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A Kinetic Model of Persulfate-Bisulfite-Initiated Acrylonitrile Polymerization

L. H. PEEBLES, JR.,* *Chemstrand Research Center, Inc., Durham, North Carolina 27702*

Synopsis

The molecular weight distribution has been derived for a homopolymer polymerized in a continuous-feed reactor under homogeneous conditions. The derived equations are then compared with data obtained on polymers of acrylonitrile–co(vinyl acetate) prepared under heterogeneous conditions with the potassium peroxydisulfate–sodium bisulfite–iron redox system. The termination reaction is assumed to be effected completely by recombination of active radicals with no disproportionation. The only transfer reaction considered is the transfer-to-activator reaction

$$R_n^* + HSO_3^- \rightarrow P_nH + SO_3^{-*}$$

The transfer and termination reactions produce polymers with different acid groups as endgroups. Each molecule, on the average, contains one sulfonate group, whereas the concentration of sulfate groups depends upon the extent of the transfer-to-activator reaction. The basic dye acceptance of the polymer depends on the number of acid groups in the polymer and hence on the activator and catalyst concentrations. Analysis of the basic dye acceptance and conversion data at a variety of catalyst and activator concentrations yields the following parameters at 50°C: $k_p/k_t^{1/2} = 1.01$ (l./mole sec)$^{1/2}$, $k_{tr}/k_p = 0.2063$, and k_1 [see eq. (1)] = 50.7 l./mole sec. Owing to the heterogeneous nature of the polymerization, the weight-average molecular weight of the polymer depends only on the activator concentration and the conversion and not directly on the catalyst concentration as predicted.

INTRODUCTION

In the usual commercial preparation of acrylic polymers, the monomers, water, catalyst (potassium peroxydisulfate), activator (SO_2 in water), and bicarbonate (to adjust pH) are continuously fed to a well-stirred reactor to produce polymer. The production of radicals by the initiator system has been studied in detail by Fritzche and Ulbricht.[1] In general, with the peroxydisulfate–bisulfite–iron system, one can write

$$S_2O_8^{2-} + Fe^{2+} \xrightarrow{k_1} SO_4^{-*} + Fe^{3+} + SO_4^{2-} \quad (1)$$

$$HSO_3^- + Fe^{3+} \xrightarrow{k_2} HSO_3^* + Fe^{2+} \quad (2)$$

A typical recipe calls for an iron content of 0.25 ppm, based on monomer, while the peroxydisulfate and sulfur dioxide concentrations are approxi-

* Present address: Office of Naval Research, 495 Summer Street, Boston, Massachusetts 02210.

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mately 0.75 and 1.50 wt-%, based on monomer. For a system at 50°C with a water-to-monomer ratio of 5/1, these concentrations are 6.0×10^{-7}, 3.7×10^{-3}, and 3.1×10^{-2} moles/l., respectively. In this scheme, the iron content should be the controlling factor in the initiation; in the presence of excess bisulfite, most of the iron should remain in the ferrous state. Many studies have been concerned with optimizing the iron–peroxydisulfate–bisulfite system to produce better-quality polymers and fibers, but the guiding chemical principles were not understood because the properties vary as the activator-to-catalyst ratio is varied.

Bamford,[2] Jenkins,[3] and others have shown that the termination reaction in acrylonitrile polymerization consists of recombination of radicals rather than of disproportionation. With the peroxydisulfate–bisulfite system, the recombination reaction would cause each polymer molecule to have two strong acid endgroups. The total concentration of sulfonate (RSO_3^-) endgroups should be exactly equal to the total concentration of sulfate ($ROSO_3^-$) endgroups; hence there should be no effect of activator-to-catalyst ratio on the strong acid group content or the basic dyeability of the polymer. The strong acid contents have been determined for polyacrylonitriles prepared with either radioactive peroxydisulfate or with radioactive bisulfite.[4] On the average, each molecule contained one sulfonate group per molecule whereas the sulfate group content varied with the polymerization recipe. Further, about 0.75 chain ends per molecule did not contain strong acid groups. Patron and Mazzolini[5] have suggested that these effects can be explained by invoking the transfer-to-activator reaction

$$R_n^* + HSO_3^- \rightarrow P_nH + SO_3^{-*} \tag{3}$$

The present work was undertaken to set up a kinetic model of the polymerization, to derive the molecular weight distribution as a function of the activator-to-catalyst ratio, and to see if the derived equations could be correlated with polymerization variables and the polymer properties such as dyeability and molecular weight. (A similar program with somewhat different emphasis has been undertaken by Montedison Fibre S.P.A., Milan, Italy.[5] It is particularly gratifying that the results of the two laboratories are in essential agreement with respect to the mechanism of polymerization and the values of the determined kinetic constants. Their results will be submitted to this journal independently.)

RESULTS AND DISCUSSION

Kinetic Model

The following symbols represent chains with different acid groups:

R_n^* = active polymer chains containing a SO_4^- fragment and n monomer units

Q_n^* = active polymer chains containing a SO_3^- fragment and n monomer units

The terminated polymer chains are:

$$\left.\begin{aligned} P_n &= {}^{-}SO_4\sim\sim H \\ S_n &= {}^{-}SO_3\sim\sim H \end{aligned}\right\}\text{formed by transfer}$$

and

$$\left.\begin{aligned} T_n &= {}^{-}SO_4\sim\sim SO_4^{-} \\ U_n &= {}^{-}SO_3\sim\sim SO_3^{-} \\ W_n &= {}^{-}SO_4\sim\sim SO_3^{-} \end{aligned}\right\}\text{formed by termination}$$

The problem is to find the concentration of the species P_n, S_n, T_n, U_n, and W_n as a function of the catalyst and activator concentrations. With the concentrations of the individual species we can also determine the number of the various endgroups per molecule. Specifically, the average number of sulfonate groups per molecule is

$$SO_3^{-}/\text{molec.} = \frac{\sum_{n=1}^{\infty} [(S_n) + 2(U_n) + (W_n)]}{\sum_{n=1}^{\infty} [(P_n) + (S_n) + (T_n) + (U_n) + (W_n)]}, \tag{4}$$

the average number of sulfate groups per molecule is

$$SO_4^{-}/\text{molec.} = \frac{\sum_{n=1}^{\infty} [(P_n) + 2(T_n) + (W_n)]}{\sum_{n=1}^{\infty} [(P_n) + (S_n) + (T_n) + (U_n) + (W_n)]} \tag{5}$$

and the average number of hydrogen-terminated ends per molecule is

$$H/\text{molec.} = \frac{\sum_{n=1}^{\infty} [(P_n) + (S_n)]}{\sum_{n=1}^{\infty} [(P_n) + (S_n) + (T_n) + (U_n) + (W_n)]}. \tag{6}$$

The total number of ends per molecule is just

$$SO_3^{-}/\text{molec.} + SO_4^{-}/\text{molec.} + H/\text{molec.} = 2 \tag{7}$$

because branching reactions will not be considered in this derivation.

Initiation is assumed to occur only by reactions (1) and (2); the radicals so produced are assumed not to react wastefully, hence they react only with monomer. Transfer reactions occur only to activator and not to monomer or to solvent (water). As stated above, no branching reactions are assumed to occur; termination is only by coupling. With these assumptions we write the following kinetic scheme in addition to reactions (1) and (2):

$$SO_4^{-*} + M \rightarrow R_1^* \tag{8}$$

$$R_n^* + M \rightarrow R_{n+1}^* \tag{9}$$

$$R_n^* + HSO_3^{-} \rightarrow P_n + SO_3^{-*} \tag{10}$$

$$R_n^* + R_s^* \rightarrow T_{n+s} \tag{11}$$

$$HSO_3^* + M \rightarrow Q_1^* \tag{12}$$

$$Q_n^* + M \rightarrow Q_{n+1}^* \tag{13}$$

$$Q_n^* + HSO_3^- \rightarrow S_n + SO_3^{-*} \tag{14}$$

$$Q_n^* + Q_s^* \rightarrow U_{n+s} \tag{15}$$

$$Q_n^* + R_s^* \rightarrow W_{n+s} \tag{16}$$

$$SO_3^{-*} + H^+ \rightarrow HSO_3^* \tag{17}$$

For simplicity, we will assume that all radicals propagate with the same velocity constant k_p, all radicals transfer with the same velocity constant k_{tr}, and all radicals undergo termination with the same velocity constant k_t, and that all species are soluble in the solvent. We know that the polymerization of acrylonitrile in water occurs in two or three separate phases rather than in a homogeneous solution.[6] However, we do not know enough about the heterogeneous phases, the concentration of material in these phases, or the process by which reactions can transfer from one phase to another. Hence, in order to proceed, we must invoke the simplifying assumption of homogeneous polymerization. As far as the other assumptions are concerned, the only error is in the formation of the species R_1^* and Q_1^*. Thus, R_1^* can be formed either from SO_4^{-*} or HSO_4^*, if the latter exists. Q_1^* can be formed from either SO_3^{-*} or HSO_3^*. Now the rate of reaction of an ion radical with monomer most surely will be different from the rate of reaction of the nonionized radical, but no information is available for these reactivities, so the differences will be ignored. Similarly the differences between the reactivity of SO_3^{-*} and SO_4^{-*} will be ignored. After one or two monomer units have been added to R_1^* or Q_1^* to make R_n^* and Q_n^*, any initial difference in reactivity will disappear. In acid media, at pH 3, the HSO_4^* concentration is probably very low, at least an order of magnitude below that of the HSO_4^- ion; the sulfonate radical may not be ionized.

Concentration of Molecular Species

The polymerizations are conducted in a continuous-flow, stirred-tank reactor with constant rates of monomer, catalyst, and activator feed and constant rates of overflow. The average lifetime of a molecule in the tank is θ, the dwell time, hence the concentrations of each species is independent of time. All rate equations can be set equal to zero to provide algebraic relations among the various species, as is shown in the Appendix.

With the following definitions

$$y = k_{tr}(HSO_3^-)/z \tag{18}$$

$$z^2 = 2k_tk_1(Fe^{2+})(S_2O_8^{2-}) = 2k_tk_2(Fe^{3+})(HSO_3^-) \tag{19}$$

$$\alpha = k_p(M)/[k_p(M) + z(1 + y)] \tag{20}$$

we can write for the total weight-fraction molecular weight distribution

$$W(n) = \frac{(1 - \alpha)^2 n \alpha^{n-2}}{2(1 + y)} [2\alpha y + (n - 1)(1 - \alpha)], \tag{21}$$

which is just the distribution obtained for a polymer where both transfer and termination are important.[7]

For high molecular weight polymer,

$$\alpha \approx 1 \quad \text{i.e.,} \quad k_p(\mathrm{M}) \gg z(1 + y), \tag{22}$$

hence,

$$\bar{r}_n = 2k_p(\mathrm{M})/z(1 + 2y) \tag{23}$$

$$\bar{r}_w = k_p(\mathrm{M})(3 + 2y)/z(1 + y)^2. \tag{24}$$

The rate of disappearance of monomer is given by

$$-d(\mathrm{M})/dt = k_p(\mathrm{M})[(\mathrm{SO_4}^{-*}) + (\mathrm{HSO_3}^*) + \Sigma(R_n^*) + \Sigma(Q_n^*)] - (\mathrm{M})_0/\theta + (\mathrm{M})/\theta \tag{25}$$

where $(\mathrm{M})_0$ is the initial monomer concentration in the absence of polymerization. By making the proper substitutions from the Appendix and eq. (22),

$$\mathrm{M} = (\mathrm{M})_0/[(z\theta k_p/k_t) + 1]. \tag{26}$$

By defining the conversion as

$$c = [(\mathrm{M})_0 - (\mathrm{M})]/(\mathrm{M})_0 \tag{27}$$

we obtain

$$c/(1 - c) = z\theta k_p/k_t. \tag{28}$$

The number of sulfonate and sulfur groups per molecule can be obtained by substitution of eqs. (A14) through (A19) into (4) through (6). The results are

$$\mathrm{SO_3}^-/\text{molec.} = 1 \tag{29}$$

$$\mathrm{SO_4}^-/\text{molec.} = 1/(1 + 2y) \tag{30}$$

$$\mathrm{H}/\text{molec.} = 2y/(1 + 2y). \tag{31}$$

The sum of eqs. (29) through (31) shows that eq. (7) is true.

Application of Kinetic Results to Continuous-Reactor Data

When the transfer-to-activator reaction is considered in the kinetic expressions to the exclusion of all other transfer-type reactions, the average number of sulfonate groups per molecule is unity, regardless of the mode of polymer formation, that is, at different activator-to-catalyst ratios in the feed.

The number of strong acid groups per gram (SAG/g) is obtained by adding eqs. (29) and (30), then dividing by eq. (23), and dividing by the molecular weight of the monomer:

$$\mathrm{SAG/g} = z(1 + y)/k_p(\mathrm{M})W_m \tag{32}$$

where (M) is the monomer concentration leaving the reactor and W_m is the molecular weight of monomer.

We can express (M) in terms of conversion by eq. (27) and write y and z in terms of the *input* catalyst and activator concentrations in weight per cent, based on monomer, eqs. (A30) and (A31):

$$\mathrm{SAG/g} = \frac{\mathrm{A}^*}{a}\frac{(\mathrm{cat})^{1/2}}{1 - c} + \frac{b\mathrm{D}^*[(\mathrm{act}) - \mathrm{B}^*(\mathrm{cat})]}{(1 - c)\,[1 + ab\mathrm{C}^*(\mathrm{cat})^{1/2}]} \tag{33}$$

where

$$\left.\begin{aligned}
\mathrm{A}^* &= \left[\frac{k_1(\mathrm{Fe}^{2+})\theta}{1 + k_1(\mathrm{Fe}^{2+})\theta}\cdot\frac{2\times10^{-2}}{\theta(\mathrm{M})_0W_mW_{kps}}\right]^{1/2} = \mathrm{C}^*/\theta(\mathrm{M})_0W_m\\
\mathrm{B}^* &= \frac{k_1(\mathrm{Fe}^{2+})\theta}{1 + k_1(\mathrm{Fe}^{2+})\theta}\cdot\frac{W_{\mathrm{SO}_2}}{W_{kps}} = \mathrm{C}^{*2}W_{\mathrm{SO}_2}10^{+2}/2\theta(\mathrm{M})_0W_m\\
\mathrm{C}^* &= \left[\frac{k_1(\mathrm{Fe}^{2+})\theta}{1 + k_1(\mathrm{Fe}^{2+})\theta}\cdot\frac{2\theta(\mathrm{M})_0W_m10^{-2}}{W_{kps}}\right]^{1/2}\\
\mathrm{D}^* &= 10^{-2}/W_{\mathrm{SO}_2}
\end{aligned}\right\} \tag{34}$$

$$a = k_p/k_t^{1/2} \qquad b = k_{tr}/k_p \tag{35}$$

W_i is the molecular weight of component i, (kps = $K_2S_2O_8$): and $(\mathrm{M})_0$ is the initial monomer concentration in the absence of polymerization.

At the present time, we do not have strong acid data on a sufficient number of polymers prepared by continuous polymerization. However, independent work in this laboratory[4] has shown that the number of dye sites (DS) (μeq/g) is related to the acid group content by

$$\mathrm{DS} = \mathrm{SAG} + \mathrm{NWAG} \tag{36}$$

where

$$\mathrm{DS} = 3.87(\mathrm{BDA} - 2.48) \tag{37}$$

BDA is the basic dye acceptance of the polymer in percent (4, 8), NWAG is the nonchromophoric weak acid group present in the polymer either due to partial hydrolysis of nitrile groups or to an added weak-acid containing comonomer. The NWAG content is determined by photometric titration[9] or by correcting the total amount of weak acid groups determined by potentiometric titration[10] for the amount of chromophoric weak acid groups present.[9] The parameter 2.48 in eq. (37) represents the amount of Sevron Blue

TABLE I
Polymers Prepared at Various Activator and Catalyst Levels[a]

Cat, % (b.o.m.)	Act, % (b.o.m.)	BDA, %	c	$\bar{M}_w \times 10^{-5}$
0.75	0.25	7.63	0.750	1.854
0.75	0.375	7.93	0.720	2.022
0.75	0.75	9.34	0.707	1.740
0.75	1.50	11.07	0.723	1.169
0.75	2.25	13.78	0.715	1.858
1.00	0.33	8.62	0.744	2.149
1.00	0.50	9.40	0.717	1.959
1.00	1.00	11.22	0.718	1.414
1.00	2.00	14.75	0.731	0.849
1.00	3.00	17.09	0.724	0.733
1.50	0.50	11.25	0.771	1.678
1.50	0.75	12.13	0.771	1.325
1.50	1.50	15.33	0.763	0.923
1.50	3.00	19.91	0.763	0.620
1.50	4.50	23.86	0.709	0.470
0.25	0.75	6.38	0.604	2.375
0.375	0.75	7.41	0.635	2.096
2.25	0.75	15.00	0.813	1.149
0.33	1.00	7.51	0.611	1.781
0.50	1.00	8.64	0.674	1.627
2.00	1.00	14.79	0.795	1.025
3.00	1.00	20.65	0.833	0.795
0.50	1.50	9.70	0.675	1.315
3.00	1.50	20.22	0.819	0.715
4.50	1.50	24.81	0.833	0.586
0.70	0.70	8.97	0.704	1.896
0.85	0.85	10.27	0.710	1.525
1.20	1.20	12.87	0.747	1.111
1.40	1.40	14.92	0.766	0.941
1.60	1.60	16.63	0.755	0.822
1.80	1.80	18.07	0.787	0.759
2.00	2.00	20.00	0.787	0.672
2.50	2.50	24.97	0.802	0.536

[a] The polymers were prepared at a water-to-monomer ratio of 5/1, pH 3, t = 50°C, Fe = 0.25 ppm b.o.m. (based on monomer), 91% acrylonitrile, 9% vinyl acetate, in a continuous-flow, stirred-tank reactor with a dwell time of 75 min.

2G dyestuff taken up by a polymer of infinite molecular weight, e.g., the amount of physically adsorbed dyestuff which is independent of polymer molecular weight. Its value will depend upon the parameters used to obtain a measure of the molecular weight from the specific viscosity of the polymers. The factor 3.87 is obtained from the best estimate of the molecular weight and the purity of Sevron Blue 2G.[11] BDA values are known for a series of 33 polymers prepared in a continuous-flow, stirred-tank reactor under a variety of catalyst and activator concentrations; they are listed in Table I. The NWAG content of most of these polymers is small, rela-

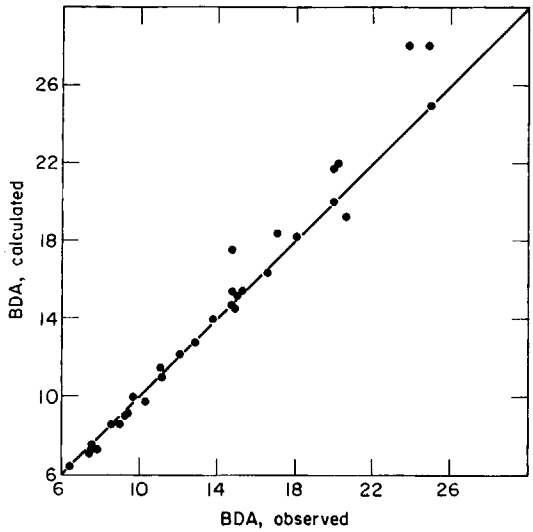

Fig. 1. Comparison of basic dye acceptance (BDA) calculated from eqs. (38) and (39) with the observed values (Table I).

tive to the SAG content, hence it is neglected in the present work. Therefore, we can replace SAG/g in eq. (33) by BDA in per cent:

$$\mathrm{BDA} = \mathrm{BDA}_0 + \frac{\mathrm{A}^*}{3.87a}\,\frac{(\mathrm{cat})^{1/2}}{1-c} + \frac{b\mathrm{D}^*}{3.87(1-c)}\left[\frac{(\mathrm{act}) - \mathrm{B}^*(\mathrm{cat})}{1 + ab\mathrm{C}^*(\mathrm{cat})^{1/2}}\right]. \quad (38)$$

This equation involves the undetermined parameters a, b, and C*, all in the third term on the right-hand side, hence are not independent of one another. However, by writing eq. (28) in the form

$$\frac{c}{1-c} = a\mathrm{C}^*(\mathrm{cat})^{1/2}, \quad (39)$$

an independent estimate of the product aC* can be made. The data of Table I were substituted into eq. (39) and the value of aC* found by the least-squares procedure:

$$a\mathrm{C}^* = 2.742\ (\text{wt-\% catalyst, based on monomer})^{-1/2}.$$

The values of a and b were estimated by using a cyclic procedure. Initial values of a and b were assumed in order to calculate the parameters A*, B*, and C* and the term $(1 + ab\mathrm{C}^*(\mathrm{cat})^{1/2})$ from the known conditions of polymerization and taking $(\mathrm{M})_0 = 806/6W_m$ moles/l. These calculated terms were then substituted into eq. (38). The values of a, b, and $(\mathrm{BDA})_0$ were estimated by the least-squares procedure. The cycle was repeated using the new values of a and b until constant values were obtained:

$$(\mathrm{BDA})_0 = 3.224$$

$$a = k_p/k_t^{1/2} = 7.868\ (\text{l./mole min})^{1/2} = 1.01\ (\text{l./mole sec})^{1/2}$$

$$b = k_{tr}/k_p = 0.2631.$$

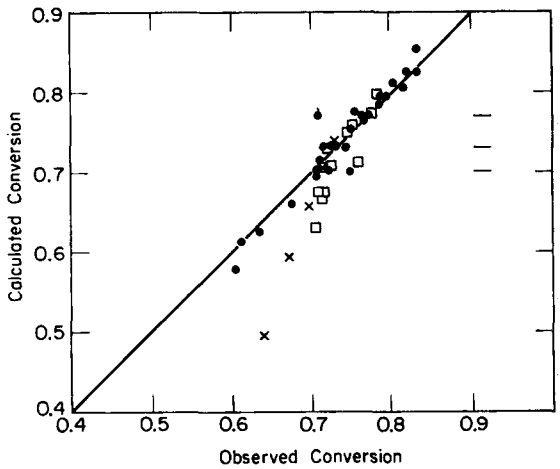

Fig. 2. Comparison of conversion calculated from eq. (39) with those reported in Tables I–III: (●) constant iron concentrations and dwell time, varying catalyst and activator concentrations. The three horizontal lines indicate polymers prepared at constant catalyst concentration while varying the activator concentration by a factor of 9; (×) constant catalyst, activator, and iron concentrations, varying dwell time; (□) constant dwell time, varying catalyst, activator, and iron concentrations.

A comparison of computed versus observed values of BDA are shown in Figure 1. The different values of the parameter $(BDA)_0$, 3.22 given here and 2.38 given earlier, is not considered significant because in both cases the values are based on least-squares estimates. The important point is that we have a single common correlation between the number of dye sites and the catalyst and activator concentrations.

The value of $k_p/k_t^{1/2}$ is in reasonable agreement with that obtained by extrapolating Dainton and Eaton's data[12] on photosensitized acrylonitrile polymerization in water to 50°C, 0.58 l./mole sec)$^{1/2}$.

The parameter C* in eq. (39) is a function of both the iron concentration which was held constant at 0.25 ppm iron, based on monomer, and the dwell time, 75 min, for the data in Table I.
Hence,

$$k_1 = 0.007373/(\text{ppm}) \text{ min} = 50.7 \text{ (l./mole sec)},$$

which is not inconsistent with the value determined by Fritzche and Ulbricht[1] at 25°C: 71 l./mole sec by varying the catalyst, activator, and iron concentrations. On the other hand, Saal[13] determined the rate constant for the peroxydisulfate–ferrous iron reaction in the absence of monomer and activator at 13°C. He obtained a value of 9.3 l./mole sec in the presence of 0.1*N* KCl and 0.02*N* H_2SO_4.

The conversion data of Tables I to III are plotted in Figure 2 against the value calculated from the initial catalyst, iron concentration, and dwell time. The three small horizontal lines indicate polymers where the cata-

lyst concentration was held constant while the activator concentration varied over a factor of 9. Thus, the conversion depends primarily on the catalyst concentration and is practically independent of the activator concentration.

TABLE II
Polymers Prepared at Various Dwell Times[a]

θ	c	$\bar{M}_w \times 10^{-5}$
30	0.640	1.657
45	0.671	1.545
60	0.697	1.335
75	0.715	1.315
90	0.726	1.295

[a] The polymers were prepared under the conditions listed in Table I, except that (cat) = (act) = 1.00 wt-% (b.o.m.). For these data, $\bar{M}_w \times 10^{-5} = 4.56(1 - c)$.

TABLE III
Polymers Prepared at Various Iron Levels[a]

Fe, ppm (b.o.m.)	Cat, % (b.o.m.)	Act, % (b.o.m.)	c	$\bar{M}_w \times 10^{-5}$
		$\bar{M}_w \times 10^{-5} = 3.94(1 - c)$		
0.03	0.70	1.60	0.599	1.596
0.18	"	"	0.705	1.178
0.28	"	"	0.708	1.130
"	"	"	0.705	1.140
"	"	"	0.718	1.149
0.38	"	"	0.717	1.140
0.53	"	"	0.720	1.073
		$\bar{M}_w \times 10^{-5} = 3.34(1 - c)$		
0.03	0.95	2.20	0.678	1.140
"	"	"	0.695	1.101
"	"	"	0.646	1.169
0.18	"	"	0.713	0.904
0.28	"	"	0.724	0.858
0.38	"	"	0.727	0.804
0.53	"	"	0.752	0.840
		$\bar{M}_w \times 10^{-5} = 4.14(1 - c)$		
0.03	1.45	1.45	0.727	1.111
"	"	"	0.725	1.130
"	"	"	0.727	1.111
0.18	"	"	0.760	1.082
0.28	"	"	0.745	0.978
0.38	"	"	0.776	0.969
0.53	"	"	0.781	0.895

[a] The polymers were prepared under the conditions listed in Table I, except that the iron level varied.

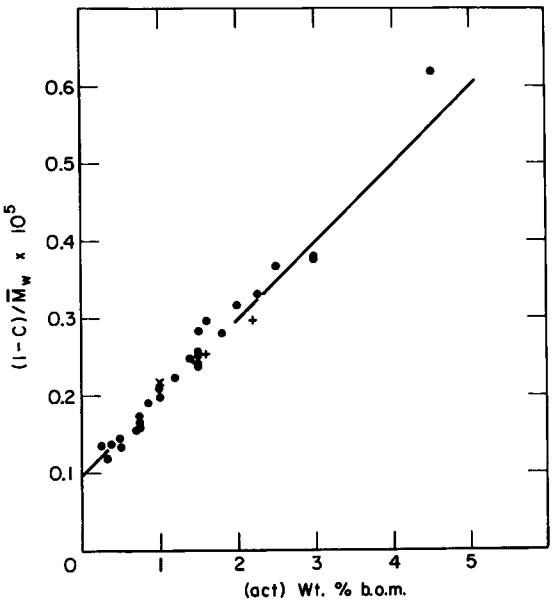

Fig. 3. Correlation between weight-average molecular weight and the conversion and activator concentrations. Data of Tables I–III.

According to eq. (24), the weight-average molecular weight of the polymer should vary as

$$\frac{1}{\bar{M}_w} = \frac{z(1 + y)^2}{k_p(\mathrm{M})W_m(3 + 2y)}. \tag{40}$$

For the polymers under consideration, the weight-average molecular weight can be calculated from the specific viscosity through the relation

$$\bar{M}_w = K/(1/\eta_{sp} + 0.24)^{4/3}$$

which is based on the Cleland-Stockmayer[14] equation for polyacrylonitrile and an approximation for converting specific viscosity, measured at 0.1 g/100 ml, to the intrinsic viscosity.[15] The molecular weights calculated by eq. (40) are lower than those obtained by viscosity measurements by about a factor of 1.5. This is not inconsistent with the observations of the previous paper[4] that the $\bar{M}_w/\bar{M}_n$ ratio is roughly 2.7. Computation of the $\bar{M}_w/\bar{M}_n$ ration by means of eqs. (23) and (24) gives a range of values, from 1.5 to 2.0, depending on the initial catalyst and activator concentrations. The molecular weight ratio calculated from the measured specific viscosities and the computed number-average molecular weight gives a range of 2.2–3.7. This means that the molecular weight distribution of the actual polymers is broader than that predicted from the assumed mechanism of polymerization. In this mechanism, we have assumed homogeneous conditions, which indeed do not exist. How heterogeneity influences the mech-

anism of polymerization is one of the unsolved problems in polymer kinetics.

A rather accurate correlation equation has been obtained relating the weight-average molecular weight, the conversion, and the activator concentration:

$$(1 - c)/\bar{M}_w = [0.0920 + 0.1079(\text{act})]\times 10^{-5}. \tag{41}$$

Figure 3 contains data from Tables I–III. Why such a relation is dependent on the catalyst concentration only as the catalyst concentration affects the conversion is not known at this time.

Despite the fact that the observed molecular weight distribution is not consistent with that calculated from the mechanism, let us examine the distribution equations to see what implications result.

The first term in the square brackets of eq. (21) comes from the molecules formed by transfer, whereas the second term comes from molecules formed by recombinative termination. The fraction f of molecules of size n formed by transfer within a given polymer, is

$$f = 2\alpha y/[2\alpha y + (n - 1)(1 - \alpha)] \tag{42}$$

or, with the aid of eq. (19),

$$f = u/[u + (n - 1)/\bar{r}_n] \tag{43}$$

where

$$u = \alpha y(1 + 2y)/(1 + y) \tag{44}$$

$$\approx y(1 + 2y)/(1 + y) \tag{45}$$

for high molecular weight polymers. Equation (43) shows that the fraction of molecules formed by transfer, and hence the number of strong acid groups per molecule, is going to vary across the molecular weight distribution of the polymer. Curves of this function are given in reference 7. Under our assumptions, the number of strong acid groups per molecule is

$$\text{SAG/molec.} = 2 - f. \tag{46}$$

The number of strong acid groups per molecule is shown in Figure 4 as a function of $(n - 1)/\bar{r}_n$ for a variety of u values. The curves give the distribution of strong acid groups per molecule as a function of molecular weight for a number of different polymers. Note that the molecular weight distribution is becoming broader as the parameter u becomes larger.

The distribution equations are derived on the basis of a homogeneous polymerizing system in which both ionic and nonionic initiator fragments are assumed to be equally reactive. Adjustments can be easily made in the theoretical equations to include various initiator reactivities. The effects of heterogeneity are more difficult to include. It is known[6] that copolymerization in heterogeneous phases depends significantly upon the locus of polymerization: polymerization can occur either in solution or on the

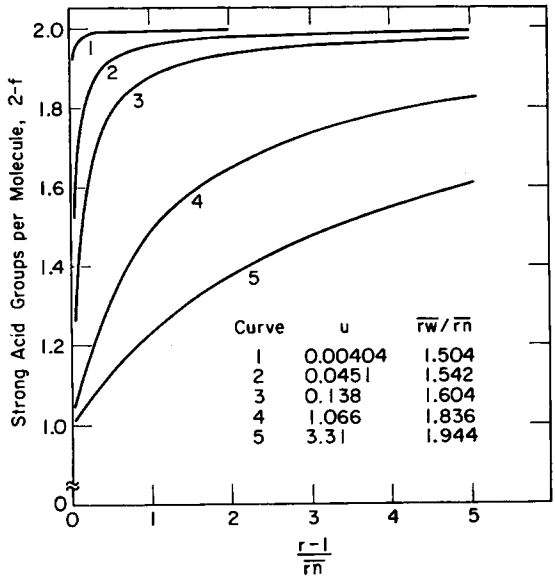

Fig. 4. The lines represent the distribution of strong acid groups per molecule within a single polymer as a function of molecular weight.

sorbed surface layer of monomers on the polymer particles. The effect of surface polymerization on molecular weight distributions have not been determined. A similar situation exists in the bulk polymerization of poly(vinyl chloride). Here, again, the polymer is insoluble in the monomer, and the molecular weight is independent of the catalyst concentration.[16] The theoretical equations derived here predict for a homogeneous system a shift in molecular weight distribution as the (act)/(cat) ratio is varied from low to high values. Such shifts were demonstrated in the semibatch polymers described elsewhere.[4] It would be interesting to have osmotic molecular weights for the polymers described here, as previous data did show a correlation with strong acid groups; but, unfortunately, this is not possible.

EXPERIMENTAL

Copolymers of acrylonitrile–co(vinyl acetate) (91:9 monomer feed) were prepared in a continuous-feed, stirred-tank reactor under the conditions described in the tables. The exit active liquors were short-stopped by cooling with ice. The reaction was allowed to proceed for 5 to 6 dwell times before equilibrium polymer was collected, washed, dried, and examined. Conversion was calculated from the measured rate of polymer production and the rate of monomer input. Specific viscosity measurements were made by the usual method with dimethylformamide as solvent at 25°C.

The polymers were prepared before suitable methods for measuring the strong acid group content became available, hence we must use the basic dye acceptance as a measure of the strong acid group concentration. A 1:1

relation does exist between the acid group content and the basic dyeability as defined in eq. (36) and demonstrated on more recently prepared polymers.[4] The basic dye acceptance method is described by Masson.[8]

Appendix

The kinetic equation for each species in a continuous-flow, stirred-tank reactor, assuming instantaneous mixing and equilibrium after 5 to 6 dwell times is independent of time, hence we write

$$d(R_1^*)/dt = k_p(M)(SO_4^{-*}) - k_p(R_1^*)(M) - k_{tr}(R_1^*)(HSO_4^-) - k_t(R_1^*)\sum_{s=1}^{\infty}(R_s^*) - k_t(R_1^*)\sum_{s=1}^{\infty}(Q_s^*) - (R_1^*)/\theta = 0 \quad (A1)$$

$$d(R_n^*)/dt = k_p(M)(R_{n-1}^*) - k_p(M)(R_n^*) - k_{tr}(R_n^*)(HSO_3^-) - k_t(R_n^*)\sum_{s=1}^{\infty}(R_s^*) - k_t(R_n^*)\sum_{s=1}^{\infty}(Q_s^*) - (R_n^*)/\theta = 0 \quad (A2)$$

$$d(Q_1^*)/dt = k_p(M)(HSO_3^*) - k_p(Q_1^*)(M) - k_{tr}(Q_1^*)(HSO_3^-) - k_t(Q_1^*)\sum_{s=1}^{\infty}(R_s^*) - k_t(Q_1^*)\sum_{s=1}^{\infty}(Q_s^*) - (Q_1^*)/\theta = 0 \quad (A3)$$

$$d(Q_n^*)/dt = k_p(M)(Q_{n-1}^*) - k_p(M)(Q_n^*) - k_{tr}(Q_n^*)(HSO_3^-) - k_t(Q_n^*)\sum_{s=1}^{\infty}(R_s^*) - k_t(Q_n^*)\sum_{s=1}^{\infty}(Q_s^*) - (Q_n^*)/\theta = 0 \quad (A4)$$

$$d(P_n)/dt = k_{tr}(R_n^*)(HSO_3^-) - (P_n)/\theta = 0 \quad (A5)$$

$$d(S_n)/dt = k_{tr}(Q_n^*)(HSO_3^-) - (S_n)/\theta = 0 \quad (A6)$$

$$d(T_n)/dt = {}^1/_2 k_t \sum_{s=1}^{n-1}(R_s^*)(R_{n-s}^*) - (T_n)/\theta = 0 \quad (A7)$$

(the factor $^1/_2$ is included so that each species will not be counted twice)

$$d(U_n)/dt = {}^1/_2 k_t \sum_{s=1}^{n-1}(Q_s^*)(Q_{n-s}^*) - (U_n)/\theta = 0 \quad (A8)$$

$$d(W_n)/dt = k_t \sum_{s=1}^{n-1}(R_s^*)(Q_{n-s})^* - (W_n)/\theta = 0 \quad (A9)$$

We define α as

$$\alpha = k_p(M)/[k_p(M) + k_{tr}(HSO_3^-) + k_t\{\Sigma(R_s^*) + \Sigma(Q_s^*)\} + 1/\theta], \quad (A10)$$

then solve eq. (A2) for (R_n^*):

$$(R_n^*) = \alpha(R_{n-1}^*). \quad (A11)$$

From eq. (A1),

$$(R_1^*) = \alpha(SO_4^{-*}); \tag{A12}$$

hence,

$$(R_n^*) = \alpha^n(SO_4^{-*}). \tag{A13}$$

Likewise,

$$(Q_n^*) = \alpha^n(HSO_3^*) \tag{A14}$$

$$(P_n) = \theta k_{tr}(HSO_3^-)(SO_4^{-*})\alpha^n \tag{A15}$$

$$(S_n) = \theta k_{tr}(HSO_3^-)(HSO_3^*)\alpha^n \tag{A16}$$

$$(T_n) = {}^1/_2\theta k_t(SO_4^{-*})^2\alpha^n(n - 1) \tag{A17}$$

$$(U_n) = {}^1/_2\theta k_t(HSO_3^*)^2\alpha^n(n - 1) \tag{A18}$$

$$(W_n) = \theta k_t(SO_4^{-*})(HSO_3^*)\alpha^n(n - 1) \tag{A19}$$

$$\sum_{n=1}^{\infty} (Q_n^*) = \alpha(HSO_3^*)/(1 - \alpha) \tag{A20}$$

$$\sum_{n=1}^{\infty} (R_n^*) = \alpha(SO_4^{-*})/(1 - \alpha). \tag{A21}$$

To find the values of (SO_4^{-*}) and (HSO_3^*), we write the equation for ferric ion:

$$d(Fe^{3+})/dt = -Fe^{(3+)}/\theta + k_1(Fe^{2+})(S_2O_8^{2-}) - k_2(Fe^{3+})(HSO_3^-) = 0. \tag{A22}$$

But, as discussed earlier, in the presence of excess (HSO_3^-) most of the iron will be in the ferrous state, hence the first term on the right-hand side of eq. (A22) is negligible relative to the other terms. This gives the initiation continuity equation

$$k_1(Fe^{2+})(S_2O_8^{2-}) = k_2(Fe^{3+})(HSO_3^-). \tag{A23}$$

The differential equations for initiator fragments are

$$d(SO_4^{-*})/dt = k_1(Fe^{2+})(S_2O_8^{2-}) - k_p(M)(SO_4^{-*}) - (SO_4^{-*})/\theta = 0 \tag{A24}$$

$$d(HSO_3^*)/dt = k_2(Fe^{3+})(HSO_3^-) + k_{tr}(HSO_3^-)[\Sigma(R_n^*) + \Sigma(Q_n^*)] - k_p(M)(HSO_3^*) - (HSO_3^*)/\theta = 0; \tag{A25}$$

hence,

$$(SO_4^{-*}) = k_1(Fe^{2+})(S_2O_8^{2-})/k_p(M) \tag{A26}$$

$$(HSO_3^*) = \frac{k_1(Fe^{2+})(S_2O_8^{2-})}{k_p(M)}\left[\frac{k_p(M) + k_{tr}(HSO_3^-)\alpha/(1 - \alpha)}{k_p(M) - k_{tr}(HSO_3^-)\alpha/(1 - \alpha)}\right]. \tag{A27}$$

In eqs. (A26) and (A27), the term $1/\theta$, ($\sim 3\times 10^{-4}$ sec^{-1}) is negligible when compared to k_pM ($\sim 1\times 10^{+5}$ sec^{-1}). Equation (20) can be obtained directly from eq. (A10).

The values of (HSO_3^-) and $(S_2O_8^{2-})$ given in eqs. (18) and (19) are the instantaneous values present in the reactor. To relate these values with those introduced into the reactor, we write

$$d(S_2O_8^{2-})/dt = -k_1(Fe^{2+})(S_2O_8) + (S_2O_8^{2-})_0/\theta - (S_2O_8^{2-})/\theta \tag{A28}$$

$$d(HSO_3^-)/dt = -k_2(Fe^{2+})(HSO_3^-) - k_{tr}(HSO_3^-)[\Sigma(R_n^*) + \Sigma(Q_n^*)] - (HSO_3^-)/\theta + (HSO_3^-)_0/\theta. \tag{A29}$$

Setting these equations to zero and using eq. (A23), we obtain

$$(S_2O_8^{2-}) = (S_2O_8^{2-})_0/(1 + k_1(Fe^{2+})\theta) \tag{A30}$$

$$(HSO_3^-) = \frac{(HSO_3^-)_0 - k_1(Fe^{2+})\theta(S_2O_8^{2-})_0/(1 + k_1(Fe^{2+})\theta)}{1 + \theta^{1/2}(k_{tr}/k_t^{1/2})[2k_1(Fe^{2+})\theta(S_2O_8^{2-})_0/(1 + k_1(Fe^{2+})\theta)]^{1/2}}. \tag{A31}$$

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