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A Numerical Approach to the Estimation of Reactivity Ratios: Application to the Styrene-DMAEMA System

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ABSTRACT

The reactivity ratios for the styrene dimethylaminoethyl methacrylate (DMAEMA) copolymerization have been determined by accurate experimental procedures. The experimental results were analyzed using a completely numerical procedure developed from the equations of Skiest. The results obtained differ significantly from those previously published.

INTRODUCTION

In the prediction and control of the composition of a copolymer for given initial compositions of monomers and a given degree of conversion, the important parameters are the copolymerization reactivity ratios. Unfortunately, there are many discrepancies in values of reactivity ratios reported in the literature. Two major reasons for the inaccuracy of the many reported values are 1) the polymer compositions have not been determined with sufficient accuracy, and 2) the data obtained have been analyzed by subjective methods [1].

It is the purpose of this paper to present a method of determining copolymerization reactivity ratios which uses an accurate experimental procedure and a completely numerical method of data analysis. This numerical method required no subjective judgments and no approximations as to the extent of polymerization. We are prompted to report our results by the publication of a similar approach by Makarov et al. who do not present any experimental verification of their method [2].

The method has been applied to the system styrene-DMAEMA. Interest in these particular monomers arose out of a project to develop coatings for the protection of amino acids as they pass through the rumen of sheep. In this work the chemical distribution in the polymer was an important parameter and accurate values of reactivity ratios were required to control this distribution.

DISCUSSION

Theory

The determination of copolymerization reactivity ratios has three aspects: 1) the reaction kinetics model, 2) the choice of estimation procedures, and 3) experimental procedures and practices. Tidwell and Mortimer have discussed the many difficulties associated with each of these aspects [3].

In this work the usual model for the kinetics of copolymerization [4]

$$\begin{aligned} M_1\cdot + M_1 &\xrightarrow{k_{11}} M_1\cdot \\ M_1\cdot + M_2 &\xrightarrow{k_{12}} M_2\cdot \\ M_2\cdot + M_1 &\xrightarrow{k_{21}} M_1\cdot \\ M_2\cdot + M_2 &\xrightarrow{k_{22}} M_2\cdot \end{aligned} \qquad (1)$$

was used, where $M_1\cdot$ and $M_2\cdot$ represent chain radicals having monomer residues from M_1 and M_2, respectively, as their terminal free radical bearing units.

If the chains are long and initiation and termination reactions rare compared to the above reactions, we can write the steady-state equation

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \tag{2}$$

and then

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1]/[M_2] + 1}{[M_1]/[M_2] + r_2}\right) \tag{3}$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the copolymer reactivity ratios.

If the concentration terms are written in mole fractions, defining F_1 as the mole fraction of monomer M_1 in the increment of copolymer formed at a given stage in the polymerization and f_1 as the mole fraction of that component in the feed, then

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \tag{4}$$

Skiest [5] introduced a method of calculating the average composition of the polymer formed over a finite range of conversion. Let $[M] = [M_1] + [M_2]$. The number of moles of monomer 1 converted to polymer is $-F_1 d[M]$; meanwhile f_1 changes by df_1 and the number of moles of unreacted M_1 changes from $f_1[M]$ to $(f_1 + df_1)([M] + d[M])$. So we have

$$f_1[M] - (f_1 + df_1)([M] + d[M]) = -F_1 d[M] \tag{5}$$

and

$$\ln\left(\frac{[M]}{[M]_0}\right) = \int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)} \tag{6}$$

The degree of conversion is

$$D = 1 - \frac{[M]}{[M]_0} = 1 - \exp\left(\int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)}\right) \tag{7}$$

In the experimental procedures developed, $(f_1)_0$, (f_1), and D are measured and the problem is to estimate r_1 and r_2 from the experimental data.

Analysis of Data

A method suggested by Flory [4], which in the days before large computers was very cumbersome, has been used in this project. This method calculates D from Eq. (7) by a numerical integration technique (Simpson's rule) for various values of r_1 and r_2 taken from a predetermined grid. The best fitting values of r_1 and r_2 are found by minimizing the function

$$\sigma^2 = \frac{1}{N - 1} \sum_{i=1}^{N} (D_{i,\mathrm{exptl}} - D_{i,\mathrm{calc}})^2$$

consistent with N data points.

The procedure is completely numerical and converges rapidly. A typical estimation of r_1 and r_2 from 14 data points takes less than 0.5 sec on a CD6600.

Tidwell and Mortimer [3, 6] have recently reviewed the various methods which have been used to estimate reactivity ratios from experimental data. All of the methods suggested make the approximation that the differentials in Eq. (3) can be replaced by the instantaneous composition of the polymer. This approximation can only be true for low degrees of conversion. The method described above is valid for all degrees of conversion.

Most of the previous methods then use additional approximations in order to estimate r_1 and r_2 in some least squares sense.

The nonlinear least squares method using Eq. (3) suggested by Tidwell and Mortimer is an analytical version of our numerical method and as such is amenable to detailed statistical analysis. However, it has the disadvantage that it can have some convergence problems. The numerical search least squares method has the advantage of being easily programmed for a computer and in our experience rapidly gives the least squares estimates of r_1 and r_2.

The least squares analysis of Tidwell and Mortimer indicates that some regions of the F-f curve are more sensitive to r_1 and r_2 than others. Also there is some evidence [7] that better results are obtained using these methods if particular degrees of conversion are used. These problems are overcome in the numerical search method by using data covering much of the composition range and a wide range of degree of conversion.

RESULTS

The copolymerization between styrene and DMAEMA was studied using methods outlined in the experimental section of this paper.

It should be noted that polymer compositions were determined by two independent methods which gave good agreement. The values obtained for r_1 and r_2, where the subscript 1 refers to styrene, were $r_1 = 0.22$ and $r_2 = 0.42$, and these differ significantly from the previously reported values of $r_1 = 0.53$ and $r_2 = 0.37$ [8]. Plots of the F_1 against f_1 for the two sets of reactivity ratios are shown in Fig. 1. Price-Alfrey [9] Q-e values were calculated from the reactivity

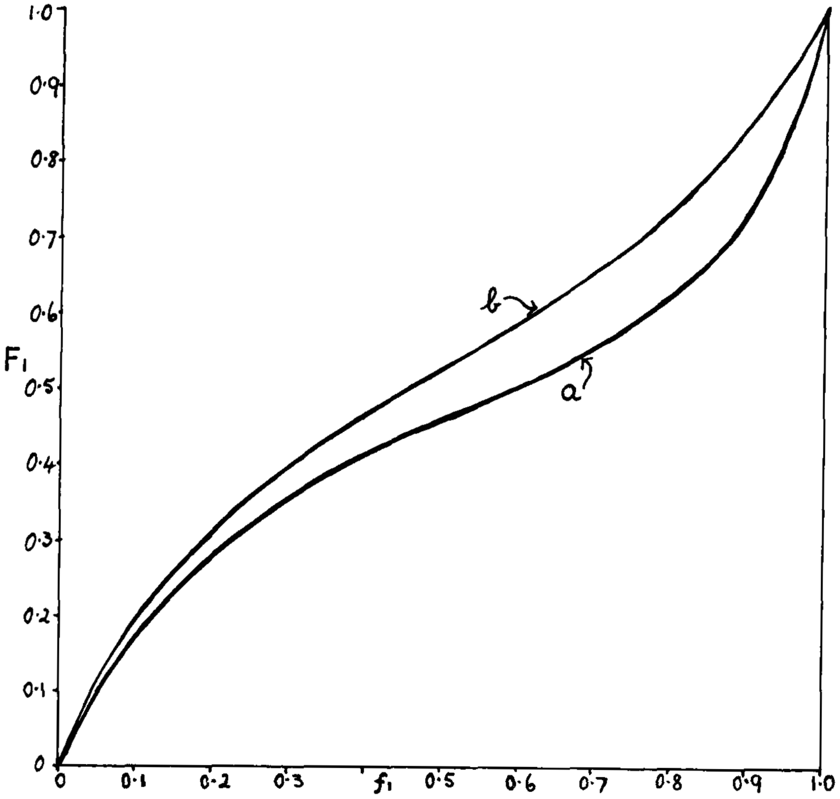

FIG. 1. A plot of the instantaneous polymer composition (F_1) against the feed composition (f_1) using Rohm and Haas reactivity ratios (b) and the present values (a).

ratios. Taking $Q_1 = 1.0$ and $e_1 = -0.8$, the values $Q_2 = 1.346$ and $e_2 = 0.751$ were calculated. The point on the F_1-f_1 curve where $F_1 = f_1$ is known as the critical point $(f_1)_c$. This point is quite different for the two sets of reactivity ratios. For the Rohm and Haas values $(f_1)_c = 0.57$ and for our values $(f_1)_c = 0.42$.

EXPERIMENTAL

The purity of monomers used in the feed was checked using both gas-liquid chromatography and elemental analysis.

The copolymers formed were analyzed directly after isolation by elemental analysis and by a monomer disappearance method using gas-liquid chromatography [10, 11]. There was no significant difference in the copolymer compositions obtained by either method.

The nature of the polymer suggests that polymer fractionation may occur on isolation if precipitation methods using water as the nonsolvent for the polymer are used.

The polymers were therefore isolated by two methods, viz., precipitation with water, and removal of solvent and unchanged monomers by rotary evaporation. There was no significant difference in analyses figures of the same polymers isolated by each method. It was shown that a straight line relationship existed between monomer concentration and peak height, using GLC, except at high concentrations where there was a departure from linearity, especially in the case of styrene. All samples obtained from experimental runs were diluted to bring the residual monomer concentrations into the linear range. Monomer concentration, peak height relationships were not altered by the presence of polymer.

Results of GLC analysis were used to calculate the degree of conversion. There was no significant difference in the value of the degree of conversion calculated in this way and that obtained by isolation of the polymer and subsequent gravimetric calculation.

Reagents

Styrene was washed free of inhibitor with 1 M sodium hydroxide, washed with water, dried over sodium sulfate, and finally distilled over copper turnings under reduced pressure and an atmosphere of nitrogen.

Dimethylaminoethyl-methacrylate was obtained from Rohm and Haas and was distilled over copper turnings under reduced pressure and an atmosphere of nitrogen.

Methyl ethyl ketone (MEK) was distilled in a vacuum-jacketed column packed with Fensky rings. The fraction boiling between 79.3 and 79.8°C collected.

The α,α'-azoisobutyronitrile (ADIB) was recrystallized from hot methanol.

Copolymer Preparation

To a 250-cm flask fitted with stirrer, reflux condenser, nitrogen inlet tube, and separating funnel was added 72.00 g of MEK and 0.48 g of ADIB as initiator. ADIB was used as the initiator to minimize chain branching and to avoid the amine decomposition sometimes encountered with peroxide catalysts.

Styrene and DMAEMA in appropriate proportions, depending on the initial monomer concentration required (e.g., 24.00 g styrene, 24.00 g DMAEMA), were added to the separating funnel and purged with nitrogen for 15 min.

The purged monomers were added to the polymerization flask under nitrogen and the separating funnel replaced by a suba seal to facilitate subsequent withdrawal of samples by syringe and hypodermic needle during the reaction.

The reaction mixture was kept under nitrogen and heated with stirring to reflux temperature (85 to 90°C).

ADIB (0.24 g in 1 g of MEK) was added at 70 min intervals from the time of monomer addition. The differential rate law for copolymerization shows that the initial rate of polymerization is proportional to the square root of the initiator concentration [12]. To keep the ADIB concentration at approximately its initial level, ADIB was added every half life, which is approximately 70 min at the reflux temperature [13].

Samples were removed every half hour, cooled immediately using ice, and stored in a refrigerator.

Isolation of Polymers

Polymers were isolated from solution by two methods.

1. The polymer solution was placed in a rotary evaporator flask and most of the MEK removed at room temperature. Some styrene was then removed at 40°C (1.0 Torr). Acetone was added to the partially evaporated solution and the resulting solution dropped into an ice-water mixture.

The white precipitate which formed was filtered off, air dried, finely ground in a mortar and pestle, and dried at 35°C.

2. The residual monomers and MEK were removed in a rotary evaporator at 60°C. The remaining white solid was removed, broken up with a mortar and pestle, and dried under vacuum at 35°C.

Analysis of Copolymer

Gas-Liquid Chromatography

A gas chromatograph model PYE SERIES 104 equipped with a flame ionization detector was used. The $\frac{1}{4}$ in. × 5 ft column was packed with 10% SE 30 on Gaschrome Z.

In order to separate the polymer present in samples, a 6-cm glass precolumn packed with 10% SE30 on Gaschrome Z was used. A freshly packed precolumn was used for every run.

Column temperature was 120°C, inlet port temperature 130°C, and detector temperature 155°C.

Sample size was 0.5 μliter.

Peak heights were measured and the peak height of the solvent was used as the internal standard.

Elemental Analysis of Polymer

Elemental analysis was carried out by the Microanalytical Laboratory of the Division of Applied Chemistry.

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