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Determination of Radical Concentrations in Copolymerization

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ABSTRACT

The determination of the individual conversion rate of each monomer in a radical copolymerization allows the absolute concentration of each kind of growing radical to be derived, provided the reactivity ratios and the homopropagation rate constants are known. The procedure is applied to the following binary copolymerizations: styrene-methyl methacrylate, vinyl chloride-vinyl acetate, acrylonitrile-vinyl acetate, and acrylonitrile-vinyl chloride. In the two latter cases, the anomalous behavior, probably caused by the internal cyclization reaction involving CN bonds, is well evidenced.

INTRODUCTION

The determination of the absolute concentrations of radicals in radical polymerization is a difficult task, which involves generally nonsteady-state conditions (intermittent illumination, posteffect, etc.). In radical copolymerization of a binary system with monomers A and B, the steady state assumption leads to the ratio of the radical concentration $A°/B°$:

$$\frac{A^{\circ}}{B^{\circ}} = \frac{k_{BA}}{k_{AB}} \frac{A}{B} \tag{1}$$

where A and B are the monomer concentrations k_{AB} and k_{BA} are the rate constants for the two propagation reactions involving a change in the nature of radicals. These two rate constants are derived from the reactivity ratios $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$ of the rate constants of the propagation reaction of the same radical reactivity with the different monomers. These reactivity ratios are derived in turn using the copolymerization equation

$$n_A = \frac{dA}{dB} = \frac{1 + r_A x_A}{1 + r_B/x_A} \tag{2}$$

where $x_A = A/B$ and dA and dB are the amounts of monomers A and B polymerized during the time dt.

The use of analysis of the reaction medium by gas chromatography, as developed in our laboratory [1], allows the determination of the consumption rate of each monomer dA/dt and dB/dt:

$$-\frac{dA}{dt} = k_{AA} A^{\circ}A + k_{BA} B^{\circ}A \tag{3}$$

$$-\frac{dB}{dt} = k_{AB} A^{\circ}B + k_{BB} B^{\circ}B \tag{4}$$

Systems (3) and (4) may be solved for A° and B°:

$$A^{\circ} = \frac{\dfrac{1}{A}\dfrac{dA}{dt}r_B - \dfrac{1}{B}\dfrac{dB}{dt}}{k_{AA}r_B - k_{AB}} \tag{5}$$

$$B^{\circ} = \frac{\dfrac{1}{B}\dfrac{dB}{dt}r_A - \dfrac{1}{A}\dfrac{dA}{dt}}{k_{BB}r_A - k_{BA}} \tag{6}$$

Of course, the steady-state assumption, i.e., Eq. (1), where A° and B° are replaced by their values (Eqs. 5 and 6), leads to Eq. (2).

The determination of $[A^\circ]$ and $[B^\circ]$ using Eqs. 5 and 6 again involves a knowledge of the absolute rate constants k_{AA}, k_{AB}, k_{BA} and k_{BB}, but, in fact, by taking into account the reactivity ratio, only the homopolymerization rate constants are needed. In this paper, Eqs. (5) and (6) have been applied to the study of a few systems where the useful data were available and satisfactorily established. The systems include a pair of conjugated monomers (styrene and methyl methacrylate), a pair of unconjugated monomers (vinyl chloride and vinyl acetate), and finally two mixed systems with acrylonitrile as a conjugated monomer copolymerized with vinyl acetate and vinyl chloride respectively. In the latter case we have previously shown [2] that an intramolecular cyclization reaction takes place which involves a number of vinyl chloride ended radicals transformed into CN° radicals with a very different reactivity: this anomalous behavior is again shown in the present study.

STYRENE(S)-METHYL METHACRYLATE (M) COPOLYMERS

The copolymerization have been carried out in dioxane solution at 60°C using azodiisobutyronitrile as initiator. The charge of the reactors as well as the kinetic results are reported in Table 1. Using the literature data for the homopolymerization reaction rate constants [mole/(liter)(sec)], $k_{SS} = 176$ [3] and $k_{MM} = 367$ [4], as well as the reactivity ratios derived from a Fineman-Ross plot [5] of the data of Table 1, $r_S = 0.58$ and $r_M = 0.52$, the absolute values of (A°) and (B°) for styrene (S°) and methyl methacrylate (M°) ended radical concentrations are plotted in Fig. 1 in the whole range of monomer feed composition. Actually, in order to eliminate the effect of initiator concentration, the plots involve the ratios $R^\circ/I^{1/2}$, where R is the absolute value of radical concentration (mole/liter) and I is the initiator concentration.

A smooth curve is obtained for the methyl methacrylate ended radicals. In the case of styrene, the experimental points are more dispersed. This shows that these kinds of measurements are very sensitive to the accurary of the kinetic measurements. However, the ratio of $[M^\circ]/[S^\circ]$ may be compared with the calculated one by using Eq. (1). The agreement is good for three out of the five points. Then, using the results for $[M^\circ]$ and Eq. (1), the calculated curve for $[S^\circ]$ is shown as a full line on Fig. 1.

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TABLE 1. Styrene-Methyl Methacrylate Copolymerization

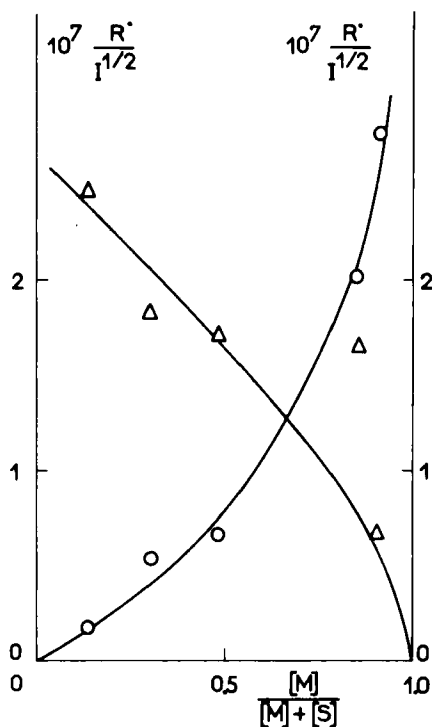| Styrene (mole)	MMA (mole)	Dioxane (moles)	AIBN = I [(mole/liter) × 10²]	$x_M = \dfrac{M}{S}$	$n_M = \dfrac{dM}{dS}$	$-\dfrac{1}{M}\dfrac{dM}{dt}$ (sec⁻¹ × 10⁶)	$-\dfrac{1}{S}\dfrac{ds}{dt}$ (sec⁻¹ × 10⁶)	$M°/S°$, calcd by Eq. (1)
	0			0	-	-	5.16	-
0.96	0.153	3.38	1.2	0.160	0.236	9.60	6.46	0.069
0.73	0.32	2.70	1.43	0.438	0.467	8.66	8.14	0.303
0.32	0.30	3.09	1.50	0.935	0.98	10.5	10.8	0.382
0.157	0.937	3.04	1.31	5.97	4.65	16.18	23.2	1.174
0.083	0.798	3.0	1.43	9.60	6.05	16.25	28.3	4.510

FIG. 1. Styrene (S, △) and methyl methacrylate (M, ○) copolymerization. Corrected concentration of radicals $R/I^{1/2}$ vs monomer feed composition.

VINYL CHLORIDE (C)-VINYL ACETATE (Ac) COPOLYMERS

The data used are taken from the experiments described in Ref. 6 for polymerization in dimethylformamide (DMF) solution at 60°C and from the literature [7, 8] for the homopolymerization rate constants. We have used $r_C = 1.60$, $k_{CC} = 13,400$, $k_{CAc} = 8,400$, $r_{Ac} = 0.29$, $k_{AcAc} = 9,500$, and $k_{AcC} = 32,800$.

The results are illustrated in Fig. 2, the useful data being given in Table 2. Owing to the greater reactivity of the radicals born from unconjugated monomer units, the number of radicals is lower than in the previous case. The last two columns in Table 2 compare the ratio or radical concentrations as calculated from Eq. (1) or experimentally
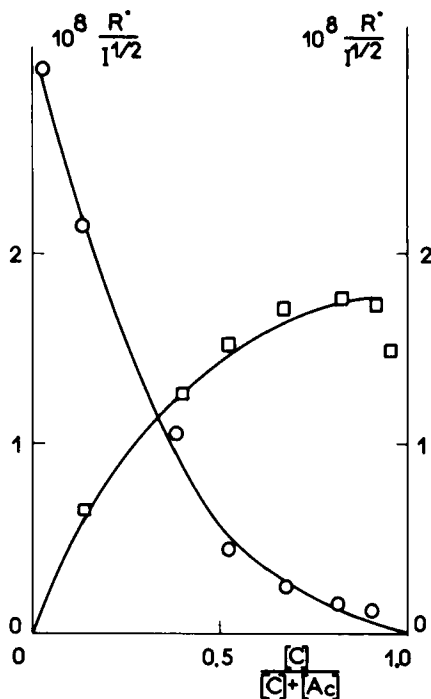
FIG. 2. Vinyl chloride (C, □) and vinyl acetate (Ac, ○) copolymer-
ization. Corrected concentration of radicals vs monomer feed
composition.

determined using Eqs. (5) and (6). The agreement is rather good,
except at the extreme part of the composition range.

ACRYLONITRILE (AN) -VINYL ACETATE (Ac)
COPOLYMERS

Copolymerization has been carried out in DMF solution at 60°C.
The data are reported in Table 3. Owing to the curvature of the Fineman-
Ross plot, the reactivity ratios have been derived by the extrapolation
method to give r_{AN} = 4.0 and r_{Ac} = 0.08.

From the literature [8, 9] and these reactivity ratios, we have used
k_{ANAN} = 1,960, k_{ANAc} = 490, k_{AcAc} = 9,500, and k_{AcAN} = 1,190,000.

TABLE 2. Vinyl Chloride–Vinyl Acetate Copolymerization

$\begin{bmatrix}Ac\end{bmatrix}$ (mole)	$\begin{bmatrix}C\end{bmatrix}$ (mole)	$\begin{bmatrix}DMF\end{bmatrix}$ (moles)	AIBN = I $[(\text{mole/liter}) \times 10^2]$	$x_{Ac} = \dfrac{Ac}{C}$	$n_A = \dfrac{Ac}{C}$	$-\dfrac{1}{Ac}\dfrac{dAc}{dt}$ $(\sec^{-1} \times 10^6)$	$-\dfrac{1}{C}\dfrac{dC}{dt}$ $(\sec^{-1} \times 10^6)$	$\dfrac{[Ac^\circ]}{[C^\circ]}$ calcd
0.0190	0.815	5.50	1.04	0.023	0.0156	14.20	26.60	0.0059
0.0210	0.733	5.06	1.13	0.030	0.0175	15.00	26.70	0.0076
0.055	0.812	5.63	1.04	0.068	0.0388	15.50	26.90	0.0174
0.0916	0.820	5.85	0.970	0.112	0.0615	15.80	27.50	0.028
0.2343	1.055	5.56	0.958	0.222	0.133	16.25	28.70	0.056
0.342	0.736	5.50	0.98	0.465	0.213	16.66	31	0.119
0.275	0.288	5.85	1.01	0.950	0.408	17.00	35	0.243
0.617	0.278	6.02	0.92	2.22	0.82	20.00	50	0.568
0.570	0.086	5.95	1.02	6.66	2.22	25.80	79	1.704
0.593	0.018	5.48.	1.04	33	9.60	27.30	96	8.45

TABLE 3. Acrylonitrile–Vinyl Acetate Copolymerization

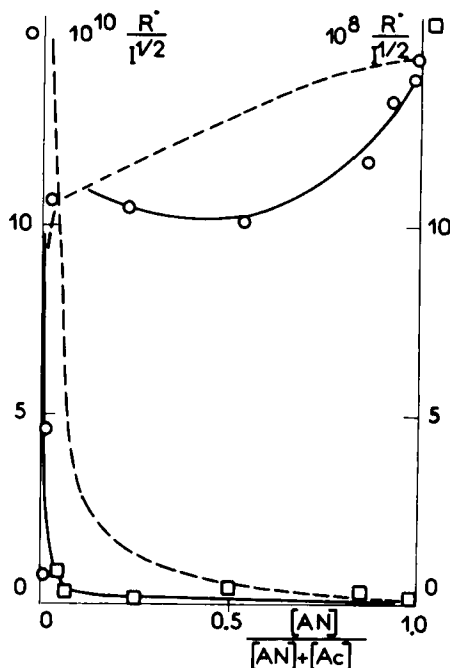| $[AN]$ (mole)	$[Ac]$ (mole)	$[DMF]$ (moles)	$(AIBN) = I$ $[(mole/liter) \times 10^2]$	$x_{AN} = \dfrac{AN}{Ac}$	$n_{AN} = \dfrac{AN}{Ac}$	$-\dfrac{1}{AN}\dfrac{dAN}{dt}$ $(sec^{-1} \times 10^6)$	$\dfrac{1}{Ac}\dfrac{dAc}{dt}$ $(sec^{-1}) \times 10^6$	$[AN°]/[Ac°]$, calcd by Eq. M
0.012	0.856	6.108	0.91	0.0128	0.400	203	6.40	0.0313
0.028	0.870	5.63	0.97	0.0247	0.495	126.5	6.35	0.060
0.067	0.858	5.62	0.96	0.0780	0.690	50.0	5.67	0.190
0.160	0.840	5.60	0.96	0.192	1.200	33.2	5.32	0.468
0.240	0.780	5.70	0.95	0.308	1.85	30.9	5.16	0.751
0.538	0.480	5.71	1.02	1.12	6.95	26.70	4.35	2.73
0.940	0.145	5.77	0.962	6.51	29.60	25.80	5.65	15.88
1.17	0.099	6.11	0.898	11.60	46.4	26.70	6.50	28.30
0.907	0.038	6.07	0.942	22.30	89.7	25.80	6.40	54.41
1.02	0.018	6.07	0.933	52.0	211	26.70	6.57	126.88

FIG. 3. Acrylonitrile (AN, ○) and vinyl acetate (Ac, □) copolymer-
ization. Corrected concentration of radicals vs monomer feed
composition. Theoretical curve (--).

The results, shown in Fig. 3, first show a large difference between the
number of the two kinds of radicals: the vinyl acetate radicals change
very rapidly in acrylonitrile radicals. The latter show a minimum
which is not at all in agreement with theory. Because the vinyl acetate
radicals have a reactivity similar to that of the vinyl chloride radicals,
they can probably cause the same intramolecular cyclization reaction [11]
and be changed into CN° radicals. Such an event might possibly
explain the observed minimum.

ACRYLONITRILE (AN) - VINYL CHLORIDE (C)
COPOLYMERS

The data from Ref. 10 have been used for Table 4. For the calcula-
tion of the radical concentration, the following values have been used:
r_{AN} = 3.90, r_C = 0.03, k_{ANAN} = 1,960, k_{CC} = 13,400, k_{ANC} = 502, and

TABLE 4. Acrylonitrile–Vinyl Chloride Copolymerization

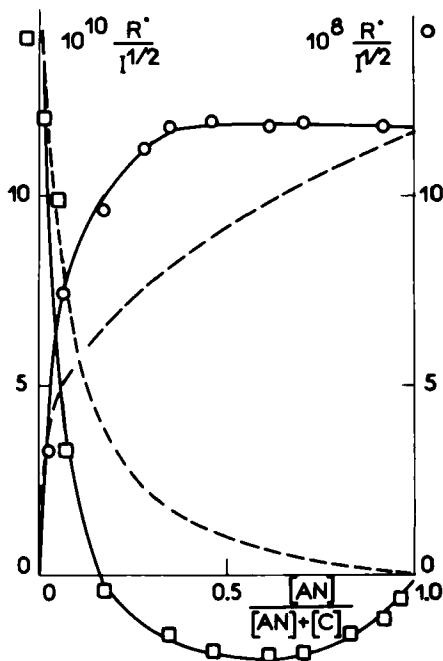| [AN] (mole)	[C] (mole)	[DMF] (moles)	AIBN = I [(mole/liter) × 10²]	$x_{AN} = \dfrac{AN}{C}$	$n_{AN} = \dfrac{AN}{C}$	$-\dfrac{1}{AN}\dfrac{dAN}{dt}$ (sec⁻¹ × 10⁶)	$\dfrac{1}{c}\dfrac{dC}{dt}$ (sec⁻¹ × 10⁶)	$(AN°)/(C°)$ calcd by Eq. (1)
0.0191	1.000	5.30	1.04	0.019	0.136	70.00	4.7	16.90
0.0247	0.825	5.54	1.03	0.030	0.376	61.10	3.3	26.70
0.084	1.05	4.88	1.10	0.080	0.545	30.60	4.4	71.2
0.160	0.82	5.11	1.08	0.195	0.780	18.10	5.0	173
0.324	0.603	5.51	1.02	0.536	1.60	14.60	5.4	476
0.616	0.648	5.53	0.98	0.940	2.36	13.90	5.6	836
0.590	0.384	5.80	0.97	1.540	3.77	13.90	5.7	1,370
0.637	0.270	5.85	0.98	2.360	6.50	14.20	5.7	2,099
0.820	0.171	5.16	1.08	4.80	15.10	16.00	5.7	4,270
1.16	0.106	5.45	1.00	10.50	36.80	18.10	5.8	9,341
1.045	0.031	5.41	1.07	33.30	127.5	20	5.8	29,620

FIG. 4. Acrylonitrile (AN, ○) and vinyl chloride (C, □) copolymer-
ization. Corrected concentration of radicals vs monomer feed
composition. Theoretical curve (--).

k_{CAN} = 446,600. Again, as shown in Fig. 4, the most frequent radicals
are the less active acrylonitrile ended radicals. A strikingly anomalous
behavior is observed: the calculated number of vinyl chloride radicals
become negative, and the concentration of acrylonitrile remains constant
in a large range of monomer feed concentrations.

   If one assumes that the intramolecular cyclization reaction is the
major cause of the discrepancies observed with the theory, because this
reaction mainly involves the attack of a CN group by an active vinyl
chloride or vinyl acetate radical, the contribution of this reaction at both
ends of the composition range becomes negligible. It is then possible to
admit that the classical theory may be applied to these part of the range.
Then from the steady-state assumption:

$$v_i = 2fk_d IM = k_{tAA}(A°)^2 + 2k_{tAB}(Å)(B°) + k_{tBB}(B°)^2 \tag{7}$$

where A° is the acrylonitrile radicals, B° the vinyl chloride or vinyl
acetate radicals, k_{tAA} and k_{tBB} the termination rate constants for A

and B homopolymerization, k_{tAB} the rate constant for the cross-termination, I the initiator concentration, k_d its decomposition rate constant, f the efficiency, and M the total monomer concentration.

In the present case there is no important steric hindrance, so that we may reasonably [12] estimate, using Eq. (8):

$$k_{tAB} = (k_{tAA} k_{tBB})^{1/2} \tag{8}$$

The efficiency f may be dependent on the monomer mixture and one has to consider the efficiencies f_A and f_B for each monomer:

$$fM = f_A (A) + f_B (B) \tag{9}$$

The values of k_{tAA} and k_{tBB} are reported in the literature. The best values [7-9] are $k_{tANAN} = 7.8 \times 10^8$, $k_{tCC} = 2.1 \times 10^9$, and $k_{tAcAc} = 3.80 \times 10^8$.

From Eq. (8) we calculate $k_{tANC} = 1.28 \times 10^9$ and $k_{tANAc} = 5.45 \times 10^8$.

For k_d at $60°$C we have $k_d = 9.15 \times 10^{-6}$/sec   [13]

Because the efficiencies are not known, we have to calculate v_i. For this purpose we used the data of Tables 3 and 4 for the extreme part of the range.

For the mixtures rich in acrylonitrile we chose $x_{AN} = 33.5$ and 52, respectively, for the vinyl chloride and vinyl acetate copolymerization. Equations (5) and (6) allow us to get $[A°]$ and $[B°]$. Then, the Eq. (8), we calculate $v_i = 1.07 \times 10^{-7}$ and 1.71×10^{-7}, respectively. These values are practically the values for acrylonitrile homopolymerization. Taking into account the value of k_d, the efficiency for acrylonitrile f_{AN} may be estimated as 0.29. The same procedure is used for the B rich mixtures. The corresponding values for vinyl chloride copolymerization ($x_{AN} = 0.02$) are $v_i = 1.01 \times 10^{-8}$ and $f_c = 0.027$, and for vinyl acetate copolymerization ($x_{AN} = 0.0128$) they are $v_i = 0.82 \times 10^{-8}$ and $f_{Ac} = 0.22$.

From Eq. (9), the values of v_i is expected to follow a linear relationship with the monomer mixture composition which is easily established. Then, using Eqs. (8) and (1), one may calculate $[A°]$ and $[B°]$ in both cases. The calculated values are illustrated in Figs. 3 and 4 as dotted lines.

The results seem surprisingly different from one case to another one. The number of acrylonitrile radicals is larger than the theoretical one in the case of vinyl chloride but the reverse is observed in the case of vinyl acetate. There is also a rather larger decrease of C° radicals than of Ac° radicals. The coloration of the copolymers is less pronounced in the case of vinyl acetate copolymers [14], but the difference cannot explain by itself the above results. It is probably better to conclude that the cyclization reaction is only one of the facts which causes the observed anomalous kinetic behavior. The other possible causes, which are obviously not of a chemical nature, remain to be discovered.

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