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ANALYSIS OF THE TERPOLYMERIZATION OF ACRYLONITRILE, STYRENE, AND 2,4,6-TRIBROMOPHENYL ACRYLATE

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ABSTRACT

Probability theory has been used to derive equations for the terminal model for free radical terpolymerization, showing how the polymer composition and triad fractions are related to the reactivity ratios and monomer composition. These relationships have been used to analyze the monomer-polymer composition data for the acrylonitrile–styrene–2,4,6-tribromophenyl acrylate system using a nonlinear least-squares method. The "best values" of the reactivity ratios which describe the polymerization have been used to calculate the triad fractions for each monomer.

INTRODUCTION

Copolymer composition data have been widely used to evaluate the reactivity ratios for a variety of models for copolymerization and to discriminate between the fit of the models to the experimental data. We have recently reviewed the techniques which can be used to evaluate reactivity ratios from copolymer composition or triad fraction data [1]. Although many workers have studied copolymerization, and the reactivity ratios for numerous copolymerizations are available in the literature [2], very little work has been directed toward the study of terpolymerizations.

The composition of the polymer formed from the polymerization of three monomers can be expressed in terms of six reactivity ratios when only terminal effects are important. Most workers who have investigated terpolymerization have estimated the terminal model reactivity ratios for the three related binary copolymerizations and applied these to model the terpolymerization [3-5]. While the set of reactivity ratios estimated in this way may provide an acceptable representation of some terpolymerization data, many exceptions to this conclusion have been found [6].

Rudin et al. [6] were the first to use a nonlinear least-squares analysis of the terpolymer compositions to obtain the terminal model reactivity ratios. These workers found that the reactivity ratios evaluated directly from the terpolymerization data provided a better fit to the experimental data than did the combined set of binary reactivity ratios obtained from studies of the appropriate copolymerizations. Duever et al. [7] later extended the techniques reported by Rudin by allowing for errors in the feed compositions as well as in the experimentally determined terpolymer compositions.

While Rudin and others have modeled terpolymerizations based upon the polymer composition relationships, to date there have been no reports expressing the triad fractions in terms of the reactivity ratios. However, it is now widely recognized that the polymer sequence distribution plays a very important role in determining many polymer properties.

Ham [8] previously reported the mathematical relationships for terpolymer compositions using a probabilistic approach for polymerizations based on a terminal model. However, he did not use these relationships to calculate directly the best values of the reactivity ratios, as has been done here. Ham suggested that the analysis of terpolymerizations may present a useful means of evaluating binary reactivity ratios, especially those which are very small or very large, and he also suggested that the presence of penultimate effects in copolymerization can be determined more precisely from compositional studies of terpolymerizations than from binary copolymerizations.

We have previously reported the analysis of copolymerization using a probabilistic approach, and we have shown how this approach can be readily used to deduce relationships for the copolymer triad fractions, as well as the composition. In this paper we describe the application of the probabilistic approach to terpolymerization, and we deduce equations for the terpolymer composition and triad fractions based on the terminal model.

We have used a nonlinear least-squares method, similar to that which we reported previously [9] for copolymerization, to analyze the data for the terpolymerization of acrylonitrile, styrene, and 2,4,6-tribromophenyl acrylate in DMF solutions as reported by Janović, Saric, and Vogl [5]. The "best values" of the terminal model reactivity ratios have been estimated from the experimental composition data, and these have been used to calculate the triad fraction sequence distribution for each of the three monomers.

ANALYSIS OF THE MODEL

A terpolymerization in which only the terminal units in the growing polymer chain influence the value of the rate constants, $k_{i,j}$ $(i, j = 0, 1, 2)$, for the addition of the three monomers (M_i; $i = 0, 1, 2$), can be represented by nine propagation reactions. For example, for addition of monomer M_0, the three propagation reactions are

$$\sim M_0\cdot + M_0 \xrightarrow{k_{00}} \sim M_0\cdot \tag{1}$$

$$\sim M_1\cdot + M_0 \xrightarrow{k_{10}} \sim M_0\cdot \tag{2}$$

$$\sim M_2\cdot + M_0 \xrightarrow{k_{20}} \sim M_0\cdot \tag{3}$$

The transition possibilities, P_{ij} ($i, j = 0, 1, 2$), which describes these nine propagation reactions, are defined for all i,j according to the relationships

$$P_{ij} = \frac{k_{ij}[\sim M_i\cdot][M_j]}{\sum_j k_{ij}[\sim M_i\cdot][M_j]} \tag{4}$$

and satisfy the condition that

$$\sum_j P_{ij} = 1 \tag{5}$$

Alternatively, the transition probabilities can be expressed in terms of a set of six terminal model reactivity ratios, defined as

$$r_{ij} = k_{ii}/k_{ij} \qquad (i, j = 0, 1, 2; j \neq i) \tag{6}$$

Accordingly, the set of conditional probabilities P_{0j} ($j = 0, 1, 2$) are given by the equations

$$P_{00} = \frac{r_{01}r_{02}[0]}{r_{01}r_{02}[0] + r_{02}[1] + r_{01}[2]} \tag{7}$$

$$P_{01} = \frac{r_{02}[1]}{r_{01}r_{02}[0] + r_{02}[1] + r_{01}[2]} \tag{8}$$

$$P_{02} = \frac{r_{01}[2]}{r_{01}r_{02}[0] + r_{02}[1] + r_{01}[2]} \tag{9}$$

The analogous equations for the conditional probabilities P_{1j} and P_{2j}($j = 0, 1, 2$) can be obtained by appropriate modifications to Eqs. (7), (8), and (9).

The terpolymer composition and sequence distribution relationships can be obtained from the transition probabilities using principles similar to those we have reported previously for copolymerization models [1]. These lead to the following relationships for the ratios of the polymer mole fractions, Y_i ($i = 0, 1, 2$).

$$\frac{Y_1}{Y_0} = p_{10} = \frac{P_{01}P_{20} + P_{01}P_{21} + P_{02}P_{21}}{P_{10}P_{20} + P_{10}P_{21} + P_{20}P_{12}} \tag{10}$$

$$\frac{Y_2}{Y_0} = p_{20} = \frac{P_{02}P_{10} + P_{02}P_{12} + P_{01}P_{12}}{P_{10}P_{20} + P_{10}P_{21} + P_{20}P_{12}} \tag{11}$$

where p_{10} and p_{20} are the probabilities of finding a 1 or a 2 unit in the polymer, relative to the probability of finding a 0 unit.

The relationships expressing the various triad fractions, F_{ijk} ($i, j, k = 0, 1, 2$), of 0, 1, and 2 units can also be obtained. These relationships are given below for 1 units.

$$F_{010} = \frac{P_{01}P_{10}(1 - P_{11})^2}{(P_{01}P_{10} + P_{01}P_{12}) + p_{20}(P_{21}P_{10} + P_{21}P_{12})} \tag{12}$$

$$F_{012+210} = \frac{(P_{01}P_{12} + p_{20}P_{21}P_{10})(1 - P_{11})^2}{(P_{01}P_{10} + P_{01}P_{12}) + p_{20}(P_{21}P_{10} + P_{21}P_{12})} \tag{13}$$

$$F_{212} = \frac{p_{20}P_{21}P_{12}(1 - P_{11})^2}{(P_{01}P_{10} + P_{01}P_{12}) + p_{20}(P_{21}P_{10} + P_{21}P_{12})} \tag{14}$$

$$F_{011+110} = \frac{(2(P_{01}P_{10}P_{11}) + P_{01}P_{12}P_{11} + p_{20}P_{21}P_{10}P_{11})(1 - P_{11})}{(P_{01}P_{10} + P_{01}P_{12}) + p_{20}(P_{21}P_{10} + P_{21}P_{12})} \tag{15}$$

$$F_{211+112} = \frac{[P_{01}P_{12}P_{11} + p_{20}(2(P_{21}P_{12}P_{11}) + P_{21}P_{10}P_{11})](1 - P_{11})}{(P_{01}P_{10} + P_{01}P_{12}) + p_{20}(P_{21}P_{10} + P_{21}P_{12})} \tag{16}$$

$$F_{111} = P_{11}^2 \tag{17}$$

Analogous relationships for the 0 and 2 centered triads are given by similar sets of equations with appropriate modifications to the subscripts for the transition probabilities.

Examination of Eqs. (10) and (11) for the copolymer compositions and of Eqs. (12)–(17) for the copolymer sequence distributions shows that the compositions and sequence distributions are determined uniquely by six conditional transition probabilities, and each of these probabilities is defined by the comonomer feed composition and the six terminal model reactivity ratios. Thus, if a sufficient number of different terpolymers is prepared at low conversion from a wide range of reactant monomer compositions, in principle it is possible to calculate "best values" for the terminal model reactivity ratios, provided the copolymer compositions or triad factions are measured experimentally.

Rudin et al. [6] and Duever et al. [7] previously described computer-based nonlinear least-squares methods for analyzing the compositions of terpolymers to yield "best values" of the terminal model reactivity ratios. We have followed similar procedures based upon the direct search method developed by Chandler [10]. In the analysis of the three terpolymer mole fractions, the sum of the squared deviations between the calculated and the experimentally determined quantities has been minimized. The analytical procedure is designed to produce the "best-fit" reactivity ratios by utilizing preliminary, approximate values. The accuracy of these preliminary values is not critical, and suitable values can be obtained from copolymerization studies or *Q–e* calculations.

The change in the feed composition with conversion of monomer to polymer can also be taken into account within the analytical procedure. This is particularly important near the extremes of the composition range. The joint confidence intervals for any pair of reactivity ratios can be generated for any particular desired level of confidence. The methods for incorporation of these features have been previously outlined for the case of copolymerization [1].

RESULTS

Janović, Saric, and Vogl [5] studied the terpolymerizations of acrylonitrile, styrene, and 2,4,6-tribromophenyl acrylate in DMF solutions at 60°C and reported

TABLE 1. Experimental and Calculated Terpolymer Mole Fractions Y_i for Polymerizations of Acrylonitrile (0), Styrene (1), and 2,4,6-Tribromophenyl Acrylate (2) in DMF Solutions at 60°C for a Series of Monomer Feed Mole Fractions X_i

No.	X_0 (feed)	Y_0 (expt)	Y_0 (calc)	X_1 (feed)	Y_1 (expt)	Y_1 (calc)	X_2 (feed)	Y_2 (expt)	Y_2 (calc)
1	0.590	0.445	0.429	0.150	0.316	0.332	0.260	0.239	0.238
2	0.190	0.267	0.244	0.660	0.506	0.519	0.150	0.227	0.236
3	0.180	0.254	0.266	0.710	0.546	0.533	0.110	0.200	0.200
4	0.355	0.446	0.450	0.615	0.500	0.502	0.030	0.054	0.047
6	0.415	0.285	0.297	0.249	0.413	0.406	0.336	0.302	0.295
7	0.650	0.559	0.564	0.328	0.413	0.411	0.022	0.028	0.024
8	0.352	0.379	0.396	0.568	0.503	0.491	0.080	0.118	0.112
9	0.098	0.112	0.084	0.492	0.460	0.493	0.410	0.428	0.422
10	0.600	0.502	0.508	0.020	0.128	0.110	0.380	0.370	0.381

the thermal and flammability behavior of the copolymers. Since these properties are dependent upon the distribution of the TBPA units in the polymer, it is important to be able to calculate the microstructure of the terpolymers from the terminal model reactivity ratios and the monomer feed compositions. Janović et al. [5] reported the feed and terpolymer mole fractions, see Table 1, for a series of 10 low conversion polymerizations. These have been analyzed using the mathematical methods described above, and the "best values" of the six terminal model reactivity ratios have been evaluated. These are shown in Table 2, together with the corresponding values reported by Janović et al. [5] which were obtained from analyses of binary copolymerization data. The experimental errors associated with each of the terpolymerization reactivity ratios represent the 95% confidence limit obtained by fixing the remaining five reactivity ratios at their "best values." The experimental and calculated terpolymer mole fractions obtained from the data fit are given in Table 1.

TABLE 2. Terminal Model Reactivity Ratios for the Terpolymerization of Acrylonitrile (0), Styrene (1), and 2,4,6-Tribromophenyl Acrylate (2) in DMF Solutions at 60°C

	Method	
Reactivity ratio	Copolymer[a]	Terpolymer[b]
r_{01}	0.16 ± 0.02	0.25 ± 0.12
r_{10}	0.30 ± 0.04	0.104 ± 0.02
r_{12}	0.14 ± 0.02	0.085 ± 0.01
r_{21}	0.08 ± 0.03	0.071 ± 0.02
r_{02}	0.96 ± 0.04	0.69 ± 0.15
r_{20}	1.25 ± 0.08	0.83 ± 0.50

[a] Reported by Janović et al. [5].
[b] Determined in this work.

TABLE 3. Calculated Triad Fractions for Polymerizations of Acrylonitrile (0), Styrene (1), and 2,4,6-Tribromophenyl Acrylate (2) in DMF Solutions at 60°C for the Feed Compositions Given in Table 1 and the Reactivity Ratios Given in Table 2

	Triads for Monomer 0 central position					
No.	F_{101}	F_{102}	F_{202}	F_{100}	F_{200}	F_{000}
1	0.1883	0.1684	0.0310	0.3303	0.1396	0.1424
2	0.7910	0.0858	0.0017	0.1117	0.0060	0.0039
3	0.8273	0.0611	0.0008	0.1038	0.0038	0.0033
4	0.7478	0.0176	0.0001	0.2163	0.0025	0.0156
5	0.5590	0.2040	0.0136	0.1782	0.0312	0.0141
6	0.3479	0.2319	0.0296	0.2607	0.0818	0.0481
7	0.4369	0.0149	0.0001	0.4333	0.0074	0.1074
8	0.7091	0.0483	0.0006	0.2179	0.0074	0.0167
9	0.6517	0.2577	0.0179	0.0600	0.0113	0.0014
10	0.0079	0.0800	0.1754	0.0909	0.4088	0.2371

	Triads for Monomer 1 central position					
No.	F_{010}	F_{012}	F_{212}	F_{011}	F_{211}	F_{111}
1	0.3142	0.4832	0.1691	0.0191	0.0141	0.0003
2	0.1750	0.3573	0.1818	0.1297	0.1322	0.0240
3	0.2070	0.3234	0.1260	0.1727	0.1348	0.0360
4	0.6003	0.1320	0.0072	0.2170	0.0239	0.0196
5	0.1357	0.4229	0.3238	0.0448	0.0691	0.0037
6	0.1862	0.4707	0.2834	0.0264	0.0325	0.0009
7	0.8237	0.0810	0.0019	0.0869	0.0043	0.0023
8	0.4628	0.2776	0.0414	0.1576	0.0472	0.0134
9	0.0190	0.2169	0.6132	0.0217	0.1230	0.0062
10	0.1668	0.5238	0.3055	0.0017	0.0022	0.0000

	Triads for Monomer 2 central position					
No.	F_{020}	F_{021}	F_{121}	F_{022}	F_{122}	F_{222}
1	0.1004	0.4089	0.3285	0.0564	0.0987	0.0072
2	0.0018	0.0930	0.8743	0.0015	0.0291	0.0002
3	0.0014	0.0847	0.8926	0.0009	0.0202	0.0001
4	0.0068	0.1782	0.8083	0.0006	0.0060	0.0000
5	0.0074	0.1696	0.7283	0.0094	0.0829	0.0024
6	0.0299	0.2859	0.5348	0.0291	0.1142	0.0060
7	0.0531	0.4040	0.5348	0.0021	0.0060	0.0000
8	0.0075	0.1838	0.7898	0.0019	0.0168	0.0001
9	0.0007	0.0559	0.8359	0.0034	0.1010	0.0031
10	0.3119	0.1873	0.0256	0.3085	0.0907	0.0759

The mathematical analysis of the terpolymerization provides a much better fit to the experimental composition data than that provided by the composite set of copolymerization reactivity ratios reported by Janović et al. [5]. The standard error in the polymer mole fractions based upon the terpolymerization analysis was $\simeq 0.01$, compared with a value of $\simeq 0.04$ obtained from the composite set of reactivity ratios. It would be expected that the reactivity ratios obtained from the terpolymerization analysis would provide a better fit to the data than the composite set. However, the expected experimental error in the measured polymer mole fractions should be in the range 0.005–0.01 (they were obtained by elemental analysis), which is much less than the error estimated from the data fit obtained using the composite set of reactivity ratios. This supports the conclusion that the set of reactivity ratios obtained by analysis of the terpolymerization data provides the better representation of the terpolymer microstructure.

Some of the ternary model reactivity ratios shown in Table 2 are not within the 95% confidence interval of the corresponding binary value. (A similar observation has been made by Rudin et al. [6] for several other terpolymerizations.) Whether these differences are reflections of some real effect or whether they represent deviations from terminal model behavior (acrylonitrile–styrene copolymerizations, for example, are believed to be influenced by penultimate group effects [11]) or whether they are simply artifacts resulting from the analysis of a relatively small number of data points which do not adequately cover the monomer feed composition range, is not yet clear. Further systematic studies are required to elucidate this anomaly.

The triad fractions for each of the monomers are given in Table 3. The acrylonitrile triad fractions show (e.g., No. 1 and 6) that AN has a clear preference for STY over TBPA as a next neighbor. However, styrene has a relatively high proportion of TBPA neighbors (e.g., No. 2, 5, and 10), and an examination of the TBPA triad fractions in Table 3 shows that in all except one case F_{121} is greater than F_{020} (AN = 0, STY = 1, and TBPA = 2). The only exception occurs for the case where the AN/STY ratio in the feed is 20.

Janović et al. [5] reported that the oxygen index measure of flammability and the thermal behavior of the terpolymers are dependent on the TBPA content of the terpolymers. They observed that, based upon TGA and DTG measurements, the thermal behavior of the terpolymers resembles that of the STY/TBPA copolymers. The triad fraction results in Table 3 show that the TBPA units in the terpolymers tend to have adjacent styrene neighbors rather than acrylonitrile neighbors, which provides an explanation for this observation.

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