

*Prepared in CCl_4 at 50°C. [ST+CA]=4.000 mol/L; [AIBN]=0.0305 mol/L

$SS = \Sigma(\text{experimental value - calculated value})^2$

$SY = \{SS/(\text{no. of data points - no. of variable parameters})\}^{0.5}$

The penultimate unit effect model [14]:

$$F_{010} = 1/[(1 + r_{01}X_1)\{1 + r_{01}X_1(1 + r_{11}X_1)/(1 + r_{01}X_1)\}] \tag{4}$$

The complex participation model [8,15]

$$F_{010} = p_1(1^1)(1 - P_{11})^2/\{p_1(1^1)(1 - P_{11})^2 + p_1(1^2)(2 - P_{11})\} \tag{5}$$

where, r's are the monomer reactivity ratios, X_1 is the mole ratio of monomer 1 to monomer 0 in feed, and p's and P's are probabilities. The original papers should be consulted for the reaction schemes and the definitions of the terms. The result of the NLLS regression analysis for F_{010} is shown in Figure 4. The values of the sum of squares (SS) and the standard error (SY) for each copolymerization model are shown in Table 2. It is seen from Table 2 and in Figure 4 that the complex participation model appears to be, although only marginally, better than other models in fitting to the experimental data. The small difference among the copolymerization models is because any difference among copolymerization models tends to disappear when the monomer unit sequence in copolymers approaches to be a rigidly alternating one and it becomes difficult to differentiate copolymerization models. Although the complex participation model appears to be a little better than others, it is difficult to draw a definitive conclusion from this evidence alone. In Figure 4, the mole fraction of alternating triads in the ST-CA copolymers prepared in MEK [16] is also shown for comparison. A substantial solvent effect is seen in a way that the copolymers prepared in less polar CCl_4, whose dielectric constant at

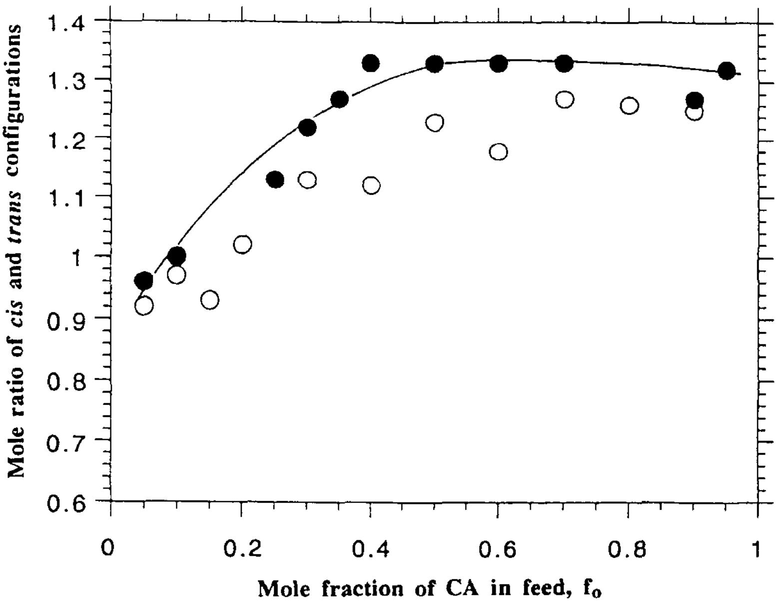

Figure 5. The mole ratio of *cis* and *trans* linkage configurations at the cyclic CA units in the copolymers of ST and CA, which are prepared in CCl_4 (●), and in MEK [16] (○).

20°C is 2.24 [17], have much more pronounced alternating tendency compared with the copolymers prepared in more polar MEK, whose dielectric constant is 18.56 at 20°C [17]. If the 1:1 EDA complex of ST and CA is participating, the more pronounced alternating tendency in the copolymers prepared in CCl_4 is consistent with the larger equilibrium constant (K) for the complexation in less polar CCl_4, in which $K = 0.142$ L/mol, as compared with that in MEK, in which the K is reported to be 0.10 L/mol [16].

The molar ratio of the *cis* configuration to the *trans* configuration at the cyclic CA units in the copolymers is plotted against the mole fraction of CA in feed in Figure 5. Since free radical intermediates, which are rather non polar, are much more susceptible to steric hindrance than very polar ionic intermediates, it would be expected that the linkage configurations at the cyclic CA units in the ST-CA copolymers would be dominated by the *trans* configuration, if the propagation reactions were entirely by the additions of free monomers. The result in Figure 5, which shows as much as more than 50% of the linkages at the cyclic CA units are in fact in the *cis* configuration, is contrary to the concept of exclusive free monomer additions.

The large proportion of the *cis* linkage configuration in the ST-CA copolymers, however, can be explained if the EDA complex formed between ST and CA is participating in the propagation step; when a propagating radical attacks the CA side of an EDA complex at an orthogonal position [7,11] or an edge-on position of the complex, followed by an intra-complex concerted addition of the ST component of the complex, a *cis* linkage will be formed at the cyclic CA unit. In Figure 5, the mole ratio of the *cis* and *trans* configurations determined for the ST-CA copolymers which are prepared in MEK [16], is shown for comparison. It appears that ST and CA form the *cis* linkage configuration slightly more efficiently in CCl_4 than in MEK especially when the composition of CA in feed is smaller. If the complex is participating in the copolymerization, this is consistent with the larger amount of the EDA complex in less polar CCl_4 than in MEK.

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Received December 20, 1996
Revision received March 30, 1997