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NON-LINEAR LEAST SQUARE CURVE FITTING OF COPOLYMERIZATION MODELS TO THE ALTERNATING TRIAD FRACTION OF COPOLYMERS OF STYRENE AND CITRACONIC ANHYDRIDE, AND COPOLYMERS OF STYRENE AND MALEIC ANHYDRIDE PREPARED IN N,N-DIMETHYLFORMAMIDE

T. H. Ha^a; Kiyohisa Fujimori^a; David J. Tucker^a; Peter C. Henry^a

^a Division of Chemistry, University of New England, Armidale, N.S.W., Australia

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NOTE

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T. H. HA, KIYOHISA FUJIMORI,* DAVID J. TUCKER,
and PETER C. HENRY

Division of Chemistry
University of New England
Armidale, N.S.W. 2351, Australia

Key Words: Alternating Copolymer, Sequence Distribution, Copolymerization Models, Non Linear Least Square Curve Fitting, Alternating Triad, Styrene, α -Methylmaleic (Citraconic) Anhydride, Maleic Anhydride

ABSTRACT

Copolymers of styrene (ST) and citraconic anhydride (α -methylmaleic anhydride) (CA) were prepared in a very polar solvent, N,N-dimethylformamide (DMF), at 50.0°C with AIBN. The monomer unit triad fractions were determined by ^{13}C NMR in acetone- d_6 solution. Non linear least square (NLLS) curve fitting was performed for the copolymerization models of the terminal

* Author to whom correspondence should be addressed.

model, the penultimate unit effect model, the complex participation model, the complex dissociation model, and the so-called *comppen* model. The theoretical equations for the ST-centered alternating triad mole fraction were fitted by NLLS minimization routine to the triad fraction data of the ST-CA copolymers and that of the ST-maleic anhydride (MA) copolymers prepared in identical polymerization conditions. It was found that for rigidly alternating copolymers of ST-MA, the difference among the copolymerization models disappeared and all models merged together. The difference among the copolymerization models were somewhat more apparent for less alternating copolymers of ST-CA copolymers. The sum of squares values indicated that the copolymerization models, which involved some complex participation, fit the data better with the *comppen* model. This was a combination of a complex participation and penultimate unit effects, which performed best.

INTRODUCTION

It has been reported that maleic anhydride (MA) and styrene (ST) form an electron donor-acceptor complex and that they form highly alternating copolymers with radical initiators [1]. In examining the copolymerization mechanism, various copolymerization models have been proposed, including the terminal model, the penultimate unit effect model, complex participation model, and, complex dissociation model. We have proposed a so-called “*comppen*” model [2], which includes both the penultimate unit effect and a participation of the monomer-monomer complex in the copolymerization mechanism. The *comppen* model may be regarded as being evolved from both penultimate unit effect model and from a complex participation model. The applicability of these copolymerization models have been assessed by curve fitting to experimental data by non-linear least square (NLLS) minimization routine [3, 4]. It has been pointed out that the monomer unit triad sequence distribution data is superior to the overall copolymer composition data for examining copolymerization models by curve fitting [3]. One major problem of applying this method to alternating copolymerization is the fact that, when the comonomer units are rigidly alternating, the differences between all these copolymerization models disappear and all the models merge together. Nevertheless, when one of the comonomers which form alternating copolymers, is capable of homopropagating, there will be some possibility of forming non-alternating copolymers. In this report, ST, which is

capable of homopolymerizing, and citraconic anhydride (α -methylmaleic anhydride) (CA) which does not homopolymerize [5], are copolymerized in a very polar solvent, N,N-dimethylformamide (DMF; dielectric constant 38.25 at 293.2 K [6]), in which it is expected that the extent of donor-acceptor complexation between ST and CA monomers is minimal and the homopropagation of ST is more encouraged. The monomer unit triad data of ST-MA copolymers copolymerized in DMF in identical polymerization conditions, reported in Reference 7, is also used together with those of the ST-CA copolymers prepared here to do the NLLS minimization curve fitting of the above mentioned copolymerization models. The equilibrium constant of complexation between ST and MA in DMF solution has been reported to be $0.035 M^{-1}$ [7].

EXPERIMENTAL

Purified monomers, DMF, and the initiator, 2,2'-azobisisobutyronitrile (AIBN), (all Fluka), were placed in glass tubes and the copolymerization was carried out in sealed glass tubes after freeze-thaw degassing, which were then placed in an oil thermostat bath. The copolymerization conditions were: [AIBN] = $3.05 \times 10^{-2} M$, in DMF at $50.0^\circ C$ with total monomer concentration [ST + CA] of $4.00 M$. The conversion was kept to less than 10% in general, and less than 5% at extreme feed monomer mole ratios.

The monomer unit triad fractions were determined from the integrated ^{13}C NMR spectra of quaternary aromatic carbon of ST units for the ST-CA copolymers and the methylene carbon of ST units for the ST-MA copolymers. An NMR technique, *distortionless enhancement by polarization transfer* (DEPT) [8], was employed at 75.46 MHz to isolate target carbon spectra and a peak simulation program *linesim* [9] was used to determine the peak area.

NMR spectra were observed in acetone- d_6 (Fluka) solution in broad band 1H dual 5 mm probe by a Bruker AC-300 NMR spectrometer with the measurement conditions of: 1H decoupler- and ^{13}C - $\pi/2$ 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 ($35^\circ C$)). Acquisition period, 15-20 hours.

The equilibrium constant of complexation between ST and CA in DMF solution was determined at an ambient temperature ($23^\circ C$) to be $0.021 M^{-1}$ from

the ultra-violet absorption spectra of the complex, which occurred around 310 nm, according to the Ketelaar Equation [10].

RESULTS AND DISCUSSION

The variation of the St-centered triad spectra of ST-CA copolymers prepared in DMF with respect to the feed CA mole fractions, f_0 , are shown in Figure 1, where “1” indicates the ST monomer unit and “0”, the CA monomer unit. According to the reported chemical shifts for similar copolymers [11, 12, 13], the chemical shift of 148 ppm is assigned to the ST-ST-ST triad, i.e., 111 triad, 146.5-143.5 ppm to a combination of 011 and 110 triads, and 141 ppm to the alternating 010 triad. It is clearly seen that as the composition of CA monomer increases in the feed, the proportion of 111 triad and the semi-alternating 110 and 011 triads decrease rapidly and predominantly alternating monomer unit sequences result. Table 1 reports values of ST-centered triad fractions of the alternating triad (F_{010}), semi-alternating triads ($F_{011+110}$) and ST-ST-ST triad (F_{111}) for the ST-CA copolymers and that of ST-MA copolymers, which were prepared in identical polymerization conditions [7]. The overall mole fraction of CA or MA unit (unit “0”) in the copolymers (F_0) in Table 1 is calculated by:

$$\frac{F_1}{F_0} = 1 + \frac{2F_{111} + F_{011+110}}{2F_{010} + F_{011+110}}, \text{ where } F_0 + F_1 = 1$$

It should be noted in Table 1 that, while the uncertainty of F_{010} data is estimated to be $\pm 3\%$ for most of the feed monomer compositions (f_0) with $\pm 5\%$ for very small f_0 's because of the strongly alternating nature of the copolymers, the uncertainty of $F_{011+110}$ and F_{111} is estimated to be quite large being $\pm 10\text{-}25\%$. The semi-alternating triads and ST-ST-ST triad are not detected for strongly alternating copolymer samples. This would render the results of NLLS curve fitting from the $F_{110+001}$ and F_{111} data less meaningful. Considering the superiority of triad data over composition data for curve fitting [3], the data for alternating triad F_{010} is chosen for fitting theoretical copolymerization equations.

The mole fraction of ST-centered alternating triad, F_{010} , in copolymers is expressed as follows for each copolymerization model.

The terminal model [14]:

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

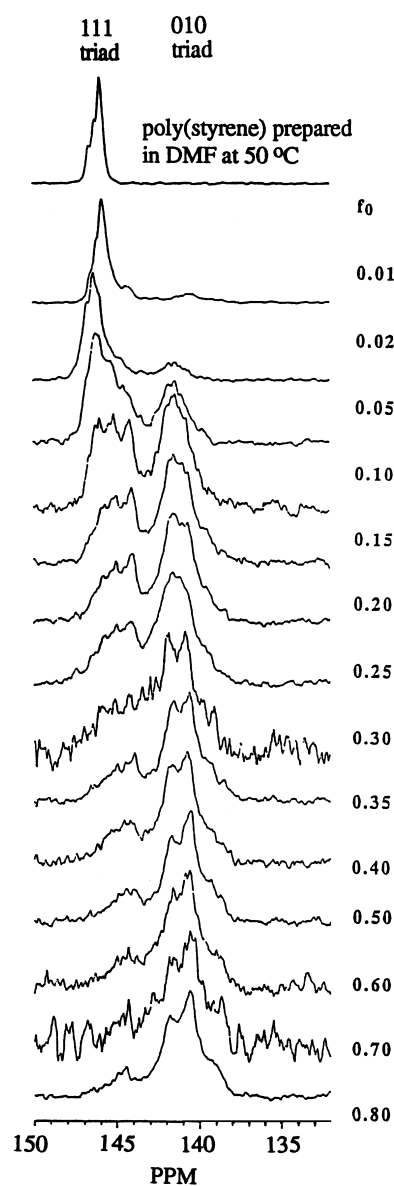


Figure 1. ^{13}C NMR spectra of the quaternary carbon of the styrene units in the copolymers of styrene (ST, 1) and citraconic anhydride (CA, 0), which are prepared in DMF solution at 50°C , with respect the mole fraction of citraconic anhydride in the feed mixture, f_0 . 111: ST-ST-ST triad, 011: CA-ST-ST triad, 110: ST-ST-CA triad, 010: CA-ST-CA triad.

TABLE 1. ST-Centered Triad Mole Fractions and Overall Copolymer Composition in Copolymers Prepared in DMF with Respect to the Mole Fraction (f_0) of CA or MA in Feed

1: ST unit and 0: CA or MA unit in copolymer.

F_{010} : alternating triad, $F_{011+110}$: semi-alternating triads, F_{111} : ST-ST-ST triad

F_0 : mole fraction of "0" units in copolymer

Polymerization conditions: Total monomer concentration in feed: 4.00 M, [AIBN] = 3.05×10^{-2} M, polymerized in DMF at 50.0°C.

f_0	ST-CA copolymers				ST-MA copolymers			
	F_{010}	$F_{011+110}$	F_{111}	F_0	F_{010}	$F_{011+110}$	F_{111}	F_0
0.0100	0.107	0.173	0.721	0.162	0.074	0.460	0.467	0.233
0.0200	0.166	0.371	0.463	0.260	0.189	0.592	0.219	0.327
0.0500	0.317	0.403	0.280	0.342	0.416	0.529	0.054	0.405
0.100	0.493	0.356	0.112	0.401	0.633	0.331	0.006	0.453
0.150	0.597	0.294	0.109	0.427	0.781	0.291	0.000	0.471
0.200	0.639	0.285	0.076	0.439	0.844	0.157	0.000	0.480
0.250	0.657	0.297	0.046	0.446	0.870	0.130	0.000	0.483
0.300	0.728	0.249	0.023	0.460	0.902	0.098	0.000	0.487
0.350	0.750	0.223	0.027	0.463	0.968	0.032	0.000	0.496
0.400	0.779	0.195	0.026	0.467	0.958	0.042	0.000	0.495
0.500	0.822	0.169	0.009	0.476	0.965	0.035	0.000	0.496
0.600	0.851	0.139	0.011	0.479	1.00	0.000	0.000	0.500
0.700	0.879	0.114	0.000	0.484	1.00	0.000	0.000	0.500
0.800	0.859	0.129	0.012	0.480	1.00	0.000	0.000	0.500
0.900					1.00	0.000	0.000	0.500

Estimated uncertainty:

F_{010} : $\pm 3\%$ (for $f_0 = 0.010$ - 0.050 , $\pm 5\%$); $F_{011+110}$ and F_{111} : ± 10 - 25%

The penultimate unit effect model [14]:

$$F_{010} = 1 / [(1 + r_{01}X_1) \{1 + r_{01}X_1(1 + r_{11}X_1) / (1 + r_{01}X_1)\}] \quad (2)$$

The complex participation model [15]:

$$F_{010} = p_1(1^1)(1 - P_{11})^2 / \{p_1(1^1)(1 - P_{11})^2 + p_1(1^2)(2 - P_{11})\} \quad (3)$$

The complex dissociation model [16]:

$$F_{010} = (p_{10} + P_{101})^2 \quad (4)$$

The *comppen* model [2]:

$$F_{010} = p_1(1^1) / \sum_{m=1}^3 p_1(1^m) \quad (5)$$

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, the definitions of the terms,

and for the expressions of other triad fractions $F_{011+110}$ and F_{111} and of the overall composition F_0 .

NLLS curve fitting of the expression for F_{010} to the two sets of experimental data, one for the copolymerization of ST with CA and the other for the copolymerization of ST with MA, in Table 1 was performed for each copolymerization model and the sum of square (SS) values observed are listed in Table 2. It is seen that, for more rigidly alternating ST-MA copolymers, the difference between the copolymerization models, which is assessed by the SS values, virtually disappears and all the copolymerization models show similar degree of fit to the experimental data. However, for less rigidly alternating ST-CA copolymers, there seems some difference in the extent of applicability among the copolymerization models. It is interesting to notice that the copolymerization models which involve some complex participation apparently show better fit to the experimental data. The very good fit of the *comppen* model to the ST-CA F_{010} triad data may suggest importance of both complex participation and penultimate unit effect in these alternating copolymerizations. Since all copolymerization models merge together for rigidly alternating copolymers, it becomes impossible to employ the NLLS curve fitting method for examining copolymerization mechanism, as demonstrated by the very similar SS values observed for the ST-MA copolymers here. It has been suggested [16] that looking for a structural evidence, which may result by a participation, or non-participation, of monomer-monomer complex may be an effective alternative for investigating the mechanism of alternating copolymerization.

TABLE 2. The Sum of Squares (SS) Values Observed in Fitting Copolymerization Models to the ST-Centered Alternating Triad Data F_{010} , Which is Shown in Table 1, for the Copolymers of ST-CA and ST-MA Prepared in DMF. The Equilibrium Constant for Complexation K in DMF Solution: ST - CA, $0.035 M^{-1}$; ST-MA, $0.021 M^{-1}$ [7].

	ST-CA copolymers	ST-MA copolymers
<i>Copolymerization models</i>	SS	SS
Terminal model	7.4×10^{-2}	7.3×10^{-3}
Penultimate model	3.8×10^{-2}	2.7×10^{-3}
Complex participation model	8.3×10^{-3}	2.4×10^{-3}
Complex dissociation model	8.3×10^{-3}	5.2×10^{-3}
The <i>comppen</i> model	2.8×10^{-3}	2.7×10^{-3}

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