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### A Kinetic Study of Free-Radical Styrene-Acrylonitrile Copolymerization by Differential Scanning Calorimeter

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## A Kinetic Study of Free-Radical Styrene-Acrylonitrile Copolymerization by Differential Scanning Calorimeter

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### ABSTRACT

The isothermal free-radical copolymerization of styrene and acrylonitrile was examined in the temperature range of 333-373 °K. Initial rate studies of styrene homopolymerization were conducted and agreed favorably with values in the literature. Initial rate studies for acrylonitrile solution polymerization in DMF were also performed. Initiator decomposition rate constants measured in the presence of AN and styrene monomer are reported for AIBN, BP, and DTBP. Rate functions for the full spectrum of comonomer compositions initiated by AIBN and benzoyl peroxide are reported. Several copolymerization kinetic models were tested and found to be inadequate. Conversion histories were found to be consistent with observed initial rates and follow a simple pseudohomopolymerization kinetic model. Autoacceleration was observed and found to increase in severity with increased AN feed compositions and decreased reaction temperatures.

### INTRODUCTION

Investigations at our laboratories have been directed toward elucidating and solving problems associated with rapid, high temperature

polymerization. In particular, emphasis has been placed upon the phenomenon of thermal runaway and its effect upon properties of the polymer product [1-6]. In our most recent work the scope of study was extended beyond chain addition homopolymerization to include copolymerization as well [5]. To lay the groundwork for experimental studies of runaway [6], it was deemed necessary to determine kinetic constants for the styrene-acrylonitrile (SAN) comonomer pair. The initial rate and isothermal copolymerization studies performed in pursuit of this end are the subject of this article.

Attempts have been made to fit our data to several of the present kinetic models for homogeneous, free-radical copolymerization. However, direct application of homogeneous models to the SAN system, whose kinetic behavior may range from entirely homogeneous to entirely heterogeneous depending upon feed composition, may press such models beyond the limits of their intended use. Nevertheless, the raw rate data and reaction profiles warrant attention on their own merits. Even in the absence of a detailed kinetic model, it will be shown that with the aid of dimensional analysis, a great deal may be learned about reaction behavior.

An experimental technique which has come to the fore only recently was employed. The use of a differential scanning calorimeter (DSC) for the kinetic study of homopolymerization has been advanced by Horie [7] as well as other investigators [8, 9]. The DSC has been an especially useful tool when applied in studies of gel-effect (GE) type autoacceleration, although it has been used in studies of other systems including cross-linking reactions [10].

Kinetic studies performed in the DSC require small sample sizes ( $\sim 12 \mu\text{L}$ ) and strictly isothermal conditions may be reproducibly obtained. The single greatest advantage of this technique is that it gives a direct measure of instantaneous rate of reaction rather than conversion. Conversion histories are readily obtained from integration of the rate data. This process is inherently more accurate than evaluating rates from the slope of the conversion curve.

The DSC actually measures rate of heat generation, but for simple homopolymerization the reaction rate is directly proportional to this. Use of the DSC for copolymerization studies is less clearcut. Heat of reaction may vary with conversion, preventing simple reduction of calorimetric data to rate data. Horie has successfully applied the method to copolymerization, but he chose a system in which both comonomers had equal heats of reaction; thus heat of copolymerization was assumed constant and independent of composition [11]. However, as a result of our numerical simulation work, it was shown that complex copolymerization kinetics could be accurately approximated by a simple lumped kinetic form provided one of the comonomers is not totally consumed prior to the completion of reaction [5, 12]. The lumped form uses a heat of reaction that is dependent upon feed composition but does not vary with composition drift during the course of reaction. This will be discussed in greater detail in a subsequent section.

## EXPERIMENTAL

Styrene and acrylonitrile monomers were vacuum distilled at a temperature of 35°C and subsequently stored at 0°C. Both solid initiators azobisisobutyronitrile (AIBN) and benzoyl peroxide (BP) were twice recrystallized from chloroform with methanol. They were vacuum dried and stored at 0°C. Initiator di-tert-butyl peroxide (DTBP) and inhibitors p-benzoquinone (BZQ) and 2,2-diphenyl picrylhydrazyl (DPPH) were used without further purification.

Reaction samples were prepared by addition of 5 mL of monomer (homopolymerization), or comonomer mix (copolymerization) to tared amounts of initiator and inhibitor held at 0°C. For all runs, an initial initiator concentration of 0.10 mol/L was used, while feed inhibitor concentration was fixed at 0.01 mol/L. After agitation the solution was frozen. For pure styrene and for comonomer mixtures containing as low as 40% styrene, Dry Ice in acetone was used to freeze the solutions. For pure AN and for mixtures of less than 40% styrene content, liquid nitrogen was required.

Thawing under tap water degassed the solution which was subsequently placed in ice water. Samples of 12  $\mu$ L were withdrawn from the stock solution and placed into standard Perkin-Elmer sealable volatile sample pans (#219-0041). The pans were sealed and the sample frozen until used. Fresh stock solution was prepared just prior to each set of experimental runs; thus samples were never more than 12-h old when used.

Time was measured from the instant the frozen sample pan was placed in the DSC. The chart recorder drive was activated 30 s after placement of the sample, and time was subsequently measured by the recorder. Addition of the inhibitor caused an induction period to precede the onset of reaction. The end of the induction period was defined as the value along the time axis determined by the intersection of the initial baseline with the tangent line drawn to the rising initial rate peak, as illustrated in Fig. 1. The initial heat generation rate was taken as the distance along the rate axis between the baseline and the intersection of the aforementioned tangent with a tangent line drawn to the downward sloping portion of the exotherm. Distance between the exotherm and baseline was taken as the instantaneous heat generation rate, and reactions were considered complete when the exotherm had fallen to the initial baseline and remained level.

## INITIATOR KINETICS

Kinetic models for copolymerization are generally formulated in terms of the kinetic constants for homopolymerization of the comonomers. Reactions involving a monomer and a radical with that monomer in the active site, or two radicals with the same monomer unit in the active site, are assumed to proceed at the same rate as a

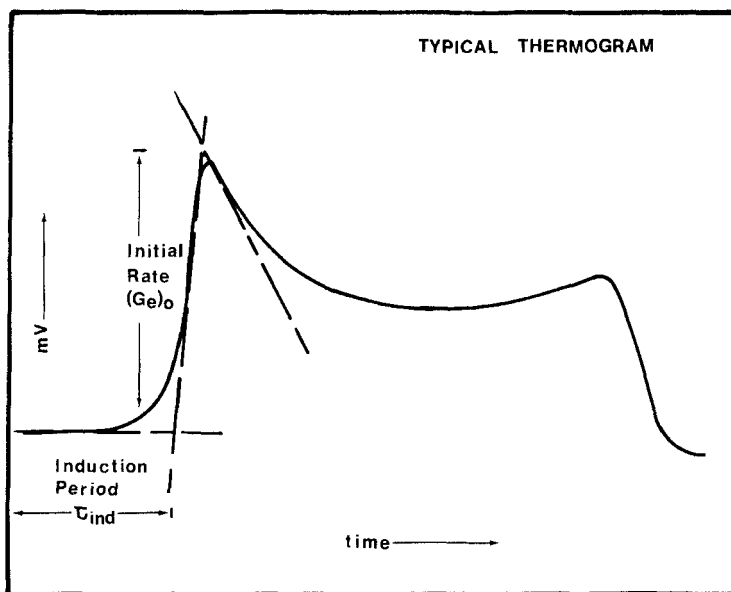


FIG. 1. Typical DSC thermogram.

similar homopolymerization reaction. Cross-reaction rate constants are often taken as some function of the homopolymerization constants for that reaction. Furthermore, interpretation of experimental rate data demands a knowledge of initiation kinetics. Thus, before embarking upon a study of SAN kinetics, it was important to verify rate constants for the homopolymerization of styrene as well as acrylonitrile. While the literature contains an abundance of values for initiator dissociation rates in various solvents [13], data for decomposition rates measured in monomers is scarce. It was our desire to determine which literature correlation best fit our experimental data for the decomposition rates of AIBN, BP, and DTBP.

Early DSC investigators abandoned the use of chemical inhibitors to establish an initial baseline when it was found that extrapolation of the final baseline coincided with the initial baseline. Since they were interested in entire reaction histories and the final baseline was always achieved, the initial baseline was superfluous. Our purposes were different, and it was chosen to use inhibitors for two reasons. First, for the many runs where only initial rates were desired, complete reaction profiles were unnecessary and their elimination saved a considerable amount of time. Second, and perhaps more importantly, the length of the induction period caused by the addition of inhibitor provided a means of calculating the in-situ initiator decay rate.

If it is assumed that one inhibitor radical consumes one initiator fragment radical, then it can be shown that the initiator decomposition rate constant,  $k_d$ , and induction period,  $\tau$ , are related by

$$k_d = \frac{1}{\tau_{\text{ind}}} \ln \left( 1 - \frac{[z]_0}{2f[I]_0} \right) \quad (1)$$

This assumption has been shown to be valid for p-benzoquinone (BZQ) in styrene provided there is no significant thermal initiation [14]. Thus induction period data for this pair may only be considered reliable for temperatures below 100°C. BZQ is not, however, an effective inhibitor of AN polymerization [15]. The stable free radical 2,2-diphenyl picrylhydrazyl (DPPH) is a powerful inhibitor for the polymerization of either monomer, but its inhibitory action is very sensitive to the presence of dissolved oxygen [16]. This was found to be a great problem in styrene polymerization, where DPPH acted more like a powerful retarder than an inhibitor. Thus initiator decay rates in styrene above 100°C were not measured. When used in AN, however, the DPPH was effective, and gave results for any given initiator that were in accord with the lower temperature BZQ/styrene results. Initiation rates of AIBN and BP were measured in both monomers. For the temperature range in which DTBP was used, thermal initiation of styrene was significant, and data were taken in AN only.

Figure 2 shows our experimental results for AIBN. Included for reference are the relationships of Tobolsky [17] and Onyon [18]. It should be noted that in our calculations of  $k_d$  from Eq. (1), a constant initiator efficiency of 0.60 was assumed for AIBN. An efficiency of unity was assumed for BP and DTBP. Initiator AIBN has been studied by many investigators [13] and all of their results lie quite close to the relations in Fig. 2. In this work the rate constant of Onyon [18],  $k_d = 2.67 \times 10^{15} \exp(-31,100/RT)$ , was chosen as that closest to our data.

Similar results were obtained for BP and DTBP. It should be noted that our decomposition data for BP produces a much higher rate than the function used in much of our earlier computational studies,  $k_d = 10^{13} \exp(-30,000/RT)$ . They do, however, agree quite well with rate constants proposed by Tobolsky [19], and thus we adopt his function,  $k_d = 6.378 \times 10^{13} \exp(-29,700/RT)$ . Results for DTBP were compared to those of other investigators [13, 20, 21], and the result,  $k_d = 2.8 \times 10^{14} \exp(-35,000/RT)$  [21] was found to agree most closely with our data. It is important to note that these are "in-situ" measurements of initiator decomposition rate, that is,  $k_d$  is measured in the reaction environment. Variation of  $k_d$  for each of the three initiators

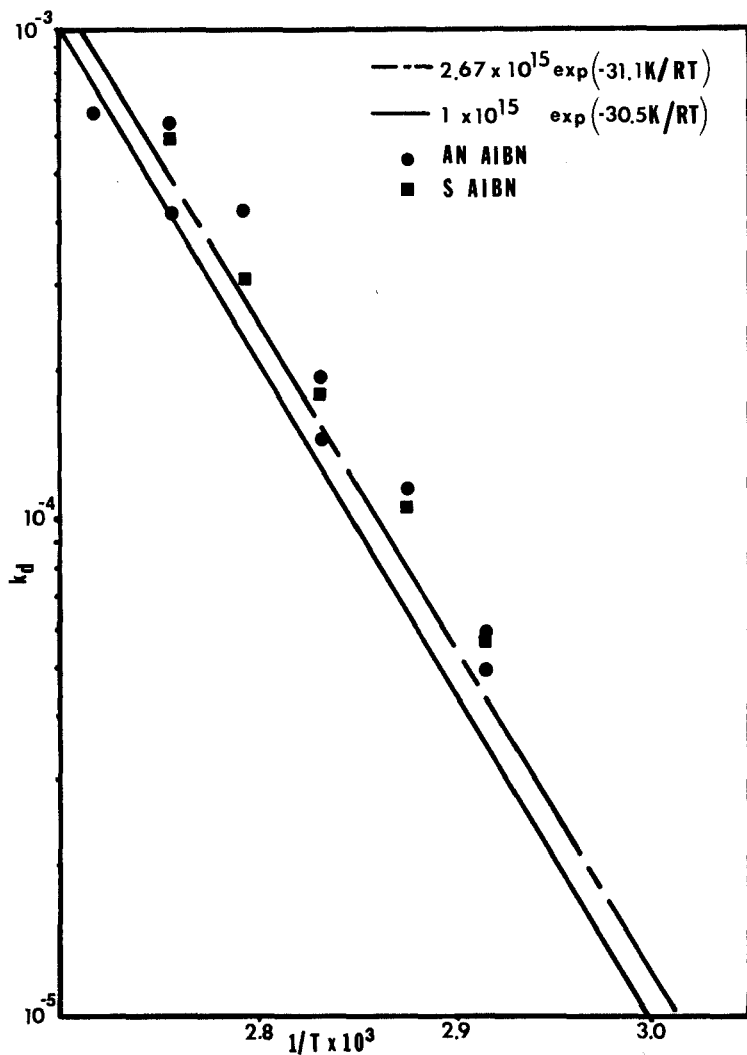


FIG. 2. Initiator decomposition rate, AIBN.

was not observed with change from styrene to AN as monomer, nor was any trend seen with compositional changes in comonomer blends. However, rate of initiator decomposition and rate of initiation need not be the same. It is generally assumed that radical attack on the monomer proceeds so much faster than initiator decay that rate of initiation is directly proportional to that decay rate.

## HOMOPOLYMERIZATION KINETICS

The conversion of styrene to polystyrene is perhaps the most thoroughly documented vinyl polymerization. Data for rate constants are readily available and the results of numerous independent investigations appear to be in accord. The copious data provides a standard against which our experimental methods can be checked before proceeding with measurements of new systems.

An initial rate study of styrene homopolymerization was undertaken. The initiators AIBN, BP, and DTBP were used to span the temperature range 343-433 K. A value of  $-\Delta H = 16.7$  kcal was used to convert DSC data to polymerization rates. Initiator conversion was calculated assuming a first-order decay, while monomer conversion was calculated from the integral of the rate curve. Dividing out the concentration dependence of the rate leaves the lumped overall rate constant for polymerization  $k_{ap} \equiv k_p (fk_d/k_t)^{1/2}$ . Using the value of  $fk_d$  computed from the expression chosen on the basis of our inhibition studies, the ratio  $k_p/k_t^{1/2}$  was extracted. This ratio is a property of the monomer only, and thus its functional dependence upon temperature should be uniform in spite of the fact that different initiators were used to span the spectrum of reaction temperatures.

Figure 3 is a graph of our data for  $k_p/k_t^{1/2}$  presented together with the literature relationships of Matheson [22], Tobolsky [23], and O'Driscoll [24]. Quite clearly the agreement is excellent. Our data yield the same activation energy as these relationships and, although Matheson's function appears to fall most closely to our data, all three lie within the limits of experimental error. It is remarkable that the data track these relationships well beyond the temperature range from which they were measured. There is generally uncertainty associated with extrapolating kinetic data far beyond the limits of their measurement. Even a small variation in activation energy can result in significant error in the calculated rate if temperature changes of the order  $100^\circ$  are considered. Nonetheless, our data extend  $70^\circ$  higher than those used to generate the relationships which match with undetectable error.

In contrast to the ready availability of styrene kinetic constants, data for AN kinetics are scarce and contradictory. Bulk homopolymerization of AN is heterogeneous, and there is no generally accepted kinetic model. One must question the meaning of single propagation and termination constants for what may be a two-phase reaction. Furthermore, it is not evident a priori as to what type of AN constants belong in a SAN copolymerization model. The SAN system is homogeneous for AN contents less than 35 mol %. Above this limit precipitation occurs, although not necessarily from the outset of reaction. It is reasonable to expect that reaction rates in solvent and nonsolvent systems will be different. Indeed, reported values for bulk AN differ



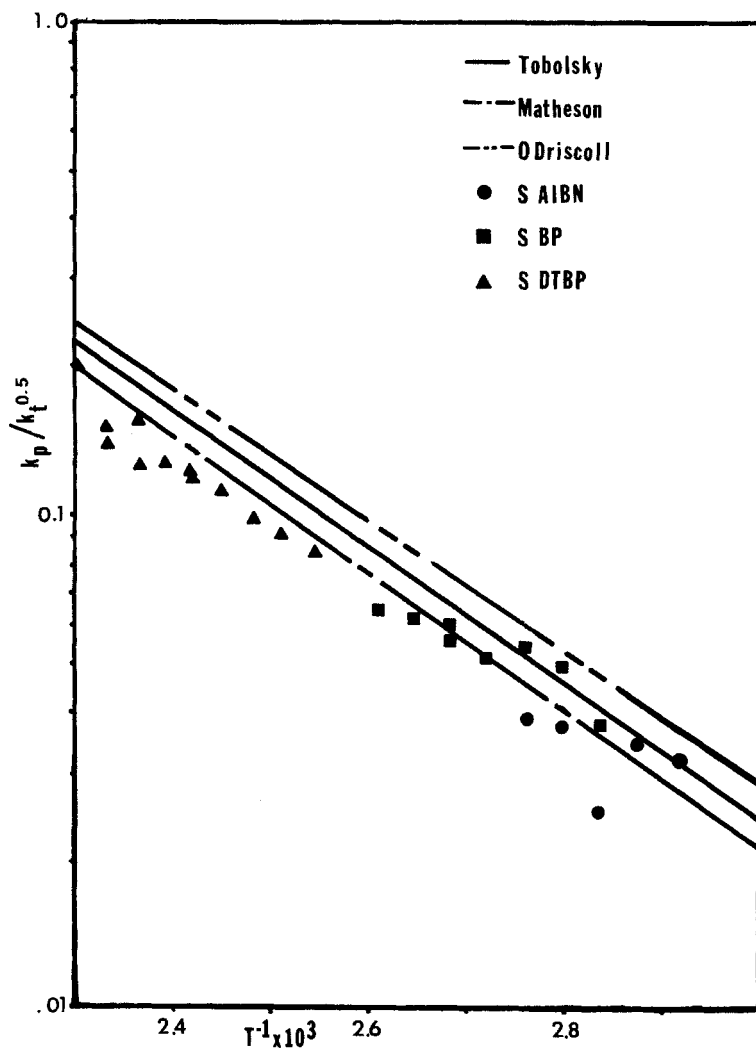


FIG. 3. Ratio of monomer rate constants for styrene.

appreciably from those for homogeneous solution polymerization. Whether either type of constant belongs in a SAN kinetic model is a question that remains to be answered.

Bulk AN homopolymerization were conducted, but under the conditions used, the initial rates could not be identified. Precipitous auto-acceleration was sufficiently severe to obscure the transition from induction period to onset of reaction and then subsequent reaction.

While the bulk reaction is precipitous from the start, it will be shown later that copolymerizations with AN composition of as much as 90% do not accelerate immediately. It is not unreasonable to speculate that at low conversions, SAN may remain homogeneous. Initial rates should then obey the usual homogeneous free-radical kinetics, and thus homogeneous AN constants would seem to be the proper choice for the SAN model.

Measurement of homogeneous AN constants proved to be a great deal easier than the bulk experiments. It has been established that the solution polymerization of AN in dimethylformamide (DMF) remains homogeneous provided monomer concentration does not exceed 5 M [25]. Kinetic constants for the AN/AIBN/DMF system have been reported by several investigators. Most data reported are confined to a single temperature of 333 K. The values for the ratio  $k_p/k_t^{1/2}$  were in close agreement; however, there was no consensus on the value for an activation energy, with estimates ranging between 5000 [26] and 7600 [27] cal. Therefore, AIBN-initiated AN solution polymerizations were conducted as part of our study. Temperatures ranging from 333 to 383 K were considered, and a single monomer concentration of 2.5 M, insuring homogeneity, was used. For simple homogeneous free-radical kinetics, the rate of monomer decay can be expressed as

$$-\frac{d[m]}{dt} = R_p \quad k_{ap}[m_0]^{1/2} [m] \tag{2}$$

If concentrations are made dimensionless by their initial values, Eq. (2) becomes

$$-\frac{dm}{dt} = k_{ap} \left[ m_0 \right]_0^{1/2} m_0^{1/2} m \tag{3}$$

With only the dimensions of reciprocal time remaining, the quantity  $(k_{ap}[m_0]_0^{1/2})^{-1}$  suggests itself as the most logical choice to make time dimensionless. Indeed, this term is a characteristic time for monomer decay formerly defined as follows [1]:

$$\lambda_m = \left( [m]_0 / \left( R_p \right)_0 \right) = k_{ap}[m_0]_0^{1/2} \quad^{-1} \tag{4}$$

If initiator consumption is assumed to be small, the reaction proceeds via pseudofirst-order kinetics. Making time dimensionless by  $\lambda_m$  ( $\tau \equiv t/\lambda_m$ ), conversion will obey

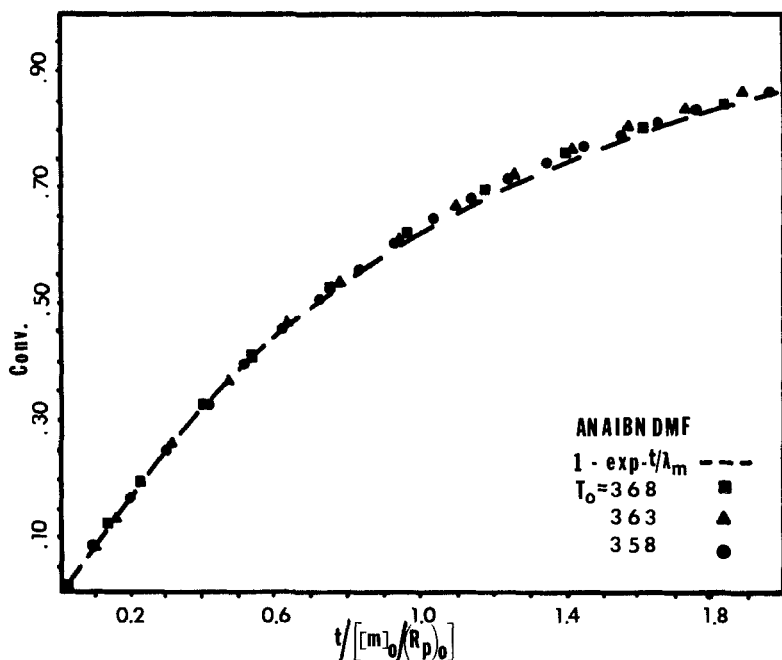


FIG. 4. Dimensionless conversion histories for solution AN polymerization.

$$\Phi = 1 - \exp(-\tau) \quad (5)$$

Using experimental values for  $(R_p)_0$  and  $[m]_0 = 2.5$ ,  $\lambda_m$  can be evaluated for each run. The results, which are shown in Fig. 4, are truly remarkable. Not only does the dimensionless form unite all conversion histories to a single profile, but the experimental data also coincide with the trend predicted by the simple relation of Eq. (5). Solution polymerization of AN proceeds in a manner consistent with the predictions of homogeneous kinetics, and a measurement of the initial rate is sufficient to estimate the entire conversion-time curve.

A least-square fit of the collected initial rate data gave rise to the following relationship:

$$(R_p)_0 = 5.561 \times 10^9 \exp(-19,842/RT) \quad (6)$$

which with knowledge of initiation kinetics can be reduced to give

$$k_p/k_t^{1/2} = (R_p)_0 / (R_i)_0^{1/2} [m]_0 = 20.44 \exp(-4292/RT) \quad (7)$$

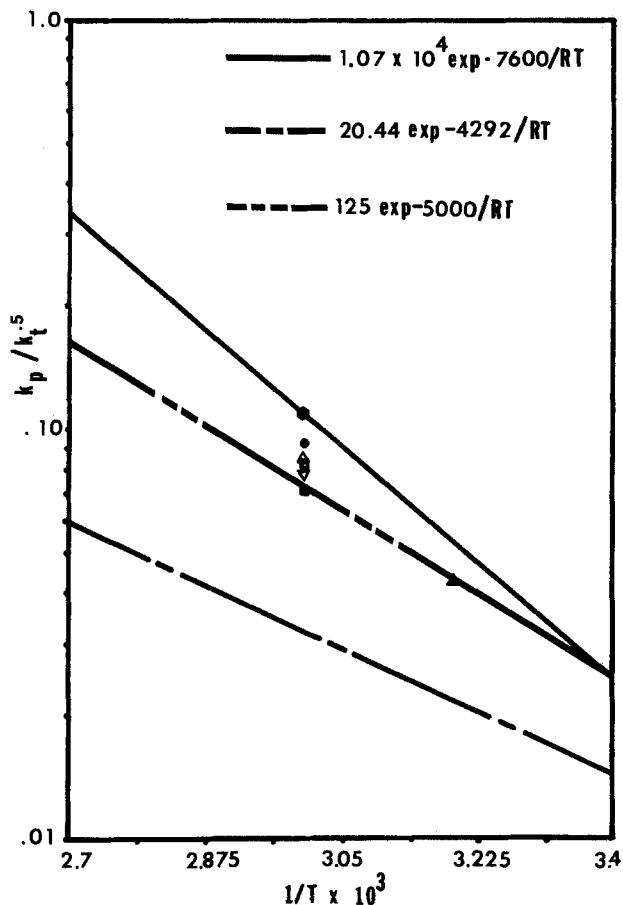


FIG. 5. Ratio of monomer constants for solution AN polymerization.

It should be noted that the dominant term in the experimentally determined activation energy of Eq. (6) is attributable to the initiation step. When the activation energy of initiation is subtracted out, all experimental error is reflected in the activation energy of Eq. (7). Thus 5% variation in the activation energy of Eq. (6) (about 1 kcal) would appear as a 25% error in Eq. (7). In Fig. 5 we present our rate function (Eq. 7) along with rate data from other investigators [25-31] and two suggested rate functions [26, 27]. While the agreement is not as impressive as the styrene results, the variation in  $(R_p)_0$  among the three functions is not very large. Since our data were taken in the temperature range and under the conditions of our experimentation, Eq. (7) was chosen.

## COPOLYMERIZATION KINETICS

The reduction of DSC data to kinetic rate data requires the expression of the heat generation rate as the product of separate functions for heat of reaction and reaction rate:

$$G_e \equiv -\Delta H R \quad (8)$$

It is generally agreed that heat of copolymerization can be attributed solely to the heats of the two homopropagation and the two cross-propagation reactions (32). Thus, for copolymerization:

$$G_e = -\Delta H_{11} R_{p11} - \Delta H_{12} R_{p12} - \Delta H_{21} R_{p21} - \Delta H_{22} R_{p22} \quad (9)$$

The rate of reaction is the sum of the same four propagation rates, provided the long-chain approximation is made, thus:

$$-\frac{d[m]}{dt} \equiv R = R_{p11} + R_{p12} + R_{p21} + R_{p22} \quad (10)$$

Clearly, the RHS of Eq. (10) is not factorable from the RHS of Eq. (9), the heat generation rate, with the exception of the rare case where all  $\Delta H$ 's are equal. Although Eq. (9) cannot be expressed in the form of Eq. (8), it is possible to define a composite heat of copolymerization,  $\Delta H_c$ , that will make this possible. Two alternative expressions are available. Alfrey has developed an expression for  $\Delta H_c$  as a function of the four propagation heats of reaction, instantaneous copolymer composition, and reactivity ratios [32].

$$\Delta H_c = \frac{1 - [1 - 4y_1y_2(1 - r_1r_2)]^{1/2}}{2(1 - r_1r_2)} (\Delta H_{21} + \Delta H_{12} - \Delta H_{11} - \Delta H_{22}) + y_1\Delta H_{11} + y_2\Delta H_{22} \quad (11)$$

In other work we have demonstrated that for a variety of systems, complex copolymerization kinetics may be approximated by a lumped form similar to the kinetic form for homopolymerization [5, 12]. This gives rise to a composite  $\Delta H_c$  and a single pseudorate constant such that generation rate may be expressed as

$$G_e = - \Delta H_c k_{ap} [m_0]^{1/2} [m] \quad (12)$$

where

$$[m] = [m_1] + [m_2] \quad (13)$$

and

$$\Delta H_c = \frac{(r_1)_0 (x_1)_0^2 \Delta H_{11} + (x_1)_0 (x_2)_0 (\Delta H_{12} + \Delta H_{21}) + (r_2)_0 (x_2)_0^2 \Delta H_{22}}{(r_1)_0 (x_1)_0^2 + 2(x_1)_0 (x_2)_0 + (r_2)_0 (x_2)_0^2} \quad (14)$$

The expression for  $k_{ap}$  depends upon the particular kinetic mechanism; however, it must conform to

$$k_{ap} = - \frac{d[m]}{dt} / [m_0]_0^{1/2} [m]_0 \quad (15)$$

In fact, substitution of the copolymer composition equation in Alfrey's expression, Eq. (11), yields our result (Eq. 14) when evaluated at feed conditions. However, our format provides a means for evaluating conversion histories from DSC data. It would seem that assumption of a constant  $\Delta H$  would be highly restrictive. The simplified homopolymerization form tracks total monomer conversion only, neglecting compositional changes. Similarly a lumped  $\Delta H$  ignores the drift of  $\Delta H_c$  with compositional changes. Nonetheless, the ability of the approximate form to track numerical integration of exact kinetics has been demonstrated for both isothermal conversion and nonisothermal temperature histories [5].

Alfrey's expression predicts the instantaneous value of  $\Delta H_c$  while the substitution of initial values of  $x_1$ ,  $x_2$ ,  $r_1$ , and  $r_2$  limit us to a constant value of  $\Delta H_c$ . However, on the basis of computer-simulated reaction histories, it was concluded that results obtained from the approximate kinetics, Eq. (14), match those of the exact kinetics provided one comonomer is not exhausted before the completion of reaction [5, 12]. Since the DSC does not permit in situ evaluation of composition, our approximation provides a valuable tool for examining complete copolymerization reaction profiles. It is of the desired form shown in Eq. (8), and determination of copolymerization conversion histories may be conducted with the same techniques applied to

homopolymerization. The utility of the DSC is thus extended beyond the ideal system considered by Horie.

### Initial Rate Study

Bulk copolymerizations of SAN initiated by AIBN and BP were conducted which spanned the full range of initial comonomer compositions. Solution copolymerizations in DMF were also conducted for high AN content copolymers. Initial temperatures lay between 343 and 373 K. In contrast to the problems encountered during bulk polymerization of AN, initial rate peaks were discernible for bulk copolymerizations at all levels of composition, including 90% AN. While most runs were stopped after an initial peak had been established, a number of reactions were allowed to proceed to completion. The results of these will be discussed in a subsequent section of this work.

Arrhenius plots of  $\log (R_p)_0$  versus  $1/T$  were linear in all cases.

Bulk AIBN-initiated reactions showed a slightly steeper slope (higher activation energy) than bulk BP-initiated ones. This is consistent with the fact that the activation energy for AIBN decomposition is roughly 1500 cal greater than that for BP. A sample plot for the composition of 60% SAN is shown in Fig. 6. The solid lines are best fit determined by a least-squares analysis. Rates of solution polymerization were significantly lower than their bulk counterparts owing to reduced monomer concentrations (2.5 M for solution as compared to 9-15 M for bulk). Initial rate functions can be reduced via Eq. (17) to expressions for the lumped pseudohomopolymerization rate constant  $k_{ap}$ .

Table 1 lists the functions for  $k_{ap}$  determined for each experimental case studied. Note the general trend of increasing activation energy with increasing styrene content, although the two AIBN bulk copolymerizations with highest AN content do deviate from this trend. Solution copolymerizations show significantly higher activation energies than reactions in bulk. This is evident in both the functions of Table 1 and the plot in Fig. 6, and is somewhat surprising. For AN homopolymerization quite the opposite is true [28]. Here the higher activation energy is attributed to the precipitous nature of the bulk reaction, and lumped activation energies of 37 kcal have been reported [30]. However, bulk AN polymerization is clearly heterogeneous from the outset, while this has not been established for bulk copolymerizations. Reaction profiles to be presented later suggest a delayed onset of heterogeneity. The contrasting activation energies for bulk and solution reactions may reflect the chemical difference between reacting in a strongly polar medium (DMF) and a nonpolar one (SAN comonomer mix).

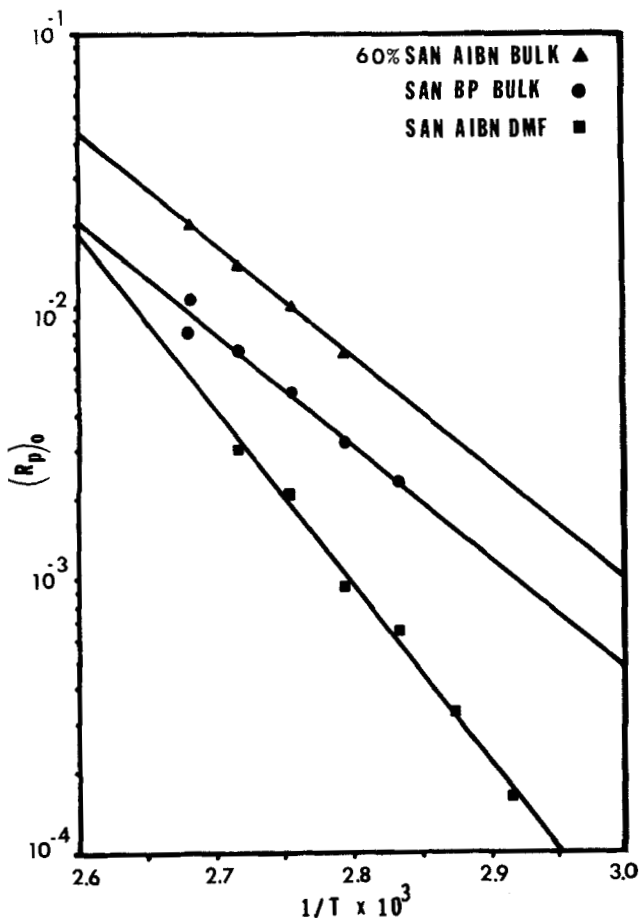


FIG. 6. Initial rate for 60% SAN copolymerization.

Kinetic Models

Several termination models for free-radical copolymerization have been reported in the literature. Perhaps the oldest is the geometric mean (GM) model [14]. The cross-termination reaction rate constant is assumed to be the geometric mean of the two homotermination rate constants. Very few systems have been found to obey this model, with the exception of styrene-methylstyrene. Of more widespread use is the phi factor (PF) model [33]. The termination rate constant for radicals with unlike monomers in the termination active site is



TABLE 1. Lumped Rate Constant—Experimentally Determined

$(x_1)_0$	$(k_{ap})_0$		
	SAN/BP	SAN/AIBN	SAN AIBN/DMF
0.1	$1.37 \times 10^6$ exp (-15,237/RT)	-	$7.32 \times 10^{10}$ exp (-22,513/RT)
0.2	$4.57 \times 10^8$ exp (-19,344/RT)	$8.69 \times 10^{12}$ exp (-25,976/RT)	$4.2 \times 10^{10}$ exp (-22,081/RT)
0.3	$5.15 \times 10^7$ exp (-17,739/RT)	-	$2.32 \times 10^{11}$ exp (-23,369/RT)
0.4	$8.5 \times 10^8$ exp (-19,718/RT)	$1.34 \times 10^{11}$ exp (-22,902/RT)	$1.59 \times 10^{12}$ exp (-24,775/RT)
0.5	$6.65 \times 10^6$ exp (-16,309/RT)	-	-
0.6	$1.91 \times 10^8$ exp (-18,727/RT)	$4.17 \times 10^8$ exp (-18,756/RT)	$7.7 \times 10^{14}$ exp (-29,337/RT)
0.7	$3.93 \times 10^8$ exp (-19,365/RT)	$1.48 \times 10^8$ exp (-18,120/RT)	-
0.8	$5.79 \times 10^8$ exp (-19,677/RT)	$9.55 \times 10^9$ exp (-21,292/RT)	-
0.9	$8.0 \times 10^8$ exp (-20,029/RT)	$1.83 \times 10^{10}$ exp (-21,748/RT)	-

assumed to be proportional to the geometric mean of the rate constants, and  $\phi$  is the constant of proportionality. Rate constants for the homotermination reactions are assumed to be identical to those of the respective homopolymerization reactions. The GM model is actually a special case of the PF model, where  $\phi$  is 1. The expression for the rate of polymerization according to the PF model is

$$R_p = \frac{(r_1 x_1^2 + 2x_1 x_2 + r_2 x_2^2) R_i^{1/2} [m]}{(r_1 x_1 \delta_1)^2 + 2\phi r_1 x_1 \delta_1 r_2 x_2 \delta_2 + (r_2 x_2 \delta_2)^2}^{1/2} \quad (16)$$

where  $\delta_1$  and  $\delta_2$  are the reciprocal of the ratio of monomer rate constants  $k_p/\sqrt{k_t}$ , which were determined for styrene and AN in the first part of this study. The model contains only one constant,  $\phi$ , that might account for copolymerization behavior different from that of homopolymerization.

There are systems which have been reported to obey Eq. (16), with a single value of  $\phi$  adequately describing the rate for all compositions. Styrene methyl methacrylate (S/MMA) is one such system [33]. Others, SAN included, show a marked dependence upon composition [34]. The temperature dependence of  $\phi$  is not considered, but this of course would imply a wholly separate termination constant  $k_{12}$ , with no utility in maintaining the  $\phi$ -factor nomenclature.

With independent means of calculating the rate of initiation, measurement of the initial rate makes possible the determination of  $\phi$ . By solving Eq. (16) for  $\phi$ , it is found that

$$\phi = \frac{\{[r_1(x_1)_0^2 + 2(x_1)_0(x_2)_0 + r_2(x_2)_0^2](R_1)_0^{1/2} [m]_0 / (R_p)_0\}^2 - [(r_1 \delta_1 x_1)_0]^2 - [(r_2 \delta_2 x_2)_0]^2}{[2(r_1 \delta_1 x_1)_0 (r_2 \delta_2 x_2)_0]} \quad (17)$$

A single experiment uniquely specifies a value for  $\phi$ .

A second more recent and more complex termination scheme is the penultimate effect (PE) model [35]. It has been successfully used to reproduce initial rate data for the system S/MMA for a broad range of compositions, and at several different temperatures [36]. It should be noted that S/MMA is one of the few systems that has been adequately represented by  $\phi$ -factor kinetics. The rate of polymerization according to the PE scheme is expressed as shown in Eq. (18). The constants  $\delta_{21}$  and  $\delta_{12}$  refer to the termination of two-like radicals with unlike monomers in the ultimate and penultimate position. This is a two-parameter model, unlike PF kinetics where a single experiment uniquely specified the copolymerization parameter.

$$R_p = \frac{(r_1 x_1^2 + 2x_1 x_2 + r_2 x_2^2) R_i^{1/2} [m]}{r_1 x_1 \left[ \frac{r_1 \delta_{11} x_1 + \delta_{21} x_2}{r_1 x_1 + x_2} \right] + r_2 x_2 \left[ \frac{r_2 \delta_{22} x_2 + \delta_{12} x_1}{r_2 x_2 + x_1} \right]} \quad (18)$$

To calculate values for  $\delta_{12}$  and  $\delta_{21}$ , initial rate data from reactions spanning the full range of compositions at a fixed temperature are necessary. These are used to evaluate constants  $C_1$  and  $C_2$ , and a least-squares fit generates the value for  $\delta_{12}$  and  $\delta_{21}$  at that temperature [36]. Employing a series of initial temperatures, the functional dependence of  $\delta_{ij}$  on  $T$  can be determined. Experiments with S/MMA showed, as might be expected, that this is an Arrhenius-type relationship, and therefore activation energies may be evaluated.

When applying either the PF or PE models to our SAN data, the values for  $(R_p)_0$  substituted into Eqs. (17) or (18) were calculated from the functions in Table 1. Changes in initial rate with composition were slight over most of the range of compositions, often on the order of experimental error. To help reduce the introduction of noise from the data, the rate determined from the line of best fit was used rather than the actual datum point. The functions were not used to generate rates beyond the temperature range of experimentation, and as previous Figures have illustrated, scatter in the data about the line of best fit is small. Thus it is our contention that no undue bias is introduced by this method. Indeed, it will be shown that these models are extremely sensitive to the kinetic constants, and small changes in the experimental data are of secondary importance.

Neither kinetic model proved satisfactory in reproducing our SAN copolymerization rate data. Particularly poor was the agreement with PF kinetics. For the three modes (bulk AIBN, bulk BP, solution AIBN), the rates for copolymers of 60% styrene composition and higher gave negative values for  $\phi$ . For lesser styrene content,  $\phi$  showed random variation between 1 and 20 with the comonomer composition.

Negative values of  $\phi$  may arise through Eq. (17) primarily by two means. If the experimental rate observed is too large, then the first term of the numerator on the RHS of Eq. (17) will be too small and the second two terms may dominate. Also, if the true rate of termination is smaller than can be expressed by this model, the denominator on the RHS of Eq. (16) will be too large. Carried to Eq. (17), the second and third terms of the numerator may be too large. If the homotermination rates proceed at a different rate in the comonomer mixture than in their respective monomer solutions, phi-factor analysis based upon homopolymerization constants must fail.

Consider the copolymerization of 70% SAN/AIBN conducted at 363 K. Substitution of kinetic constants into Eq. (17) would show

$$\phi = \frac{5.91 \times 10^{-3}}{(R_p)_0^2} - 53.81 - 0.02$$


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$$2.376$$
(19)

The rate must be less than  $1.05 \times 10^{-2}$  in order that  $\phi$  will be greater than zero, but the experimentally measured rate was  $1.13 \times 10^{-2}$ . The second term in the numerator seems to be dominant, and it contains the kinetic constants for styrene homopolymerization. For most comonomer compositions the major component entering the copolymer is styrene. Even when the styrene comonomer composition is as low as 10%, the product contains nearly 50% styrene. It is not surprising that styrene associated terms dominate the kinetics; the product  $r_1(x_1)_0$  may be as much as 200 times the value of  $r_2(x_2)_0$  (90% SAN), and even at 10% SAN it is three times as great. Although the greatest uncertainty surrounds our AN kinetic constants, it is the well-established styrene constants that are most influential in determining the copolymerization termination parameters. The failure of PF kinetics to describe even the totally homogeneous SAN copolymerizations of 70% and higher styrene composition suggests that perhaps bulk styrene homopolymerization constants cannot be used for copolymerization. The presence of AN in the reaction media may sufficiently influence the rate of styrene-styrene reactions that homopolymerization constants are inadequate to describe them.

The penultimate effect model was unable to rectify the problems encountered with the phi-factor model. It of course presumes that the data will form a linear relationship and that the parameters  $\delta_{12}$  and  $\delta_{21}$  evaluated will be positive. This was not always found to be the case, and again the high styrene content vs comonomer compositions proved to be the most troublesome. For bulk BP-initiated copolymerizations, the rate calculated from Eq. (18) using  $\delta_{12}$  and  $\delta_{21}$  values generated from the full range of compositions showed a sharp deviation from the experimental rates for 80 and 90% SAN. Similarly, for AIBN-initiated reactions, the predicted and observed rates for 90% SAN did not coincide. It may seem somewhat arbitrary, but it was found that if these data points were eliminated from the calculation of  $\delta_{12}$  and  $\delta_{21}$ , the resulting values produced rates that not only correlated better to the remaining data, but also satisfactorily matched the unused data. In Figs. 7 and 8 we show the data and predicted rates for BP and AIBN initiation, respectively. The solution polymerization results are shown in Fig. 9. Note that the sharp transition in rate between pure AN and 10% SAN is not unlike the sharp rise in the copolymer composition curve between these same two compositions.

While it is not expected that initiator choice should in any way influence the value of the parameters, the bulk BP and AIBN results clearly do not coincide. It has been reported that the rate of initiation

TABLE 2. Penultimate Effect Model Termination Parameters

T (°K)	SAN/AIBN		SAN/BP		SAN/AIBN/DMF	
	$\delta_{12}$	$\delta_{21}$	$\delta_{12}$	$\delta_{21}$	$\delta_{12}$	$\delta_{21}$
373	44.9	12.8	70.0	15.1	41.4	13.3
368	70.9	12.0	66.1	16.4	36.1	18.1
363	99.3	11.1	62.0	17.0	29.0	24.4
358	131.8	9.7	59.0	19.0	19.6	33.0
353	169.0	7.6	56.0	21.0	6.94	44.6
348	212	4.6	53.0	21.0	-	-
	$\delta_{12} = 3.42 \times 10^{-8} \exp(+5652/RT)$		$\delta_{12} = 3.24 \times 10^3 \exp(-2848/RT)$			
	$\delta_{21} = 8.46 \times 10^6 \exp(-9836/RT)$		$\delta_{21} = 5.92 \times 10^{-2} \exp(4100/RT)$			

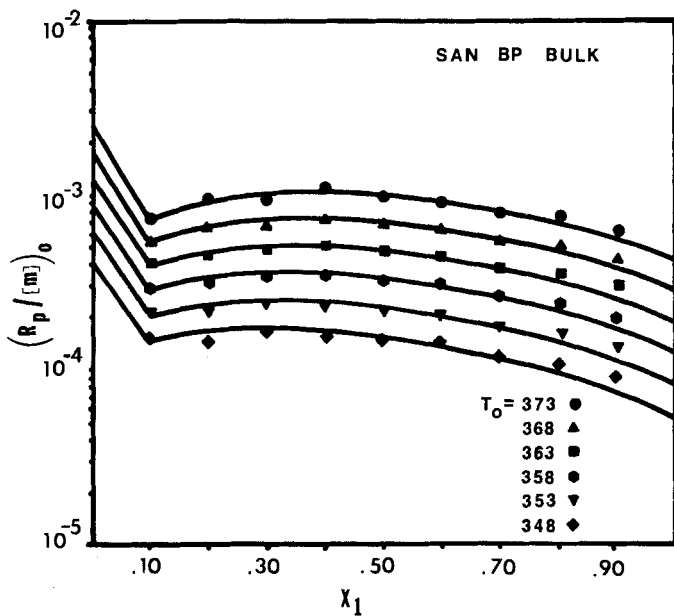


FIG. 7. PE model predicted rates, SAN/BP.

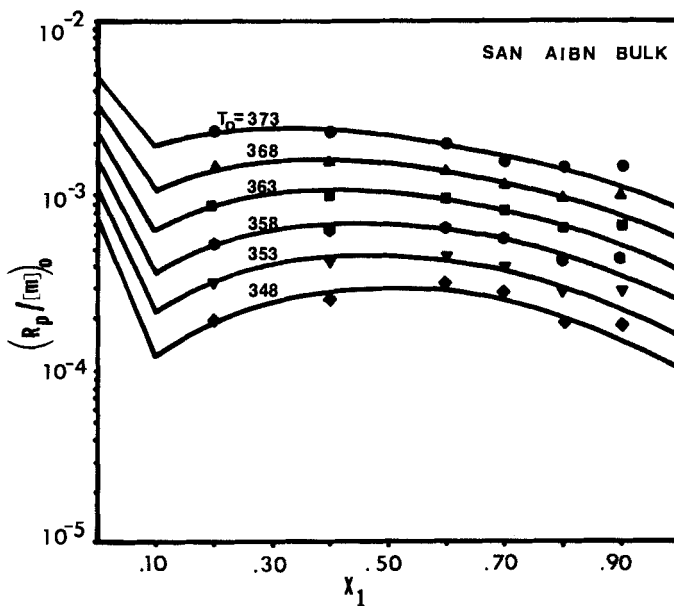


FIG. 8. PE model predicted rates, SAN/AIBN.

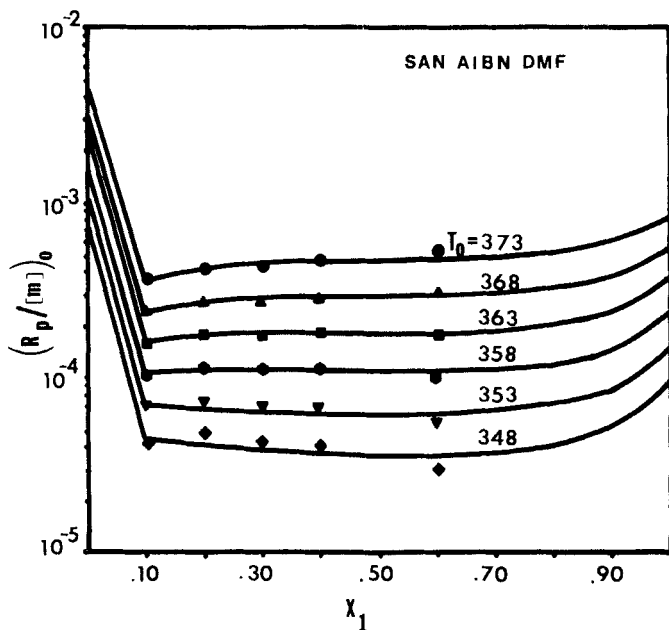


FIG. 9. PE model predicted rates, SAN/AIBN/DMF.

of styrene and AN by AIBN are the same. Thus the rate of initiation is composition-independent, which was an assumption of the PE model. There is evidence, however, that in a mixture of styrene and AN, BP will preferentially initiate styrene [37]. Our assumption of a composition-independent  $R_i$  would be invalid, and an independent means of measuring  $R_i$  at each composition would be necessary.

Solution polymerization behavior may be expected to differ significantly from bulk since the reaction rates of styrene in a polar solvent such as DMF are probably not accurately represented by bulk polymerization constants.

The PE model is as equally sensitive to styrene kinetic constants as the PF model. The data points eliminated in the calculation of  $\delta_{12}$  and  $\delta_{21}$  gave rise to negative values of one of the parameters that relate the two. Analysis parallel to that giving rise to Eq. (17) for PF kinetics would show that again the styrene term dominates the expression for this parameter. One still has the choice of finding fault with either the data or the kinetic model. It will be shown in the next section, however, that reaction profiles are consistent with initial rate data. In particular, the troublesome high styrene compositions reactions track the path predicted by the homopolymerization approximation

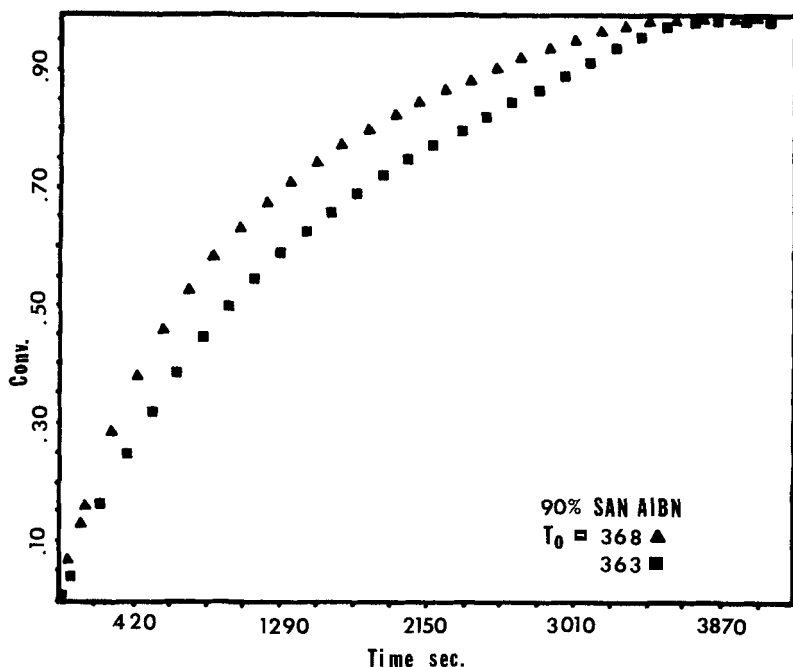


FIG. 10. Experimental conversion histories, 90% SAN/AIBN.

and the constants for this model are generated solely from the experimental rate data. Thus we are led to conclude that neither the PF nor PE models adequately describe SAN copolymerization.

### REACTION PROFILES

Our earlier numerical simulation studies demonstrated that the complex reaction kinetics of copolymerization could be approximated by balances similar in form to those of homopolymerization [5]. It was shown that if one comonomer is exhausted before the completion of the reaction, it may cause a steplike transition in the reaction behavior. This happens when the copolymer composition changes drastically with small changes in comonomer composition as one comonomer is depleted, and an example is the SAN system as the styrene composition goes to zero.

The importance to this work of these observations is that use of a single conversion independent value of  $\Delta H_c$  will not introduce a large error when converting DSC data to rate data. The relation for  $\Delta H_c$  in Eq. (15) as well as the heat generation rate in Eq. (14) are



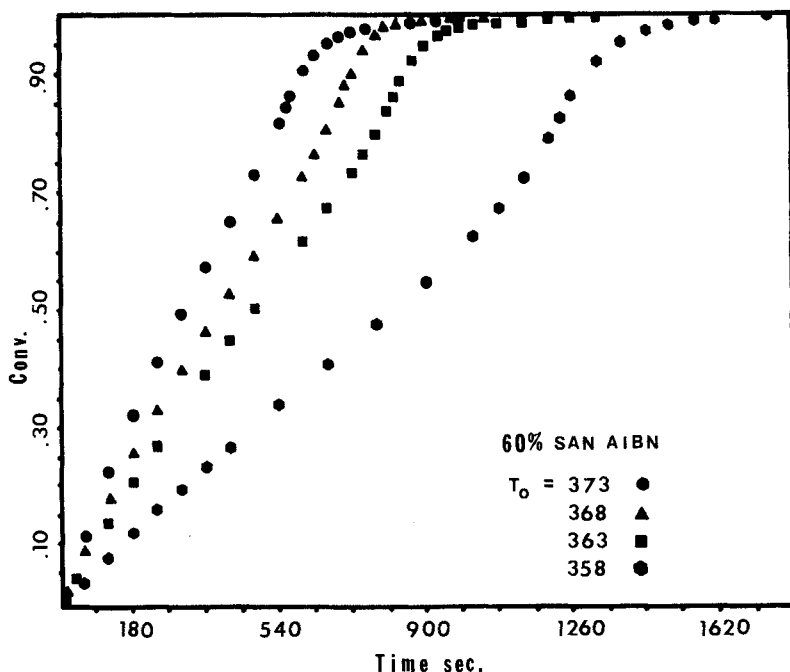


FIG. 11. Experimental conversion histories, 60% SAN/AIBN.

identically equal to the exact values at initial conditions. However, since Eq. (14) also approximates Eq. (9), it can be used to determine rates throughout the course of reaction. Furthermore, for the determination of conversion histories from rate data, a numerical value for  $\Delta H_c$  is not necessary, the mere assumption of its constancy is sufficient. By way of the numerical integration process, conversion is found from cumulative areas normalized by the total area under the DSC thermogram. The value of  $\Delta H_c$  is factorable from each term if assumed conversion independent, and thus cancels from all calculations.

The plots in Figs. 10 and 11 are samples of conversion histories obtained from numerical integration of DSC rate data. They correspond to AIBN-initiated bulk copolymerizations. It has been reported elsewhere that lowering styrene feed composition from 90 to 70% brings the onset of autoacceleration [38] which was attributed to the gel effect (GE). Our results certainly corroborate these observations. Ninety percent SAN shows a slight trace of GE only at the lowest temperature considered and late in the reaction. Successive increases in AN content bring about increasingly severe accelerations, with

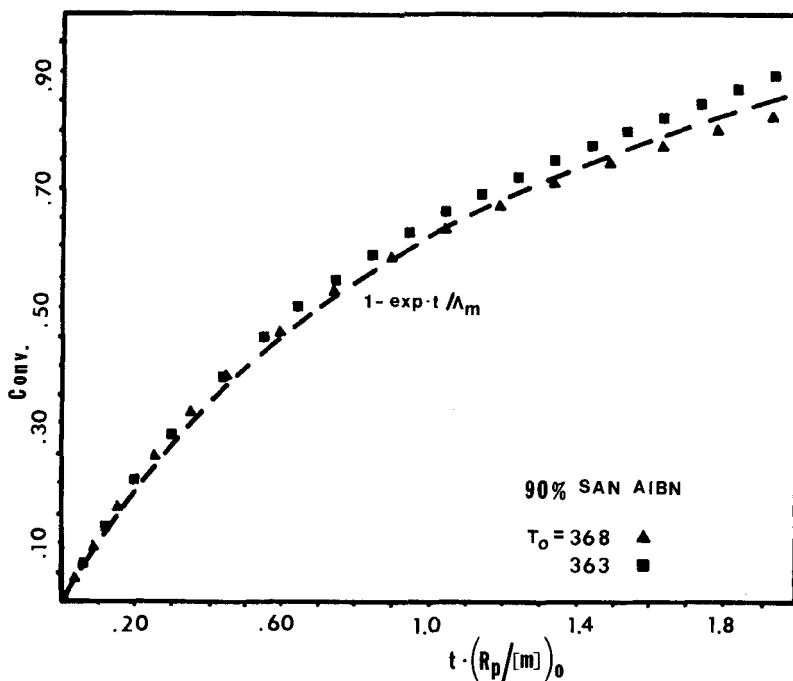


FIG. 12. Dimensionless conversion profiles, 90% SAN/AIBN.

onset at successively lower conversions. At a given composition, decreasing temperature has a similar effect. Such behavior is consistent with both precipitous acceleration and GE. For high styrene compositions (greater than 60%), the reactions are homogeneous and acceleration must be attributed to GE. When AN compositions are increased, both types may exist since the onset of heterogeneity is not immediate. From the results it is not possible to ascribe the acceleration solely to one cause or the other.

In the study of AN solution polymerization, the utility of dimensional analysis for unifying reaction behavior was demonstrated. The differences in conversion histories caused by differing initial conditions were eliminated. It would be useful to apply a similar analysis to the copolymerization reaction profiles. Our previous work showed that a characteristic time for copolymerization could be defined in a manner analogous to Eq. (4) [5, 12]:

$$\Lambda_m \equiv ([m]_0 / (R_p)_0) \quad (20)$$

Furthermore, in parallel to Eq. (14),

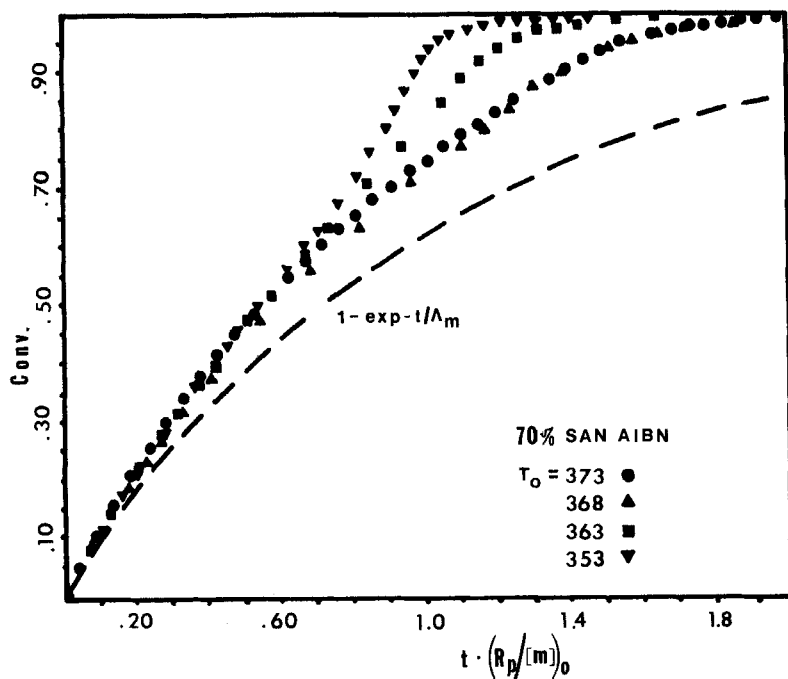


FIG. 13. Dimensionless conversion profiles, 70% SAN/AIBN.

$$-d[m]/dt = k_{ap}[m]_0^{1/2}[m] \quad (21)$$

where Eqs. (13) and (15) still serve to define  $k_{ap}$  and  $[m]$ . If Eq. (21) is made dimensionless in the way of Eq. (3), the result is

$$-dm/d\tau = m_0^{1/2}m \quad (22)$$

where

$$\tau \equiv t/\Lambda_m \quad (23)$$

Subject to the assumption of  $[m_0] \approx [m_0]_0$ , conversion will be approximated by Eq. (5). Our copolymerization initial rate data provide the means to evaluate  $\Lambda_m$  from Eq. (20), and reaction profiles may thus be checked for consistency with the predictions of Eq. (5).

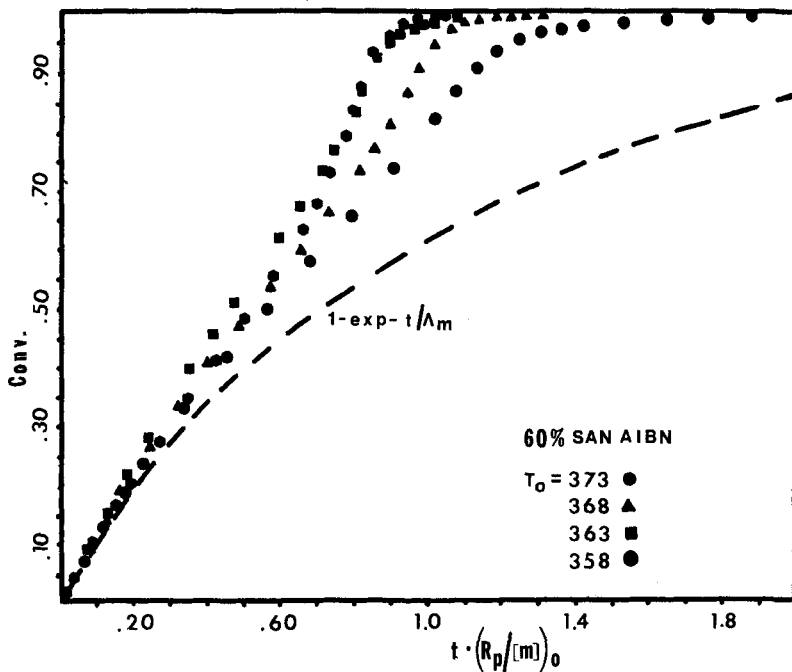


FIG. 14. Dimensionless conversion profiles, 60% SAN/AIBN.

Furthermore, the initial condition of Eq. (22) is unity, so the initial slope of the conversion-dimensionless time curve should be 1.

Replotting the conversion versus time data in dimensionless form, as described above, results in the conversion histories shown in Figs. 12-16. Notice in Fig. 12 that the 368° profile is virtually identical to that predicted by Eq. (5). The 363° run also follows closely. The high conversion deviation is a manifestation of the GE, also seen in the dimensionless plot (Fig. 1). As expected, the initial slope of the experimental profiles is 1.

As styrene composition decreases, several features of the dimensionless plots remain intact. In all cases the conversions follow the same path prior to autoacceleration. The dimensionless plots clearly demonstrate that decreased temperature creates an earlier occurring and more severe autoacceleration. Initial slope of these plots is consistently unity. Agreement with the approximation, even before the onset of GE, is not as good as the 90% SAN case, although no trend with composition is evident. It must be noted that final conversions were not experimentally determined and were tacitly assumed to be 100%. Were this not the case, the experimental profiles would be displaced upwards along the conversion axis. This is

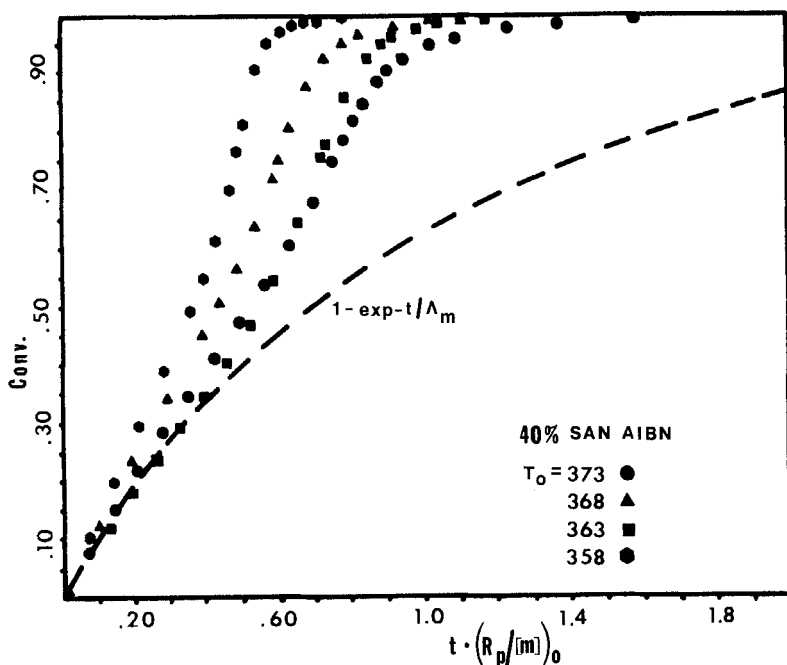


FIG. 15. Dimensionless conversion profiles, 40% SAN/AIBN.

the qualitative nature of the disagreement between data and prediction in Figs. 13-16. It is certainly not expected that a simple homogeneous free-radical model would adequately describe the complex kinetics of high AN composition copolymerizations.

The 90% system most closely matches the assumption of homogeneity and ideal kinetics (no GE), and the approximate form actually makes quantitatively accurate predictions of reaction behavior. The success of this technique suggests that there might be other complex kinetic schemes that can be approximated in a similar manner. For example, the characteristic time for conversion of any reactant is defined by

$$\Lambda_A \equiv [A]_0 / (R_A)_0 \quad (24)$$

where

$$-d[A]/dt = R_A \quad (25)$$

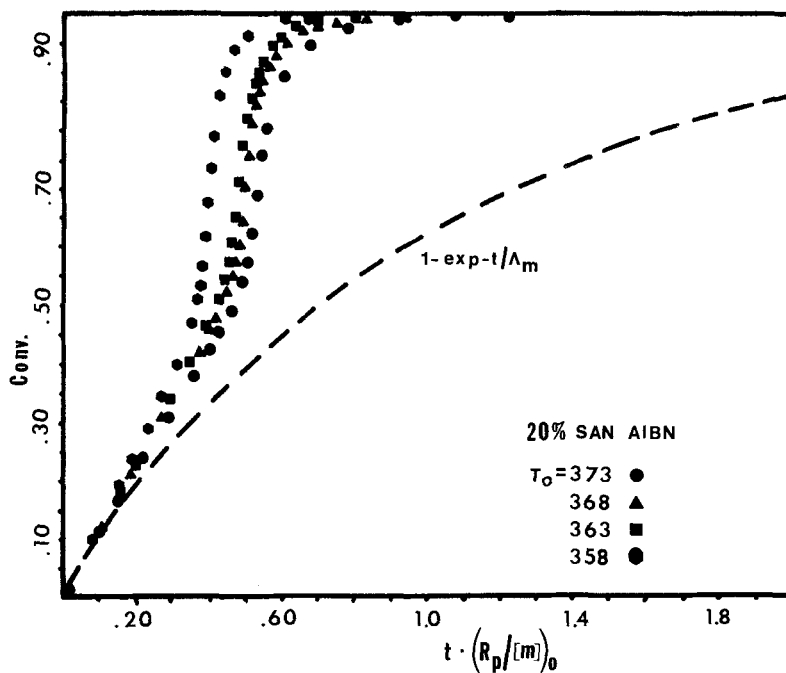


FIG. 16. Dimensionless conversion profiles, 20% SAN/AIBN.

and  $R_A$  may be a measured quantity rather than a kinetic expression. If the reaction is known to follow some arbitrary dependence on reactant A, the kinetics might be approximated by

$$-dA/dt = \Lambda_A^{-1} A^n \quad (26)$$

where  $A \equiv [A]/[A]_0$  and  $n$  represents the functional dependence of the rate on concentration.

## CONCLUSIONS AND RECOMMENDATIONS

It has been shown that present kinetic models do not adequately describe the reaction behavior of free-radical styrene-acrylonitrile copolymerization. While these models have been shown by others to be satisfactory for systems such as styrene-methyl methacrylate, where both comonomers are chemically similar, they are ineffective

when applied to a system whose kinetics vary from homogeneous to heterogeneous. It is our feeling that a major problem arises from the unaltered use of homopolymerization termination rate constants to describe copolymerization reaction rates. The different chemical nature of SAN comonomer from that of either monomer may influence these reactions. Certainly, the onset of heterogeneity makes application of homogeneous models invalid. If the available kinetic models are to be used for SAN, it is suggested that the "homo"-reaction termination constants be altered to show compositional dependence. Perhaps a study of solution polymerizations, AN in ethyl benzene, and styrene in ethyl cyanide, might further elucidate the problem.

In spite of the lack of a precise kinetic model, a great deal of reaction behavior could be described based solely upon initial rate information. The approximate kinetics presented in this work are a valuable tool, and all necessary parameters can be obtained from simple experiments.

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#### SYMBOLS

$[A]$	concentration of reactant A; without brackets, dimensionless $\equiv [A]/[A]_0$
C	constants for calculation of PE termination parameters defined in text
$E_{ap}$	lumped activation energy for polymerization $= E_p + \frac{1}{2}(E_d - E_t)$
f	initiator efficiency
$G_e$	heat generation rate
$\Delta H$	heat of reaction
$[I]$	initiator concentration
k	reaction rate constant
$[m]$	monomer concentration; without brackets, dimensionless $= [m]/[m]_0$
$[m]_0$	fictitious initiator concentration $= 2[I]_0$ ; without brackets, dimensionless $\equiv [m_0]/[m_0]_0$
r	reactivity ratio, $r_i = k_{pii}/k_{pij}$
R	reaction rate

t	time
x	mole fraction in comonomer pool, $x_i = [m_i]/[m]$
y	mole fraction in copolymer product
[z]	inhibitor concentration

### Greek Symbols

$\delta$	ratio of rate constants, $\delta_{ij} = \sqrt{k_{tij}}/k_{pii}$
$\phi$	phi factor termination parameter $\equiv k_{t12}/\sqrt{k_{t11}k_{t22}}$
$\Phi$	monomer conversion $\equiv [m] - [m]_0/[m]_0$
$\lambda$	homopolymerization time constant
$\Lambda$	lumped time constant
$\tau$	dimensionless time

### Subscripts

A	of reactant A
ap	apparent for polymerization
i	initiation
ind	induction
m	monomer
0	initial condition
p	propagation
t	termination

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