A novel mechanistic study of the radical copolymerization of styrene with citraconic anhydride via ^{13}C n.m.r. spectroscopy

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The composition and monomer unit sequence distributions of copolymers of styrene with citraconic (α-methylmaleic) anhydride (CA) prepared in methyl ethyl ketone at 50.0 ± 0.1°C have been determined over a range of comonomer feed mole fractions using ^{13}C n.m.r. spectroscopy. The monomer units in these copolymers were found to display an increasingly strong tendency to alternate as the mole fraction of CA in the feed increased. The terminal, penultimate, complex-participation and complex-dissociation models were each tested for applicability to the mechanism of copolymerization for this comonomer system by applying reactivity ratio related test functions to the experimental sequence distribution data, enabling a direct visual assessment of the applicability of each model to be made. On the basis of these test functions, the terminal, penultimate and complex-dissociation models were each found to provide inadequate descriptions of this copolymerization system.

(Keywords: radical copolymerization; styrene; citraconic anhydride)

INTRODUCTION

The mechanism of the radical alternating copolymerization of comonomers that can form 1:1 electron donor–acceptor (EDA) complexes has long been a subject of debate, with the main point of contention surrounding the participation of these complexes during chain propagation. In addition to the classical terminal[1,2] and penultimate[3] models for the mechanism of copolymerization, models have been developed incorporating EDA complex participation in the propagating step, as an alternative means of describing the strong alternating tendency of the comonomer units in these types of copolymers. Two of the more popular of this latter type of model are the complex-participation[4] and complex-dissociation[5] models.

One such comonomer system that has received little attention is the styrene (ST)/citraconic (α-methylmaleic) anhydride (CA) system. The existence of an EDA complex formed between ST and CA has been confirmed by Yang and Otsu[6] who have studied this system in bulk at 60°C, using copolymer compositions to compare the applicability of the terminal, penultimate and complex-participation models to the mechanism of copolymerization. Whilst they found the penultimate model to provide a relatively adequate description of the copolymerization, they concluded that the 1:1 EDA complex formed between ST and CA takes a certain but small part in the propagation reaction of the copolymerization. In recent work, mechanistic studies of the *p*-methoxystyrene/maleic anhydride (*p*-MST/MA)[7], *p*-MST/CA[8] and *p*-chlorostyrene/CA[9] copolymerization systems have shown that the role of the EDA complex should not be discounted when describing the mechanism of copolymerization in these types of comonomer systems. Related work[10–13] proposes that trends in the stereochemistry of the monomer units in these copolymers may have mechanistic implications. Olson and Butler and Butler *et al.* have proposed[14–18] that the participation of EDA complexes in the polymerization process, if it occurs, should affect the stereochemistry of the monomer units in the resulting copolymers.

In this work the radical copolymerization of ST with CA in methyl ethyl ketone (MEK) at 50°C was studied for a range of comonomer feed mole fractions, using ^{13}C n.m.r. spectroscopy to determine overall copolymer compositions and monomer unit sequence distributions. The terminal, penultimate, complex-participation and complex-dissociation models were tested for applicability to the mechanism of this alternating copolymerization system using a novel approach involving the application of reactivity ratio related test functions developed for the study of the ST/MA copolymerization system[19] to the experimental sequence distribution data in the form of ST centred triad fractions.

In recent times, non-linear least squares (NLLS) techniques[20] have typically been used to discriminate between copolymerization models in these types of studies. Unfortunately this lengthy and complicated type of analysis often yields inconclusive or ambiguous results. This is particularly true in the case of alternating or semi-alternting copolymerization systems, as any discernible difference between various copolymerization

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models tends to diminish as a system approaches perfect alternation. In fact, a NLLS analysis of the data presented in this work[21] failed to differentiate between the penultimate, complex-participation and complex-dissociation models in terms of their applicability to the copolymerization system despite the accuracy of the data. *Figure 1* shows the fit of these models to the experimental composition data, where it can be seen that each model provides a similarly good fit to the data, in contrast to the fit provided by the terminal model. It has recently been shown[22] that the use of reactivity ratio related test functions, as outlined in this paper, can be a simple, quick and accurate alternative to NLLS methods that can be particularly useful when such analyses return inconclusive results[8,9], providing sequence distribution data of sufficient accuracy is available. Furthermore, it has been suggested[7–9,23,24] that mechanistic studies of copolymerization systems made on the basis of sequence distribution data are better able to discriminate between copolymerization models than those made using copolymer composition data.

EXPERIMENTAL

Materials

Styrene (Unilab) was distilled under reduced pressure before use. Citraconic anhydride (Fluka) was determined to have a purity of >99.9% by ^{1}H and ^{13}C n.m.r. and was used as supplied. 2,2'-Azobisisobutyronitrile (AIBN, Fluka) was recrystallized from dry methanol. Methyl ethyl ketone (Unilab) was dried over $CaCl_2$, distilled and kept over molecular sieves until needed. Petroleum spirit was distilled and dried over sodium.

Polymerizations

The required amounts of ST, CA ($[ST+CA]=4.000$ mol l^{-1}), AIBN and MEK were added to a glass ampoule together with a trace amount of hydroquinone ($<2.7\times10^{-3}$ mol l^{-1}) to a total volume of 10.00 ml and sealed under vacuum after degassing. Hydroquinone was added to inhibit polymerization before the system became homogeneous at the reaction temperature of 50.0 ± 0.1°C[19]. In all cases the reaction mixture remained homogeneous throughout the polymerization. The reaction was terminated by pouring the reaction mixture into a 10-fold excess of low boiling point petroleum spirit (b.p. 60–80°C) at room temperature. The copolymer was then collected and washed thoroughly with boiling petroleum spirit (b.p. 80–120°C) to remove residual CA and dried *in vacuo* at 50°C for 16 h. All copolymer samples were prepared to conversions of <10 wt% after purification, with samples prepared at the extremes of comonomer feed ratios prepared to <5%.

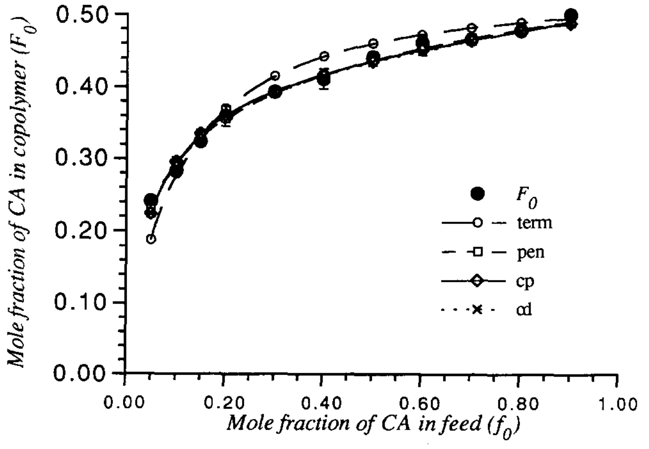

Figure 1 Composition diagram for the copolymerization of ST with CA in MEK (4.000 mol l^{-1}) at 50°C

Spectroscopy

^{13}C n.m.r. spectra of the copolymers were obtained on 25% w/v solutions in acetone-d_6 using a Bruker AC-300 spectrometer at 75.46 MHz, with a broad band/^{1}H dual 5 mm probe, over 16–19 h periods at 35°C. Spectra of quaternary carbons in the copolymers were acquired using ^{1}H and ^{13}C decoupler $\pi/2$ pulse times of 9.9 and 4.2 μs, respectively, with a 2 s recycle time, in the absence of nuclear Overhauser enhancement (NOE). The J modulation time was set to 3.2 ms, equivalent to $J=156$ Hz. Chromium (III) acetylacetonate was used as a relaxation agent in each sample. No significant increase in integrated area of the spectra was observed between acquisitions made under these conditions and those made with a recycle delay of 5 s in the absence of NOE. The presence of a transitory, contact type 1:1 ST/CA EDA complex in MEK was confirmed via u.v. spectroscopy, under conditions allowing the application of the Ketelaar equation[25]. The value of the equilibrium constant for complex formation was measured at 338 and 340 nm and its average value in MEK at ambient temperature determined to be 0.10 ± 0.02 l mol^{-1}. U.v. spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer, using 1 cm path length cells.

RESULTS AND DISCUSSION

N.m.r. analysis

The quaternary ^{13}C n.m.r. spectra of the ST/CA copolymers were assigned as in *Figure 2*, following generally, previously reported assignments for similar copolymers[10–13,18] and through the use of ^{13}C n.m.r. chemical shift tables. It has been assumed that the comonomer units add in a strict head-to-tail manner, as displayed in *Figure 2*. If regio-irregular head-to-head comonomer sequences are formed, a resonance corresponding to the C3 carbons of CA units in such sequences should appear ~10 ppm upfield of the peak shown in *Figure 2* as a result of the differences in the combined α, β and γ substituent effects on the chemical shifts of these carbons in head-to-tail and head-to-head sequences[26]. No such peak has been found in any of the spectra obtained during the course of this work. The small unassigned peaks in *Figure 2* are due to incomplete cancelling of non-quaternary carbons during acquisition of the quaternary spectrum. Conversely, if the C3 resonance in *Figure 2* itself represents head-to-head sequences, a peak corresponding to head-to-tail sequences should appear ~10 ppm downfield of this resonance. As no evidence for this has been found either, it would appear that the assumption of strict head-to-tail addition of the monomer units during propagation is a reasonable one. In any event, the formation of regio-irregular head-to-head comonomer sequences would not affect the purpose of this work providing their contributing peak areas were accounted for where such independent resonances existed. Copolymer compositions, expressed as the mole fraction of CA units in each

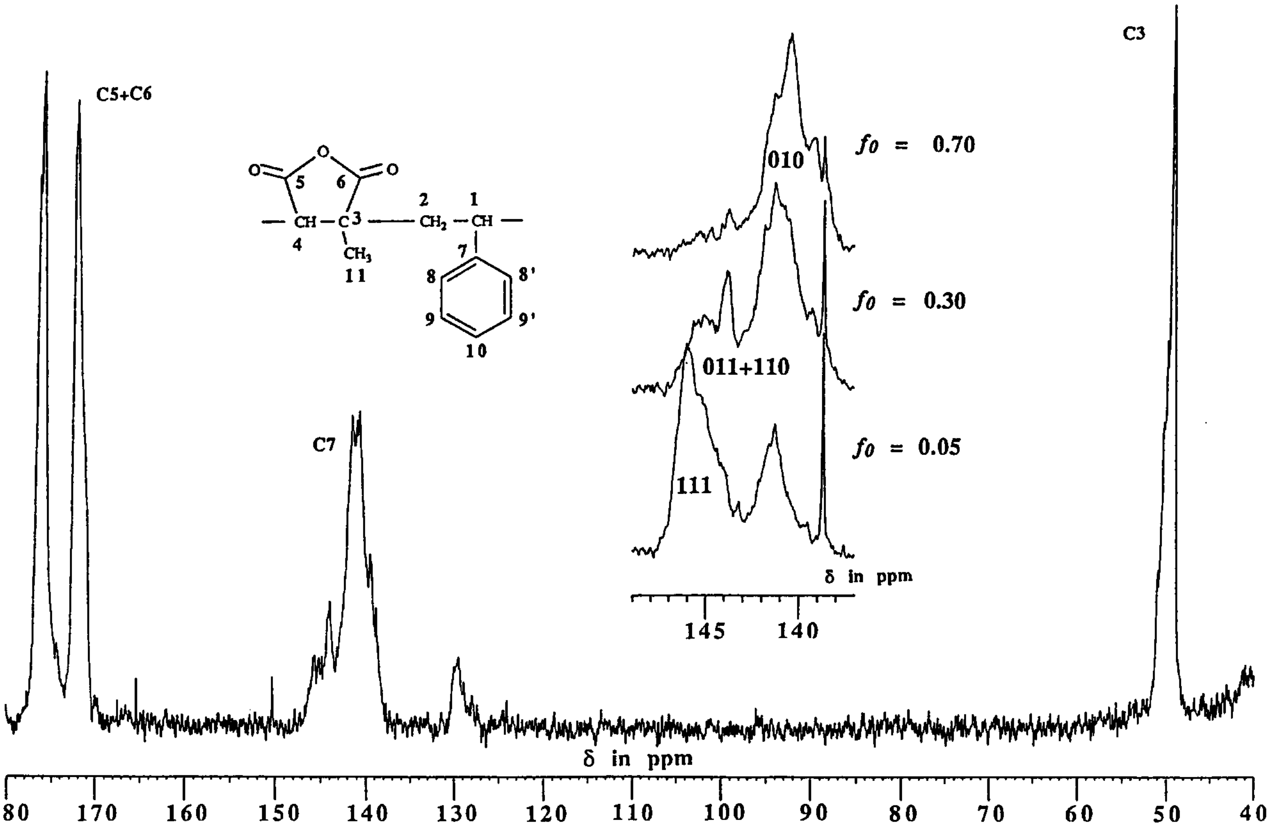

Figure 2 Typical quaternary ^{13}C n.m.r. spectrum of a ST/CA copolymer ($F_0 = 0.441$) showing assignment of the C7 aromatic resonance to monomer unit triad distributions within the copolymers

copolymer (F_0) were determined from the integrated areas of the carbonyl resonances at 175.7 and 171.8 ppm and the aromatic resonance at ~141 ppm in these spectra.

The alternating tendency of these copolymers is displayed by the experimental copolymer compositions and monomer unit sequence distributions in the form of ST centred triad fractions determined from the ^{13}C n.m.r. spectra, presented together with the initial comonomer feed compositions in *Table 1*.

The fraction of ST centred triads in each copolymer was determined from the areas of the following aromatic resonances using the linesim[27] peak simulation program, which minimizes the errors in determining individual resonance areas due to peak overlap, in the manner outlined previously[8,9]. These resonances have been characterized following the assignments initially presented by Buchak and Ramey[28], and more recently by Bhuyan and Dass[29]:

010	139–141 ppm	alternating triad
011+110	141–144 ppm	semi-alternating triad
111	144–148 ppm	non-alternating triad

where 0 = CA and 1 = ST. As CA is considered not to homopropagate under these conditions[6], there are also the only possible triads present in the copolymers with unique chemical shifts in the n.m.r. spectra, i.e. the chemical shift and contributing area of the 101 triad can be accounted for in terms of its two adjoining 1 centred triads whilst triads involving the homopropagation of CA are not possible. *Figure 3* shows the fraction of each of the 1 centred triads in the copolymers as a function of the initial fraction of CA in the comonomer feed (f_0).

Table 1 Experimental composition and triad fraction data for the copolymerization of ST (1) with CA (0) in MEK at 50°C[a]

f_0[b]	F_0[c]	F_{010}[d]	$F_{011+110}$[e]	F_{111}[f]
0.0500	0.241 ± 0.007	$0.18_7 \pm 0.030$	$0.26_0 \pm 0.050$	$0.55_3 \pm 0.055$
0.1000	0.283 ± 0.007	$0.17_1 \pm 0.060$	$0.44_9 \pm 0.060$	$0.38_0 \pm 0.038$
0.1500	0.324 ± 0.007	$0.29_2 \pm 0.029$	$0.37_6 \pm 0.050$	$0.33_2 \pm 0.033$
0.2000	$0.35_9 \pm 0.014$	$0.32_9 \pm 0.033$	$0.46_2 \pm 0.050$	$0.20_9 \pm 0.031$
0.3000	0.393 ± 0.007	$0.43_6 \pm 0.044$	$0.42_6 \pm 0.050$	$0.13_9 \pm 0.014$
0.4000	$0.41_1 \pm 0.014$	$0.50_0 \pm 0.050$	$0.39_9 \pm 0.050$	$0.10_2 \pm 0.010$
0.5000	0.441 ± 0.007	$0.65_0 \pm 0.065$	$0.27_8 \pm 0.050$	0.072 ± 0.007
0.6000	$0.46_1 \pm 0.010$	$0.76_0 \pm 0.076$	$0.19_0 \pm 0.050$	0.050 ± 0.005
0.7000	0.466 ± 0.007	$0.78_0 \pm 0.078$	$0.18_5 \pm 0.050$	0.035 ± 0.005
0.8000	0.478 ± 0.007	$0.85_0 \pm 0.085$	$0.12_9 \pm 0.060$	0.021 ± 0.005
0.9000	0.500 ± 0.007	$1.0_{00} \pm 0.100$	$0.00_0 \pm 0.050$	0.000 ± 0.005

[a] $[\mathrm{ST} + \mathrm{CA}] = 4.000 \pm 0.001\ \mathrm{mol\,l^{-1}}$; $[\mathrm{AIBN}] = 0.0305 \pm 0.0001\ \mathrm{mol\,l^{-1}}$
[b] Mole fraction of CA in feed (±0.005)
[c] Mole fraction of CA in copolymer
[d] Fraction of 010 triad in copolymer
[e] Fraction of 011 + 110 triads in copolymer
[f] Fraction of 111 triad in copolymer

It can be seen from *Figure 3* that the tendency of the monomer units to alternate increases as f_0 increases, with the copolymers becoming almost completely alternating from $f_0 \approx 0.80$.

Test functions

The reactivity ratio related test functions *a* and *b* are defined as follows:

$$a = \frac{[0]}{[1]} \frac{2F_{111}}{F_{011+110}}$$

$$b = \frac{[0]}{[1]} \frac{F_{011+110}}{2F_{010}}$$

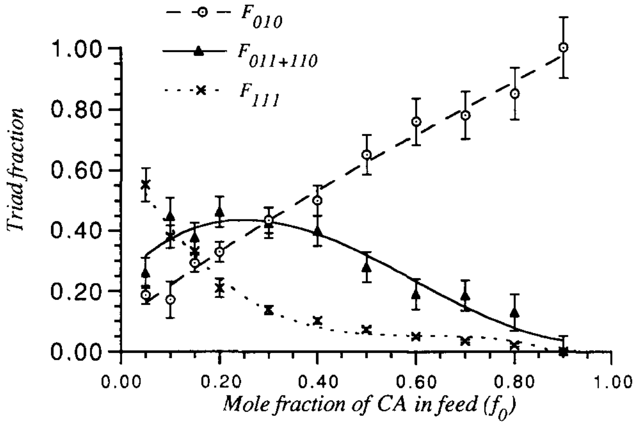

Figure 3 Triad fraction plot for the copolymerization of ST with CA in MEK (4.000 mol l^{-1}) at 50°C

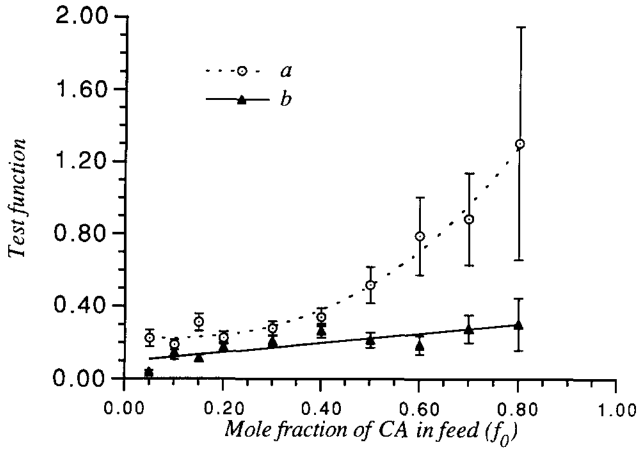

Figure 4 Test function plot for the copolymerization of ST with CA in MEK (4.000 mol l^{-1}) at 50°C

where 0 and 1 represent two different monomer units, [0] and [1] are the concentrations of these monomers in the comonomer feed (in mol l^{-1}) and F_{010}, $F_{011+110}$ and F_{111} are the fraction of 010, 011 + 110 and 111 triads in the copolymers. For the purpose of this study, ST has been designated as '1' and CA as '0'. The test functions only consider 1 centred triads, hence if triads also exist in the copolymers under study that are 0 centred, they can be accounted for separately by exchanging the assignment of 0 and 1 to the comonomer units, although this is not relevant here.

These test functions can be derived independently using the equations predicting the fraction of 1 centred triads from each of the terminal[30], penultimate[30], complex-participation[4] and complex-dissociation[5] models, the reaction schemes and reactivity ratios of which are outlined in *Table 2*. Application of sequence distribution data to these test functions in the form of 1 centred triad fractions for a given copolymerization system may have one of the following outcomes: in the case of the terminal model it can be shown that the reactivity ratio $r_1 = a = b$. Hence if the terminal model were to apply to a copolymerization system, calculation of a and b using experimental triad fraction data would yield the same value equal to r_1 for each copolymer composition. Similarly, it can be shown that for the penultimate model a and b would yield constant values equal to the reactivity ratios r_{11} and r_{01}, respectively, for each copolymer composition, whilst $a \neq b$. In the case of the complex-participation model again $a \neq b$, however a and b may vary with copolymer composition, whilst for the complex-dissociation model it can be shown that $a = b$, while a and b may also vary with copolymer composition. The result of applying the triad fraction data to these test functions is displayed in *Figure 4*, which shows the change of each test function value with the change in f_0.

It can be seen from *Figure 4* that $a \neq b$ and whilst b may have a constant value over the range of comonomer feed compositions studied, a increases with f_0. Hence, on the basis of this result it can be said that the terminal, penultimate and complex-dissociation models each display a poor degree of applicability to the data. Whilst this result appears to support the applicability of the complex-participation model to the copolymerization of ST with CA in MEK at 50°C as $a \neq b$ and a varies considerably with f_0, it is not conclusive proof for participation of EDA complexes in the propagating step during copolymerization. Rather, it exhibits the inadequacies of the terminal, penultimate and complex-dissociation models in describing the mechanism of copolymerization for this comonomer system. Remembering the fit of each model to the data shown in *Figure 1* however, it might be said that of the models investigated here, the complex-participation model provides the most adequate description of this copolymerization system, lending weight to the conclusion of Yang and Otsu[6] that ST/CA EDA complexes take a certain but small part in the propagation reaction of the copolymerization. To further investigate this point, a study of the stereochemistry of these copolymers, in line with the suggestions of Olson and

Table 2 Reaction schemes and reactivity ratios for the terminal, penultimate, complex-participation and complex-dissociation models[a]

Terminal model[b]			
$\sim 1\cdot + 1 \rightarrow \sim 11\cdot$	k_{11}		
$\sim 1\cdot + 0 \rightarrow \sim 10\cdot$	k_{10}		
$\sim 0\cdot + 1 \rightarrow \sim 01\cdot$	k_{01}		
$\sim 0\cdot + 0 \rightarrow \sim 00\cdot$	k_{00}		
Complex-participation model[c]			
As for terminal model plus:			
$\sim 1\cdot + \overline{01} \rightarrow \sim 101\cdot$	k_{101}		
$\sim 1\cdot + \overline{10} \rightarrow \sim 110\cdot$	k_{110}		
$\sim 0\cdot + \overline{01} \rightarrow \sim 001\cdot$	k_{001}		
$\sim 0\cdot + \overline{10} \rightarrow \sim 010\cdot$	k_{010}		
Complex-dissociation model[d]			
As for terminal model plus:			
$\sim 1\cdot + \overline{01} \rightarrow \sim 10\cdot + 1$	k_{101}		
$\sim 1\cdot + \overline{10} \rightarrow \sim 11\cdot + 0$	k_{110}		
$\sim 0\cdot + \overline{01} \rightarrow \sim 00\cdot + 1$	k_{001}		
$\sim 0\cdot + \overline{10} \rightarrow \sim 01\cdot + 0$	k_{010}		
Penultimate model[e]			
$\sim 11\cdot + 1 \rightarrow \sim 111\cdot$	k_{111}	$\sim 10\cdot + 1 \rightarrow \sim 101\cdot$	k_{101}
$\sim 11\cdot + 0 \rightarrow \sim 110\cdot$	k_{110}	$\sim 10\cdot + 0 \rightarrow \sim 100\cdot$	k_{100}
$\sim 01\cdot + 1 \rightarrow \sim 011\cdot$	k_{011}	$\sim 00\cdot + 1 \rightarrow \sim 001\cdot$	k_{001}
$\sim 01\cdot + 0 \rightarrow \sim 010\cdot$	k_{010}	$\sim 00\cdot + 0 \rightarrow \sim 000\cdot$	k_{000}

[a] $\sim 0\cdot$ and $\sim 1\cdot$ represent growing polymer radicals ending in 0 and 1 monomer units, respectively, 0 and 1 represent two different monomer types, $\overline{01}$ and $\overline{10}$ denote a 1:1 complex of 1 and 0 monomer units and the *k*s are rate constants for the respective propagation steps with an obvious notation identifying each

[b] $r_0 = k_{00}/k_{01}$; $r_1 = k_{11}/k_{10}$

[c] $r_0 = k_{00}/k_{01}$; $q_0 = k_{001}/k_{01}$; $s_0 = k_{010}/k_{01}$; $r_1 = k_{11}/k_{10}$; $q_1 = k_{110}/k_{10}$; $s_1 = k_{101}/k_{10}$

[d] $r_0 = k_{00}/k_{01}$; $q_0 = k_{001}/k_{01}$; $s_0 = k_{010}/k_{01}$; $r_1 = k_{11}/k_{10}$; $q_1 = k_{110}/k_{10}$; $s_1 = k_{101}/k_{10}$

[e] $r_{11} = k_{111}/k_{110}$; $r_{01} = k_{011}/k_{010}$; $r_{10} = k_{100}/k_{101}$; $r_{00} = k_{000}/k_{001}$

Butler and Butler *et al.* is presently underway in this laboratory[14–18]. Finally, the work presented in this paper further confirms the usefulness of these test functions in model discrimination, particularly where NLLS analyses have returned inconclusive results despite accurate data being available.

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