Prediction of Monomer Compositions in Terpolymerization

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SYNOPSIS

An efficient algorithm has been developed allowing iterative solution of the Alfrey–Goldfinger equation. The algorithm is shown to result in rapid convergence for terpolymerization calculations and can be extended to polymerizations with more than three monomers.

PREDICTION OF MONOMER COMPOSITIONS IN TERPOLYMERIZATION

The prediction of the composition of terpolymers produced from a monomer mixture given the six reactivity ratios, or appropriate Q–e values, has been amply demonstrated using the Alfrey–Goldfinger (A–G) equation.[1] This equation is derived using the commonly accepted assumptions that the propagating chain end's reactivity is governed only by the terminal monomer unit and that the polymerization obeys the steady-state hypothesis. Chan and Meyer,[2] as well as others,[3] demonstrated the utility of this equation in predicting terpolymer composition as well as compositional drift during the progress of the polymerization.

In synthetic practice, it is desirable to solve the terpolymerization equation for the reverse case, i.e., to predict the monomer composition needed to produce a given terpolymer. It is generally accepted that no analytic solution to the A–G equation exists.

Ham and Lipman[4] proposed a solution to a simplified form of this equation and provide several examples of its utility. Although this method does provide a method of solution, it is limited by its inherent assumption of equivalency of reversed sequences. Furthermore, the original publication contains an error in the equations for which no correction has appeared.

The A–G equation does not have this limitation. We have derived an algorithm that allows facile solution of the A–G equation. Even with a personal computer, solution to high levels of precision is quite fast. In addition, we report the correction to the equations in Ref. 4.

ALGORITHM FOR ITERATIVE SOLUTION OF THE A–G EQUATION

Slocombe[5] demonstrated the use of triangular composition diagrams to represent terpolymerizations. He used arrows to indicate the compositional change: The arrowhead represents the polymer composition, and the tail represents the monomer composition. Following this graphical representation, the length of the arrow represents the difference in composition between the monomer and polymer.

Let f_1, f_2, and f_3 represent the mol fraction of monomers 1, 2, and 3 in the monomer mixture, respectively. F_1, F_2, and F_3 are the mol fractions of the three monomers in the polymer. Then, the differential composition, as indicated by the arrow length described above, for each monomer is given by $(F_i - f_i)$, where $i = 1$, 2, or 3. This concept can be utilized by choosing an initial monomer composition, calculating the terpolymer composition, and adjusting the monomer composition for monomers 1 and 2 by moving along the differential composition vector. The concentration of monomer 3 is determined by the difference.

To iteratively solve the A–G equation, the initial values for the monomer composition (f_i^0) are chosen to be the desired terpolymer composition (F_i^*). After solving the A–G equation with these initial values, the estimated monomer composition is adjusted by the difference between the desired and calculated

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Table I Calculated Monomer Feeds for Terpolymerization of Acrylonitrile, Styrene, and 2,4,6-Tribromophenyl Acrylate

	Cald Monomer Feed (mol ratio)			Terpolymer (mol ratio)			
Run	$f1$	$f2$	$f3$	$F1$	$F2$	$F3$	n
1	.320	.482	.198	.199	.551	.250	43
2	.366	.539	.096	.279	.573	.148	33
3	.699	.252	.050	.463	.475	.062	58
5	.104	.595	.301	.061	.572	.367	94
9	.353	.335	.312	.175	.516	.309	75

From Ref. 3, Table II: monomers 1 = acrylonitrile, 2 = styrene, 3 = 2,4,6-tribromophenyl acrylate; $r_{12} = 0.1$, $r_{21} = 0.44$, $r_{13} = 0.96$, $r_{31} = 2.04$, $r_{23} = 0.21$, $r_{32} = 0.01$; n = number of iterations to achieve convergence criterion.

terpolymer composition. A problem arises with this approach for terpolymerizations in which the polymer and monomer compositions greatly differ. In these cases, the corrected monomer concentrations may become either less than zero or greater than one. The algorithm of eqs. (1) and (2) corrects this problem by scaling the adjustment by the actual value of the monomer composition. In these equations, the superscript, n, is the iteration number:

$$f_i^n = f_i^{n-1} - (F_i^{n-1} - F_i^*) f_i^{n-1} \quad (1)$$

where $f_i^{n-1} < 0.5$

$$f_i^n = f_i^{n-1} - (F_i^{n-1} - F_i^*)(1 - f_i^{n-1}) \quad (2)$$

where $f_i^{n-1} \geq 0.5$.

Iterative calculations can be continued to any desired level of accuracy. We have found that using the criterion

$$| F_i - F_i^* | < 10^{-4} \quad (3)$$

provides rapid convergence. Table I shows the calculation results for five polymerization runs extracted from table II of Ref. 3. The terpolymerization of acrylonitrile, styrene, and 2, 4, 6-tribromophenyl acrylate monomers have widely varying reactivities as indicated by reactivity ratios ranging from 0.01 to 2.04. Runs number 3 and 5 are quite close to the edges of the terpolymerization monomer–polymer composition map, i.e., less than 10 mol % of one of the monomers. Yet, convergence of the A–G equation to meet the criterion of eq. (3) is achieved in less than 100 iterations.

This iterative scheme can be generalized for multipolymerizations containing more than three monomers, for example, using the method of Seiner.[7] The iterative approach is identical, and only the equation(s) for calculating polymer composition need be changed.

Correction to Ref. 4

In their original paper, Ham and Lipman[4] presented a series of equations to solve the simplified terpolymer equation. In table 1 of Ref. 4, the coefficient A should be corrected to $(1/r_{21}) - (1/r_{21}r_{13})$.

SUMMARY

An efficient method for solving the Alfrey–Goldfinger or other multipolymerization equation set has been developed. The algorithms described provide a systematic approach to an iterative solution to the problem of predicting monomer feed compositions required for copolymerizations.

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