A Method For the Calculation of Compositions of Radical-Chain Copolymerizations

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Synopsis

In this article the straight-line relationship between $\ln A$ and $\ln B$, where A and B denote the concentrations of the two types of monomers in any reaction period, is examined to exist in the radical copolymerizations of $1.02 \geq r_1 r_2 \geq 0.25$. Utilizing this observation, we propose an easy-to-use compositions calculation method in which a single empirical parameter is included. The method is derived without involving the constant monomer reactivity ratios assumption. The copolymerizations of styrene–methyl methacrylate, vinyl chloride–vinyl acetate, methyl methacrylate–vinyl acetate, acrylic acid–acrylamide, methacrylic acid–methacrylamide, and sodium methacrylate–methacrylamide are investigated. The instantaneous and cumulative copolymer compositions and the residued monomer compositions computed by this proposal are in very good agreement with the experimental data.

INTRODUCTION

The prediction for the instantaneous copolymer composition as a function of conversion is traditionally done by virtue of the integrated forms of the copolymer composition equation due to Mayo and Lewis[1] or Lowry and Meyer,[2] which are derived involving a constant monomer reactivities assumption. Recently, Johnson et al.[3] and Zil'berman et al.,[4] however, reveal that the monomer reactivity ratios in some copolymerization reactions considerably change with conversion, and do not remain constant throughout whole reaction stages. Therefore, it is worth proposing a new method, without using the constant monomer reactivity ratios assumption, for calculating the copolymer compositions.

Watts et al.[5] observe that the relation between $\ln A$ and $\ln B$ in the copolymerization of ethylene and vinyl acetate, where A and B refer to the respective concentrations of ethylene and vinyl acetate monomers, is linear. Furthermore, they show that, theoretically, the straight-line relationship between $\ln A$ and $\ln B$ holds if $r_1 r_2 \sim 1$. Suggested by Watts' observation, we investigate several copolymerization reactions to see if the linear line relationship holds between $\ln A$ and $\ln B$. Then we propose an easy-to-use method to calculate the copolymer compositions. In this method the values of the monomer reactivity ratios are not required.

EQUATIONS PROPOSED FOR CALCULATING COMPOSITIONS

According to the usual kinetic scheme for the propagation reaction in radical chain copolymerization, the rates of disappearances for the two comonomers have been represented by[1,6-8]

$$-d \ln A/dt = k_{11}P + k_{21}Q \tag{1}$$

$$-d \ln B/dt = k_{12}P + k_{22}Q \tag{2}$$

where P and Q refer to the concentrations (and the species) of the propagation radicals, P is the propagation radical with monomer A as its end unit, and Q that with monomer B as its terminal unit. k_{11}, k_{12}, k_{21}, and k_{22} denote the respective rate constants for the appropriate elementary reactions in the propagation reaction.

Combining the above two equations results in

$$d \ln A/d \ln B = (k_{11}P + k_{21}Q)/(k_{12}P + k_{22}Q) \tag{3}$$

Putting

$$\alpha = (k_{11}P + k_{21}Q)/(k_{12}P + k_{22}Q) \tag{4}$$

we have

$$d \ln A/d \ln B = \alpha \tag{5}$$

Equation (5) is further expressed in terms of the total molar fractional monomer conversion X defined by $(A_0 - A + B_0 - B)/(A_0 + B_0)$ and the monomer compositions $f_1 = 1 - f_2$ defined as $A/(A + B)$, where the subscript 0 denotes the initial condition,

$$d \ln[(1 - X)f_1]/d \ln[(1 - X)f_2] = \alpha \tag{6}$$

Utilizing eq. (6) or eq. (7), one may determine the value of α from the slope of the plot of $\ln A$ vs. $\ln B$ or $\ln[(1 - X)f_1]$ vs. $\ln[(1 - X)f_2]$. As shown above, the plots of $\ln A$ vs. $\ln B$ for the systems being studied show the relation to be linear. This means that α is a constant. Hence, eqs. (6) and (7) can be directly integrated to become

$$\ln(A/A_0) = \alpha \ln(B/B_0) \tag{7}$$

$$\ln[(1 - X)f_1/f_{10}] = \alpha \ln[(1 - X)f_2/f_{20}] \tag{8}$$

Since α is independent of conversion, the value of α may be determined with a few experimental data of the compositions and conversions obtained at early reaction stages. After α is found, the monomer compositions at any reaction period can be computed by eq. (8) or (7).

From Skeist's equation[9] one may easily derive the relations

$$F_1/f_1 = 1 + d \ln f_1/d \ln(1 - X) \tag{9}$$

$$F_2/f_2 = 1 + d \ln f_2/d \ln(1 - X) \tag{10}$$

where $F_1 = 1 - F_2$ denote the instantaneous copolymer composition formed at f_1. Respective substitutions of eqs. (9) and (10) into the numerator and the denominator of eq. (6) yield

$$[(1/f_1) - 1]/[(1/F_1) - 1] = \alpha \tag{11}$$

Equation (11) is applicable for the calculation of the instantaneous copolymer compositions after f_1 is determined. The cumulative copolymer composition F_1' may also be calculated by either the equation of the definition of total molar fractional conversion,

$$X = (f_{10} - f_1)/(F_1' - f_1) \tag{12}$$

or the equation of the definition of weight fractional monomer conversion,[10]

$$X_w = [(M_1 - M_2)F_1' + M_2](f_{10} - f_1)/[(M_1 - M_2)f_{10} + M_2]/(F_1 - f_1) \tag{13}$$

where M_1 and M_2 refer to the molecular weights of two comonomers A and B, respectively.

RESULTS AND DISCUSSION

In this work the structural properties of the systems St–MMA, VCl–VAc, AA–AAm, MAA–MAAm and MAAm–NaM examined were shown in Table I. Analyzing the published data[4,12-15] of those systems which were collected in Table II, we have verified that the relationship between $\ln A$ and $\ln B$ for the systems (Figs. 1 and 2) where $r_1 > 1$, $r_2 < 1$ as well as $r_1 < 1$, $r_2 < 1$, in which

TABLE I
The Structural Properties of the Pairs of Monomers Cited[11] [a]

System	f_{10}	r_1	r_2	$r_1 r_2$	Remark	
St–MMA	0.80	0.52	0.46	0.239	Bulk	(60°C)
VCl–VAc	0.856	1.70	0.24	0.408	Bulk	(6)°C)
MMA–VAc	0.50	21.00	0.015	0.315	Bulk	(60°C)
AA–AAm	0.20	1.36	0.67	0.901	Aqueous	(40°C)
MAA–MAAm	0.50	2.36	0.43	1.015	Aqueous	(50°C)
MAAm–NaMA	0.493	—	—	—	Aqueous	(50°C)

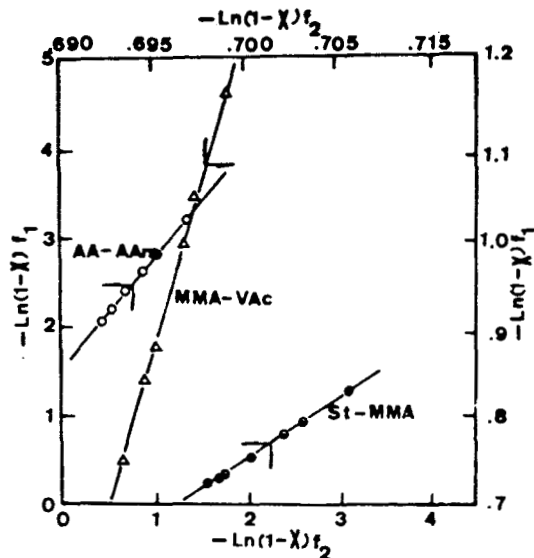[a]The subscripts 1 and 2 refer to the respective first and second monomers of the systems listed in the table.

Fig. 1. Plots for finding the values of α for various copolymerization systems of acrylic acid and acrylamide (AA–AAm), methyl methacrylate and vinyl acetate (MMA–VAc), and styrene and methyl methacrylate (St–MMA).

$1.01 \geq r_1, r_2 \geq 0.25$, is a straight line. It means that α is independent on conversions. Consequently, we have a new integrated form of the monomer composition equation, i.e., eq. (8) or eq. (7). Utilizing eq. (8) along with the published data of f_1 and X, we calculated the values of α at various conversions for the systems discussed and gave them in Figures 3–6 and their mean values were shown in Table III. It is clearly shown in the table and the figures that the variations of α with conversions are negligible. This result
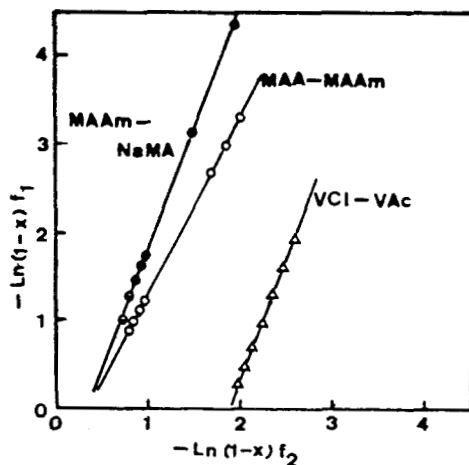

Fig. 2. Plots for finding the values of α for various copolymerization systems of methacrylamide and sodium methacrylate (MAAm–NaMA), methacrylic acid and methacrylamide (MAA–MAAm), and vinyl chloride and vinyl acetate (VCl–VAc).
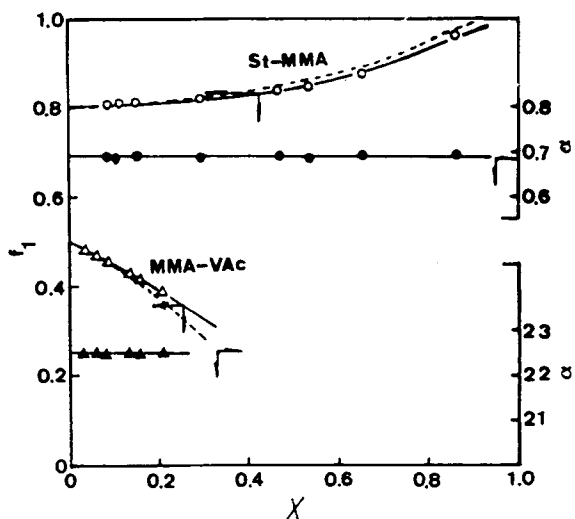
Fig. 3. Values of α determined and comparison of experimental and predicted residued monomer mixture compositions for styrene–methyl methacrylate and methyl methacrylate–vinyl acetate systems.

convinces us that the value of α may safely be determined by a few experimental data of f_1 and X obtained at early reaction stages and then may be used to predict monomer compositions at higher conversion.

Using eq. (8) along with the values of α, we obtained the f_1–X lines for the systems studied and showed them as the solid lines in Figures 3–6. We can find in these figures that the agreements between the solid lines and the experimental points are good. In the same figures we also showed the f_1–X lines computed by virtue of the integrated form of the copolymer composition equation due to Lowry and Meyer.[2] It can be seen that the f_1–X calculated by the Meyer–Lowry equation does not fall within the experimental data at moderate to high conversions, some of the systems discussed are overestimated but some underestimated, depending on the monomer feed composition and the types of the pair of monomers. This conclusion demonstrates that the
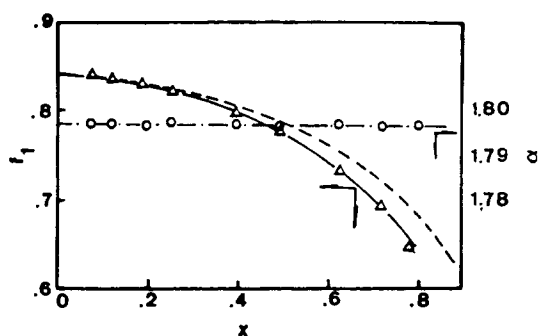

Fig. 4. Values of α determined and comparison of experimental and predicted residued monomer mixture compositions for vinyl chloride and vinyl acetate system.
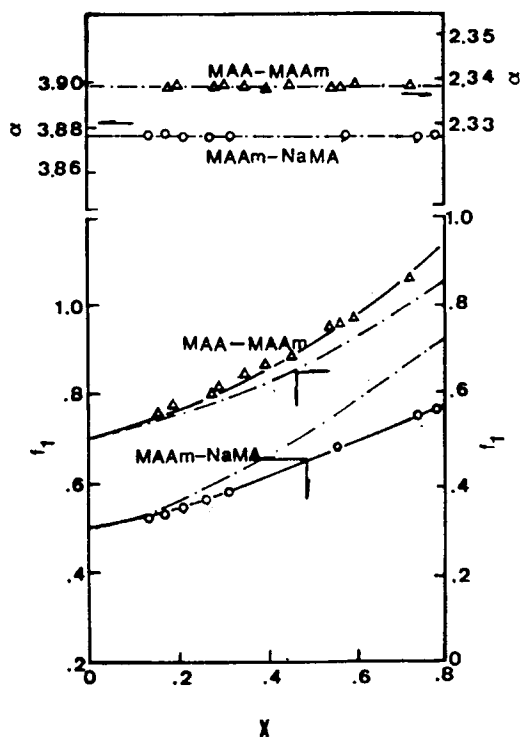
Fig. 5. Values of α determined and comparison of experimental and predicted residued monomer mixture compositions for methacrylic acid–methacrylamide and methacrylamide–sodium methacrylate systems.

classical method based on the constant monomer reactivities assumption cannot provide a good prediction for the monomer compositions at moderate to high conversions. If we look back at eq. (4), we may see that in order to keep a constant α, the monomer reactivity ratios should be varied to compensate the changes in f_1 and f_2 during polymerization progressing. This is another evidence for supporting the findings of Johnson et al.[3] and Zil'berman et al.[4]

We used eq. (11) and the values of α obtained to compute the instantaneous copolymer compositions F_1 at various monomer compositions and showed them in the ninth column of Table II. Further employing eq. (8), we obtained the F_1–f_1–X relation. We also used eqs. (8) and (12) or (13) along with the obtained value of α to determine the cumulative copolymer compositions F_1' and listed them in the eighth column of Table II. Finally we completed the relations of F_1'–F_1–f_1–X. Comparing the computed and the experimental copolymer compositions, we found that the computed values are in very good agreement with the experimental data. The difference between the computed and the experimental values were within ±0.002.

In case of chemical-controlled copolymerization the concentrations of the two types of propagating macroradicals, P and Q, are generally assumed to be

TABLE II
The Cited and Calculated Data of Monomer Compositions, Copolymer Compositions,
and Conversion

| System	T (°C)	f_{10}	X	$f_{1,\text{exptl}}$	$\bar{F}_{1,\text{exptl}}$	$f_{1,\text{calcd}}$	$\bar{F}_{1,\text{calcd}}$	$F_{1,\text{calcd}}$
St–MMA[15]	60	0.80	0.090	0.806	0.734	0.806	0.734	0.738
			0.118	0.809	0.736	0.809	0.735	0.742
			0.157	0.812	0.738	0.813	0.738	0.745
			0.294	0.823	0.745	0.823	0.747	0.759
			0.463	0.839	0.754	0.840	0.752	0.779
			0.531	0.848	0.757	0.848	0.757	0.791
			0.660	0.859	0.760	0.861	0.762	0.804
			0.717	0.877	0.774	0.875	0.773	0.828
			0.865	0.965	0.777	0.966	0.776	0.949
VCl–VAc[12]	60	0.856	0.075	0.796	0.908	0.796	0.908	0.906
			0.121	0.790	0.907	0.791	0.906	0.902
			0.180	0.782	0.905	0.781	0.905	0.898
			0.252	0.770	0.904	0.770	0.903	0.892
			0.393	0.740	0.902	0.739	0.902	0.875
			0.480	0.718	0.894	0.718	0.896	0.862
			0.609	0.669	0.886	0.668	0.885	0.833
			0.695	0.616	0.881	0.617	0.883	0.798
			0.761	0.567	0.873	0.566	0.871	0.567
MMA–VAc[13]	60	0.50	0.032	0.485	0.997	0.485	0.996	0.955
			0.061	0.471	0.996	0.470	0.996	0.953
			0.089	0.456	0.994	0.456	0.995	0.950
			0.115	0.427	0.992	0.429	0.993	0.944
			0.163	0.422	0.989	0.420	0.990	0.943
			0.205	0.386	0.983	0.388	0.982	0.934
AA–AAm[14]	40	0.20	0.197	0.178	0.288	0.178	0.288	0.240
			0.276	0.172	0.273	0.172	0.271	0.232
			0.381	0.161	0.263	0.160	0.264	0.219
			0.490	0.137	0.254	0.138	0.256	0.189
			0.621	0.136	0.237	0.135	0.235	0.187
MAA–MAAm[4]	50	0.50	0.163	0.560	0.156	0.560	0.156	0.160
			0.189	0.580	0.192	0.581	0.191	0.203
			0.275	0.600	0.202	0.598	0.204	0.215
			0.294	0.624	0.224	0.623	0.221	0.232
			0.350	0.649	0.236	0.649	0.239	0.247
			0.400	0.667	0.250	0.668	0.248	0.261
			0.451	0.679	0.282	0.678	0.281	0.290
			0.543	0.752	0.283	0.754	0.284	0.293
			0.566	0.758	0.307	0.760	0.309	0.312
			0.600	0.764	0.324	0.763	0.326	0.334
			0.727	0.830	0.276	0.832	0.378	0.387
MAAm–NaMA[4]	50	0.493	0.139	0.527	0.283	0.527	0.283	0.285
			0.176	0.533	0.284	0.534	0.285	0.288
			0.212	0.547	0.206	0.545	0.294	0.301
			0.261	0.567	0.305	0.565	0.307	0.312
			0.315	0.569	0.348	0.567	0.350	0.354
			0.561	0.680	0.377	0.678	0.375	0.381
			0.739	0.761	0.398	0.763	0.397	0.396
			0.787	0.769	0.417	0.767	0.415	0.420
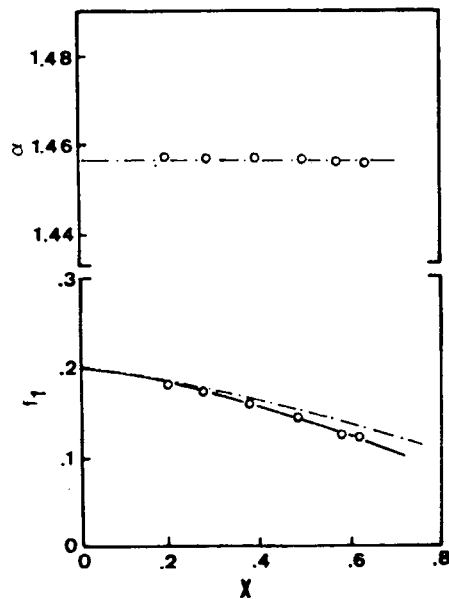
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Fig. 6. Values of α determined and comparison of experimental and predicted residued monomer mixture compositions for acrylic acid–acrylamide system.

TABLE III
The Experimental Values of α

System	f_{10}	T (°C)	α
St–MMA	0.80	60	0.691
VCl–VAc	0.856	60	2.460
MMA–VAc	0.50	60	21.675
AA–AAm	0.20	40	1.457
MAA–MAAm	0.50	50	2.350
MAAm–NaMA	0.493	50	3.876

valid for the steady-state assumption and the monomer reactivity ratios are constant. Hence according to eq. (4), the value of α is constant. Hence, eq. (8) is also applicable to the usual chemical-controlled copolymerization.

CONCLUSION

As discussed above, our method can well describe the $F_1'-F_1-f_1-X$ relation in radical-chain copolymerizations only if the copolymerizations satisfy the straight-line assumption between $\ln A$ and $\ln B$. The main advantages of this method are that the new integrated form of the composition equation includes only an empirical parameter α, unlike the classical methods, including two parameters r_1 and r_2. The parameter α may easily be determined by a few experimental points of f_1 and X at early reaction stages, and the calculation is quite simple.

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