

Introduction

- There is no doubt that multi-component polymerization is of great interest to academia and industry alike, as it enables the production of new materials with a variety of physico-chemical properties.
- Terpolymerization is a three monomer-based polymerization; the chain micro-structural composition can be predicted from the knowledge of monomer concentrations and the related reactivity ratios.
- One of the common requirements during polymer production is to maintain a homogeneous polymer composition. The 'ternary azeotropic point', similar to a binary azeotrope, is a feed composition at which the polymerization does not exhibit composition drift.
- Hence, determining both the existence of the azeotrope and its composition is important from a theoretical and practical point of view in the analysis of multi-component polymerizations.
- The question of azeotropy in terpolymerization has been discussed in the literature mainly during 1960-early 1980s. However, pervasive to these discussions, there is a certain controversy concerning the existence of the ternary azeotrope and its composition.
- Several groups have reported methods of evaluating azeotropic compositions given reactivity ratios. Some attempts have been made to calculate algebraically conditions for ternary critical points. Nonetheless, no general solutions/approaches have emerged from these efforts. Often, conflicting remarks are made with hardly any experimental verification.

Question:

- Does an azeotropic point exist for multi-component polymerizations? If yes, is it one or many? What is its composition?

Typical Literature Approach

- For terpolymerization at low conversion, the compositions of the monomer and polymer phases can be obtained by the following equations which are based on the Alfrey-Goldfinger model (ref.1):

$$\frac{F_1}{F_2} = \frac{f_1 \left(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right) \left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right)}{f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{22}} \right)}$$

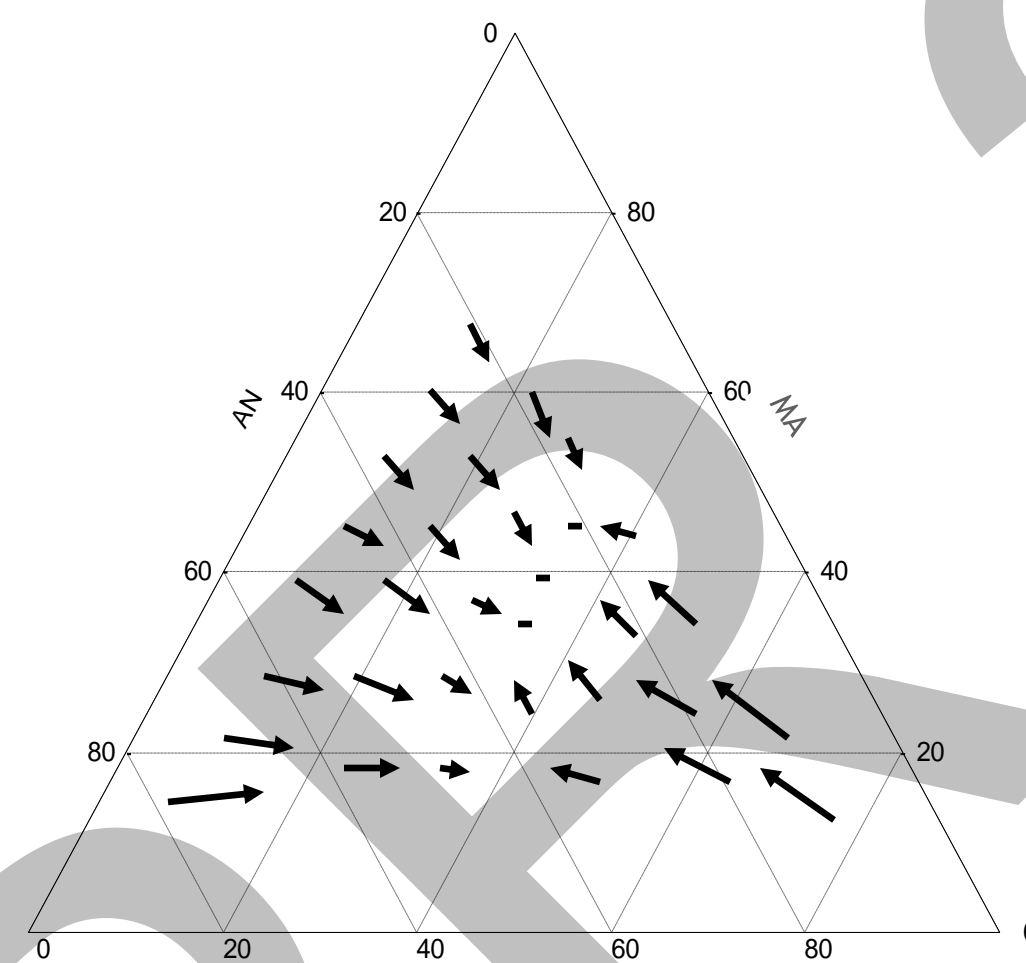
$$\frac{F_1}{F_3} = \frac{f_1 \left(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right) \left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right)}{f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right)}$$

f_i is the mole fraction of monomer i in the feed; F_i is the mole fraction of monomer i in the terpolymer; r_{ij} are binary reactivity ratios.

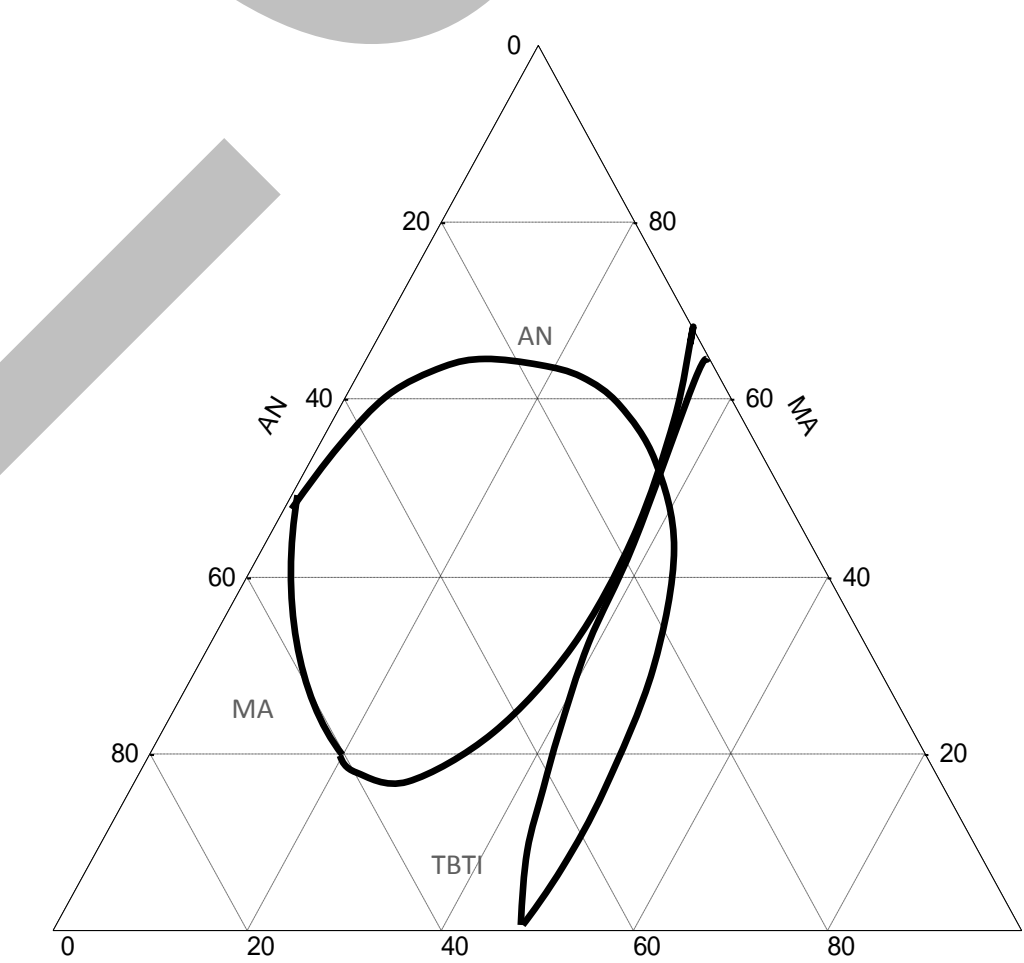
- In most cases, due to the mathematical complexity (at the time) of the terpolymerization model, no general solution methodology has been reported.
- For many of the claimed azeotropic compositions, methods of derivation have not been outlined clearly and most often the reported compositions could not satisfy the Alfrey-Goldfinger model! (see our comments in the Introduction section)

Typical Literature Approach (cont'd)

- The relationship between composition of the feed and the resulting polymer is commonly presented in the form of a triangular plot. In most cases, the ternary azeotropic composition is arrived at graphically (terpolymer compositions are illustrated by arrows pointing toward the ternary azeotropic composition (figure 1, ref. 2).
- Partial azeotropy (another potentially confusing point), namely unitary and binary, is defined when $f_i = F_i$ and $f_i / f_j = F_i / F_j$ remain constant for one or two of the three monomers during the course of polymerization (i.e., $i < m$, $m =$ number of monomers). The azeotrope is then the intersection of the unitary or binary curves inside the triangular plot. In the absence of an azeotrope, these curves do not intersect inside the triangle (figure 2, ref. 2).
- **BUT, is the graphical representation reliable enough to yield the azeotropic composition point? Furthermore, is partial azeotropy of any practical significance or help for a multi-component system? When experimental azeotropes are reported, why is the fraction of one component almost always very close to zero?**



Figure_1. Instantaneous terpolymer composition as a function of monomer composition for the methyl acrylate (MA) - di(tri-n-butyltin) itaconate (TBTI) - acrylonitrile (AN) system



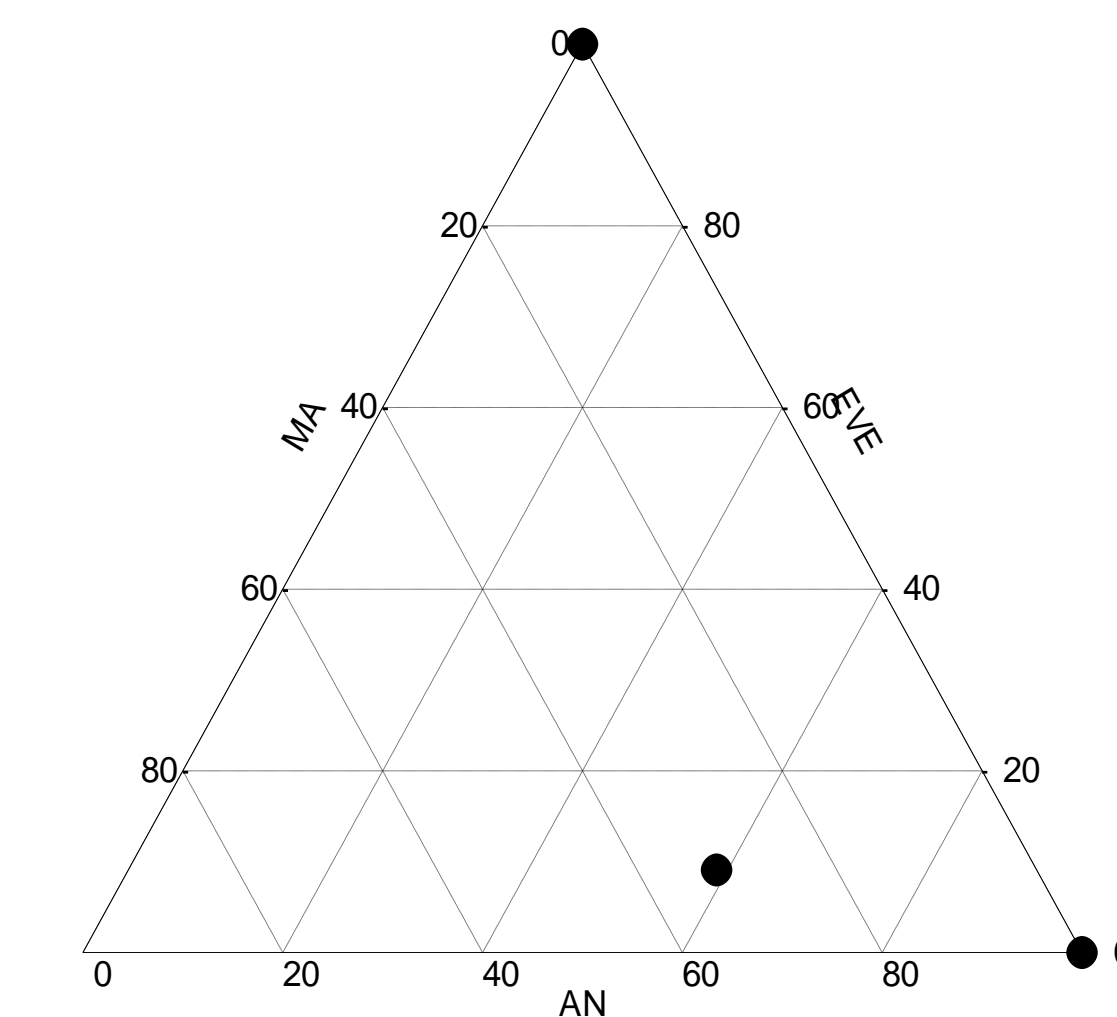
Figure_2. Unitary azeotropic lines for the methyl acrylate (MA) - di(tri-n-butyltin) itaconate (TBTI) - acrylonitrile (AN) system.

Our Approach

- **Arrive at a general numerical solution of the multi-component composition model; Is the solution feasible?**
- In order to clarify the previously stated issues, the Alfrey-Goldfinger equations were solved numerically at azeotropic conditions (solving a set of nonlinear algebraic equations using Matlab, after several bench-marking tests on the code).
The basic condition for an azeotrope is that monomer and polymer compositions are identical; in addition, the sum of monomer fractions in the feed and the resulting polymer is equal to 1 (i.e., $\sum f_i = \sum F_i = 1$, $i = 1, m$; $m =$ number of monomers).
- Binary reactivity ratios are employed in the calculations. Therefore, it is necessary to consider the effect of errors associated with the reactivity ratio estimates on the calculated azeotropic compositions.

Preliminary Results

Figure 3 (ref. 3) illustrates results for the system acrylonitrile (AN)- ethyl vinyl ether (EVE) - methyl acrylate (MA). Two trivial solutions as well as a true ternary azeotrope were found for the system.



Figure_3. Ternary azeotropic composition for the acrylonitrile (AN) - ethyl vinyl ether (EVE) - methyl acrylate (MA) system

Remarks

During the numerical testing phase with literature reports, we observed that literature results and those found by our program did not agree in most of the cases.

Poor agreement is likely due to:

- Imprecise values of reactivity ratios obtained from binary copolymerization systems.
- Modern analytical/estimation procedures/data handling methods were not used.
- Culprit seems to be again the poorly estimated reactivity ratio values!

Future Steps

- Thorough checking of our algorithm with all possible literature sources, theoretical and experimental.
- Expanding the proposed approach to higher multi-component polymerizations (with four to six components).
- Testing the feasibility of azeotropic points; significance of partial azeotropy? Possible experimental verifications?
- Further investigation on the effect of error in the reactivity ratio values on the azeotropic composition (leading to root locus analysis).

References

1. Alfrey, T. and G. Goldfinger, J. Appl. Phys., 14, 700 (1943).
2. Mahmoud, A. et al., Eur. Polym. J., 28, 555 (1992).
3. Braun, D. et al., Makromol. Chem., 182, 2951 (1981).