Seeded Heterogeneous Polymerization of Acrylonitrile

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ABSTRACT: Results are reported of an extensive study at 50 °C of the kinetics of seeded heterogeneous polymerization of acrylonitrile (a monomer which is water soluble but insoluble in its polymer). $K_2S_2O_8$ or γ-irradiation initiation were used, runs using the latter also yielding relaxation kinetics after removal from the radiation source; since free radical loss processes are likely to be similar in all three types of system, these studies permit more inferences to be made than are possible with, e.g., chemical initiation alone. It is thus shown that (i) data can be interpreted by a general kinetic scheme developed for compartmentalized polymerization, (ii) the locus of polymerization is the particle surface, (iii) the average number of free radicals per particle is high ($\simeq$250), (iv) radical capture efficiency by the particles is 100%, and (v) for the free radical fluxes used here, all loss of free radical activity is pseudo first order, consistent with the rate-determining step occurring in association with the particle and being the inhibition of propagation due to environmental constraints (e.g., when the propagating free radical grows in such a way as to become completely surrounded with glassy polymer).

Heterogeneous polymerizations involving a continuous phase and where the monomer and polymer are mutually insoluble (such as acrylonitrile and tetrafluoroethylene) are of considerable industrial importance, but there is no generally accepted theoretical framework in which to discuss them. On the other hand, there has emerged an extensive battery of theoretical and experimental techniques whereby mechanistic information can be gained on emulsion polymerization systems, where monomer and polymer are mutually soluble. An important tool here is to use both chemical initiation and initiation by γ radiation, with especial use made of the ability (with γ initiation) to remove the source of free radicals virtually instantaneously, so that relaxation kinetics can be studied. Since free radical loss processes are likely to be similar in all three types of system (chemical, in-source γ initiation, and ex-source relaxation), these studies permit more inferences to be made than are possible with chemical initiation alone.

The object of this paper is to apply these techniques to nonswelling heterogeneous polymerization systems; the archetypical monomer acrylonitrile is chosen for study. It will be seen that the methodology developed for emulsion polymerization systems can be applied with minor modifications to the heterogeneous polymerization in question and that considerable mechanistic information can be gleaned thereby.

Acrylonitrile is an especially suitable monomer for study, because there has been extensive characterization of its heterogeneous polymerization (including the establishment of suitable experimental techniques to enable one to obtain reproducible results) carried out by Elbing and co-workers.[1,2] In its heterogeneous polymerization, the addition of chemical initiator to an aqueous solution of this water-soluble monomer (its solubility at 50 °C is 1.5 mol dm^{-3}) results in a stable, monodisperse latex, even without any added surfactant.

A major problem in the mechanistic investigation of any multiple-phase polymerization system is the number and complexity of the reactions which must be taken into account. For example, in such systems one can have both latex particle formation and growth within these particles occurring simultaneously; each of these processes is itself complex. Thus it is impossible to obtain an unambiguous mechanistic interpretation of data obtained from a study of ab initio polymerizations (i.e., systems where new latex particles are formed) alone. It is now well established for emulsion polymerization systems that this impasse is avoided by first studying the seeded polymerization kinetics, i.e., determining conditions whereby one can carry out polymerization using a preformed latex such that no new particles are nucleated. It is only then that sufficient mechanistic information on particle *growth* is available for the conditions under study to enable one to obtain subsequently unique and unambiguous information on the kinetics of particle *formation* in unseeded systems. A methodology for this approach, with some examples for emulsion polymerization systems, has been given elsewhere.[3,4] As will be seen, the theoretical framework of this treatment is sufficiently general as to encompass, without major modification, special cases such as the present one of heterogeneous polymerization of a monomer which is insoluble in its own polymer.

The methodology for determining the mechanisms operative in seeded systems has now been applied to a number of monomers.[3,5] The treatment will be summarized in a later section. The object of the present paper is to apply this methodology to the seeded heterogeneous polymerization of acrylonitrile. This will lay the groundwork for the future application of related techniques[4] for studying particle formation.

One particular advantage of the methods to be used here is that (in most cases) it is not necessary to make use of data from bulk polymerization. This is particularly fortunate in the present case in view of the considerable uncertainty about the kinetics in acrylonitrile polymerization systems. Studies on the bulk and aqueous kinetics include those of Chapiro,[6] Bamford et al.,[7,8] Dainton et al.,[9] Thomas et al.[10] and Peebles.[11] It was suggested that there was an unusually high concentration of free radicals in the bulk polymerizing system,[7,8,10,11] which was associated with a number of unusual kinetic features. Peebles[11] emphasized that the principal locus for polymerization in the bulk

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is in the (discrete) polymer phase (recall that formed polymer is insoluble in its monomer), a conclusion for which Lewis et al.[12] found strong confirmatory evidence. However, this conclusion is in disagreement with that of Dainton et al.[9] These last-named workers deduced values for the rate coefficients for propagation (k_p) and termination (k_t) of 3×10^4 and 4×10^9 dm^3 mol^{-1} s^{-1} at 30 °C, which seem extraordinarily high when compared with proposed values for the bulk system at 60 °C of k_p in the range 1 to 10^2 dm^3 mol^{-1} s^{-1} and k_t in the range 1 to 3×10^3 dm^3 mol^{-1} s^{-1}.[7,8] Dainton et al. proposed that most polymerization occurs in the aqueous phase (for acrylonitrile polymerization in aqueous solution). However, it appears that this conclusion, while consistent with their own experimental observations, is in conflict with the subsequent observation that a reduction in particle number may decrease the rate in aqueous solution.[1]

Part of the origin of these discrepancies may lie in the experimental difficulties inherent in the bulk or solution polymerization of a monomer which is insoluble in its own polymer. It is opportune to point out here that many of these difficulties are completely circumvented by studying seeded polymerizations (using a well-characterized preformed seed latex) dispersed in a continuous phase (water in the present case). Some advantages of this method include the following: (i) the polymerizing system can be maintained truly isothermal; (ii) if conditions are chosen to avoid new nucleation, the growth kinetics can be studied quite separately from those of nucleation, and moreover the seed particle size can be varied at will be use of suitable monodisperse latexes; (iii) while bulk kinetics can usually only be accurately monitored up to a relatively small fractional conversion of monomer to polymer, this limitation is absent in a seeded study.

Methodology

In quantifying the kinetics of heterogeneous polymerizations where monomer and polymer are mutually insoluble, it is essential to take proper account of the compartmentalized nature of the system: that is, it is highly likely that the locus of polymerization is associated with the latex particles (at or near the particle/water interface), these particles being physically separate from each other. It is of course well-known[13] in emulsion polymerization that it is this compartmentalization which gives rise to the greatly different characteristics of polymer generation in a latex system from those in bulk or solution.

The essence of the methodology for emulsion systems is as follows. We write down a set of equations for the polymerization rate which specifically takes account of the compartmentalized nature of the system. These are generalizations of the Smith–Ewart[13] equations, incorporating (i) the creation or entry of polymerizing free radicals which become active at the locus of polymerization, (ii) first- and second-order loss of these free radicals, and (iii) aqueous-phase events that may affect the kinetics occurring at the polymerization locus. The resulting set of equations contain rate parameters that are sufficiently small in number to be uniquely specified from the amount of data available, provided certain constraints are met. These data are the chemically initiated kinetics and the kinetics in and out of the γ-radiation source. It has been shown[3,5] that there is always sufficient information in these data for an unambiguous choice of rate parameters, subject to constraints such as the first- and second-order radical loss rate coefficients being independent of initiator concentration.

In a seeded emulsion polymerization system, the rate of polymerization can be conveniently expressed in terms of the fractional conversion of monomer to polymer, x. If no monomer droplets are present ("interval III" in emulsion polymerization systems), one has (see, e.g., Gilbert and Napper[3])

$$\mathrm{d} \ln (1 - x)/\mathrm{d}t = -(k_p/N_A V_s)\bar{n} \quad (1)$$

Here k_p is the propagation rate coefficient, N_A is Avogadro's constant, V_s is the swollen volume of the particles, and $\bar{n}$ is the average number of free radicals per discrete polymerizing locus. In an emulsion polymerization system, the polymerizing locus is the whole particle; in the present system where monomer and polymer are mutually insoluble, most evidence[1,7,8,10-12] seems to indicate that the polymerization locus is the particle/water interfacial region. This conclusion will be adopted in the following development.

We now consider a heterogeneous polymerization with mutually insoluble monomer and polymer and where the monomer is soluble in the aqueous phase. For the present, we confine our attention to a system without monomer droplets present, i.e., where the only reservoir of monomer is the aqueous phase (extensions to include the presence of monomer droplets are straightforward[3]). Let $[M_L]$ denote the concentration of monomer in the locus of polymerization and $[R_L\cdot]$ denote the free radical concentration in this locus. Then the rate of polymerization in an individual locus is given by

$$R_p = -\mathrm{d}[M_L]/\mathrm{d}t = k_p[M_L][R_L\cdot] \quad (2)$$

The concentrations of monomer in the aqueous phase, $[M_{aq}]$, and in the polymerizing locus, $[M_L]$, will be related by a partition coefficient q: $[M_L] = q[M_{aq}]$. The value of q will be independent of $[M_{aq}]$, provided that the system is not in the saturation regime of the adsorption isotherm and that the solutions are sufficiently dilute so that the activity coefficients are unity. In addition, in systems with comparatively low particle number densities such as those considered here, almost all of the monomer will be present in the aqueous phase. Equation 2 can then be transformed to yield the overall rate of polymerization in the system:

$$-\mathrm{d}[M_{aq}]/\mathrm{d}t = k_p[M_{aq}]q(\bar{n}/N_A V_L)(N_c V_L) \quad (3)$$

Here $\bar{n}$ is the average number of free radicals at each polymerization locus, N_c is the number density of loci per unit volume of solution, and V_L is the volume of an individual polymerization locus (i.e., region of a latex particle wherein polymerization takes place). Equation 3 can be rewritten as

$$\mathrm{d} \ln (1 - x)/\mathrm{d}t = -k_p q \bar{n} N_c/N_A \quad (4)$$

where x is the fractional conversion to polymer. The average number of free radicals per locus is given by

$$\bar{n} = \sum_i i N_i / \sum_i N_i \quad (5)$$

where N_i is the number of loci with i free radicals associated with them. The time evolution of these last quantities is given by the generalized[3,14-16] Smith–Ewart[13] equation:

$$\mathrm{d}N_i/\mathrm{d}t = \rho[N_{i-1} - N_i] + k[(i + 1)N_{i+1} - iN_i] + c[(i + 2)(i + 1)N_{i+2} - i(i - 1)N_i] \quad (6)$$

Here ρ is the (first-order) rate coefficient for the attachment of a free radical to a polymerizing locus (ρ is the entry rate in an emulsion polymerization system), k is the rate coefficient for first-order loss of a polymerizing free radical from this locus, and c is the (pseudo-first-order) rate coefficient for second-order loss of free radical activity from this locus; c will be proportional to k_t, the second-order termination rate coefficient. The coefficients $(i + 1)$ etc. in eq 6 arise from simple combinatorics.

The physical interpretation of k is likely to be different in the present special heterogeneous system (where the locus of polymerization is at or near the particle/water interface) from what one normally has in an emulsion polymerization. The first-order loss in the latter is due to exit (desorption) by diffusion of the polymerizing free radical into the aqueous phase subsequent to transfer to a monomer or to a chain-transfer agent (this desorption occurring before the new free radical has had time to undergo significant propagation). However, in the present heterogeneous system, this first-order loss could occur by additional mechanisms as well: for example, by burial of the propagating free radical inside the particle where there is negligible concentration of monomer.[7,10]

It is essential at this point to note that if first-order loss is actually by desorption into the aqueous phase, this can have a very significant effect on the radical attachment rate coefficient ρ, for the following reasons. First, the desorbed free radical may undergo subsequent reentry.[14] Second, a desorbed free radical may instead (or as well) undergo heterotermination with an aqueous free radical that would otherwise have become attached to the polymerization locus.[15] Third, there is the possibility of self-termination between these desorbed free radicals. The first of these effects increases ρ, the second decreases it, while the third has no effect on ρ. A rigorous mathematical treatment of the various possible aqueous events[3,16] shows that one can take account of all these possibilities by writing

$$\rho = \rho_A + \alpha k \bar{n} \tag{7}$$

Here ρ_A is the contribution to radical attachment of free radicals arising directly from initiator (and background thermal sources), and α is a "fate parameter" whose values lie between ± 1. If $\alpha = +1$, reentry is dominant; it $\alpha = -1$, then the dominant fate of excited free radicals is heterotermination. If all desorbed free radicals undergo self-termination in the aqueous phase, then $\alpha = 0$ (note that this last possibility was not included in the formal derivation of eq 7; however, its inclusion is straightforward). It must also be noted here that the case (which is not unlikely in the present system) where first-order loss never results in a free radical being desorbed into the aqueous phase is also included if one has $\alpha = 0$. Indeed, in general α may take any value in the range $-1 \leq \alpha \leq +1$. Equation 7 results in eq 6 being nonlinear, even if k and c are constants independent of any change in particle size etc. during conversion, and care in solution of eq 6 is required.[3]

It is essential to note that our method of obtaining unique values for the various rate parameters involved in eq 2–7 requires that (i) N_c remain constant (no new nucleation), (ii) use be made of rate data *both* in the steady-state regime *and* during the approach to steady state (if feasible), (iii) both chemical and γ initiation be used, the latter both in and out of the radiation source, and (iv) chemical and radiolytic initiation be used over as wide a range of initiator concentration as is possible without new particle nucleation or flocculation. Only by acquiring data from all these sources can the data analysis be sufficiently overdetermined to yield unambiguous rate parameters. It should also be noted that one cannot assume a priori that free radical capture efficiency is 100% (which would imply that $\rho_A = 2k_d N_A[I]/N_c$, where k_d is the initiator decomposition rate coefficient and [I] the initiator concentration), since there exist well-tested counterexamples to this supposition.[3]

The technique of obtaining unique rate parameters can be summarized as follows. One has conversion/time data for chemical initiation over a wide range of [I] and γ-radiolytic initiation both in the radiation source (over a range of dose rate) and after removal from the source ("relaxation mode"). Various means can then be devised[3,5] for unique fits to all these data together with the computed solutions of eq 2–7, with the constraints that k and c must be independent of initiator type (chemical or γ) and concentration (or radiation flux). Means of solving eq 2–7, both in the steady-state and time-dependent regimes, have been discussed elsewhere.[3,5] It should be noted at this point that sometimes it is impossible to obtain as much of the above-mentioned data as would be desirable. For example, very often the range of initiator concentration is limited (in order to avoid flocculation or new nucleation), and for some systems the approach to steady state with chemical initiator is so rapid that it cannot be properly distinguished from the end of the induction period. Moreover, not infrequently certain of the rate parameters are so large that they are not rate determining (for example, termination in many styrene systems[17]) and, of course, as a consequence these large rate parameters cannot be determined by the above techniques.

For reasons that will become apparent later, it is useful here to note a special solution of eq 2–7. In the particular case that $c = 0$ (no second-order loss), eq 6 can be multiplied by i and summed over all i to yield

$$d\bar{n}/dt = \rho_A - (1 - \alpha)k\bar{n} \tag{8}$$

Equation 8 has the steady-state solution

$$\bar{n}_{SS} = \rho_A/(1 - \alpha)k \tag{9}$$

Note that if α is exactly +1, eq 9 is undefined; in such a case, second-order loss must become important; under such circumstances $\bar{n}_{SS}$ is no longer proportional to ρ_A.[5]

Equation 8 shows that $\bar{n}_{SS} \propto \rho_A$ if $c = 0$ (and $\alpha < +1$). Moreover, it is readily proved that these conditions are necessary as well as sufficient: proportionality of $\bar{n}_{SS}$ to ρ_A is *only* observed if c is very small and $\alpha < +1$. The proof of this statement is carried out by computing $\bar{n}_{SS}$ as a function of ρ_A, k, c, and α (or rather, as a function of the dimensionless parameters ρ_A/k, c/k, and α) over a range of values sufficiently wide as to cover all physically likely situations (the way of obtaining $\bar{n}_{SS}$ as a function of these quantities has been given elsewhere[18]). The numerical results so obtained show that $\bar{n}_{SS}$ is proportional to ρ_A/k only as $c/k \to 0$ and for $\alpha < +1$.

Experimental Section

Acrylonitrile (Fluka, AR grade, stabilized by *p*-methoxyphenol) was distilled immediately prior to use, with the fraction boiling between 77.0 and 77.3 °C being collected for use. Potassium peroxodisulfate (BDH, AR grade) was recrystallized from water. The surfactant (employed only for making the seed latex) was sodium dodecyl sulfate (Sigma, AR grade). Sodium metabisulfite (used in the preparation of seed latexes) was Ajax, Laboratory Reagent grade.

Seed latexes were prepared as follows. Recipes are given in Table I. $K_2S_2O_8$, sodium dodecyl sulfate, acrylonitrile, and $Na_2S_2O_5$ were dissolved in water at ambient temperature, which had been previously purged with high-purity nitrogen. The seed latex was formed by keeping this preparation at 50 °C for the listed times. The resulting seed was dialysed for 20 days, with daily changes of distilled water, and was characterized by calibrated electron microscopy. The mean radii and standard deviations are as listed in Table I.

Polymerization kinetics were measured dilatometrically as follows. For runs with chemical initiation, a suspension of seed latex and initiator was made up at room temperature and degassed by evacuation with a water pump. A known mass of acrylonitrile, previously purged with nitrogen, was then added under vacuum. Nitrogen was then bled in, the mixture was transferred to a dilatometer, and the system was rapidly brought to 50 °C. The

Table I
Seed Latex Recipes and Properties

	seed A	seed B
preparation		
$K_2S_2O_8$, g	0.270	0.135
sodium dodecyl sulfate, g		0.138
acrylonitrile, g	40.0	30.0
$Na_2S_2O_5$, g		0.013
water, g	1000	1000
reaction time, h	0.33	24
radius, nm	50 ± 5	113 ± 4
N_c used in runs, 10^{15} dm^{-3}	0.96	1.6

dilatometer was of sufficiently small volume (ca. 30 cm^3) and of appropriate shape so that thermal equilibration could occur rapidly. Thermal equilibration time (measured with a thermocouple inside the vessel) was always reached in under 5 min; this time is less than the induction period. The system was found to be colloidally stable with initiator concentrations of up to 10^{-3} mol dm^{-3} $K_2S_2O_8$; some gelation of the latex occurred at high initiator concentrations. The technique for initiation using γ radiation was similar to that for chemically initiated runs, except of course for the absence of $K_2S_2O_8$. Details of the γ-radiolytic apparatus and technique have been presented elsewhere.[19] The dose rate in the present system was varied between 0.84 and 17.6 krad h^{-1} (as determined by Fricke iron(III) sulfate dosimetry) through the use of lead shielding. In γ-radiolysis polymerization involving a water phase, the initiating species is virtually entirely OH·. The technique has the unique advantage that the reactor vessel can be removed from the radiation source essentially instantaneously, and (since the half-life of aqueous-phase free radicals in these systems is extremely short) the relaxation kinetics can be accurately monitored. The reactor vessel was usually inserted and removed from the source a number of times in each run, so that the relaxation kinetics could be monitored several times. It was verified that the dilatometer remained isothermal to better than 0.1 °C during a run by testing with a sensitive thermocouple. Spurious effects in dilatometric measurements arising from the heat of polymerization can thus be safely discounted.

All runs (chemical and γ) were checked for new nucleation by electron microscopy by inspection of at least 1000 particles, and only runs where no newly formed particles could be seen (at resolution down to 10 nm) were used for quantitative analysis, using methods given in the previous section. It was found that it was difficult to avoid new nucleation if monomer droplets were present and if significant amounts of surfactant were used. Since the data analysis requires no new particle formation, all kinetic runs were carried out under conditions of no added surfactant and no monomer droplets present ("interval III" in the language of emulsion polymerization systems).

All kinetic studies were carried out at 50 °C.

Results and Quantitative Interpretation

Chemical Initiation. The results of typical chemically initiated runs are shown in Figure 1, plotted as $-\ln(1-x)$ against time, as suggested by eq 4. Figure 2 shows the same data, plotted as $-\mathrm{d}\ln(1-x)/\mathrm{d}t$ against x. It is apparent that there is an extensive steady-state period, covering typically 20% of the conversion. It is worthy of note that a steady state would not be apparent in a plot of simple conversion against time, since eq 4 shows that it is $-\ln(1-x)$, not x, that is the appropriate variable whose linearity in time implies a constant $\bar{n}$. Note that, in the present system, there is no reserve of monomer droplets present as in conventional emulsion polymerization systems in interval II (which maintains constant monomer concentration in the polymerization locus). Some workers[9] have hitherto claimed that a brief apparent linearity in $x(t)$ was a steady state; in fact, it can be seen from eq 3 that this would only be a point of inflection and would not correspond to a region of constant $\bar{n}$ at all.

Figures 1 and 2 show that the chemically initiated runs exhibited a slow approach to this steady state: up to 20% conversion in some cases. It is important to ascertain whether this slow approach is actually due to the time required for $\bar{n}$ to acquire a constant value or is just an artifact due to retardation of polymerization. This was established as follows. The γ-radiolysis studies discussed in more detail below also show a slow approach to steady state upon the *initial* insertion into the radiation source. However, *subsequent* insertions (after removal from the source) show a very short time to reach the steady state. Now, as has been pointed out previously in the context of a similar effect observed with methyl methacrylate,[5] this is because with the γ source all retarders are completely scavenged during the initial insertion, and it is subsequent insertions that give the true time required to reach a steady state free of all retardation effects. The present acrylonitrile system shows slow approach to steady state both during the initial insertion into the γ source and for the chemical initiation systems. However, subsequent γ insertions show a fast approach to steady state. Hence a significant component of the time required to reach a steady state in the chemically initiated system and in the initial insertion into the γ source must be due to retardation and/or inhibition. We are thus unable to obtain any meaningful results from the approach to steady state in the chemically initiated systems.

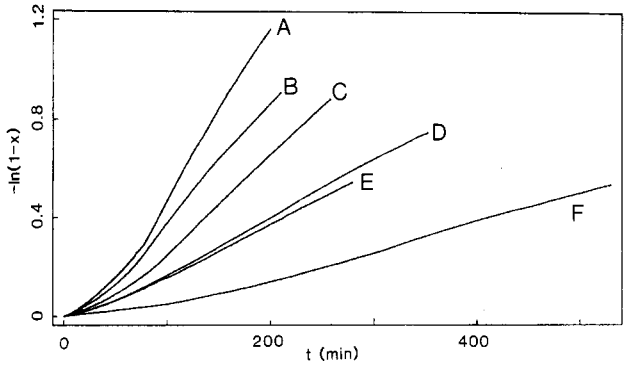

Figure 1. Fractional conversion to polymer, x [plotted as $-\ln(1-x)$], as a function of time for chemically initiated runs; $S_2O_8^{2-}$ concentrations (10^{-3} mol dm^{-3}) are 1.0 (A), 0.75 (B), 0.50 (C), 0.250 (D), 0.20 (E), and 0.10 (F). Initial concentration of monomer was 0.75 mol dm^{-3} in all cases; the seed latex used was seed A.

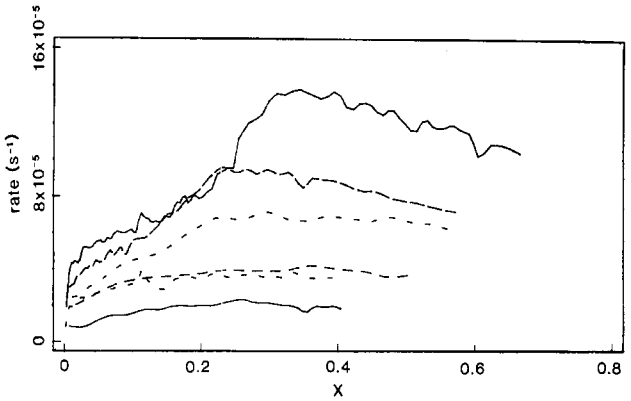

Figure 2. Data of Figure 1 plotted as polymerization rate, $-\mathrm{d}\ln(1-x)/\mathrm{d}t$, as a function of conversion, x. Rates were obtained by numerically differentiating the data without smoothing and hence show considerable noise.

Figure 3 shows a plot of the steady-state rate, $-\mathrm{d}\ln(1-x)/\mathrm{d}t$, as a function of [I]. One sees that the steady-state rate is linear in [I] and approaches a small but significant background thermal value as [I] approaches zero. It is thus apparent that the steady-state rate in excess of the background thermal value is proportional to [I] over the entire concentration range of initiator that was accessible. Ac-

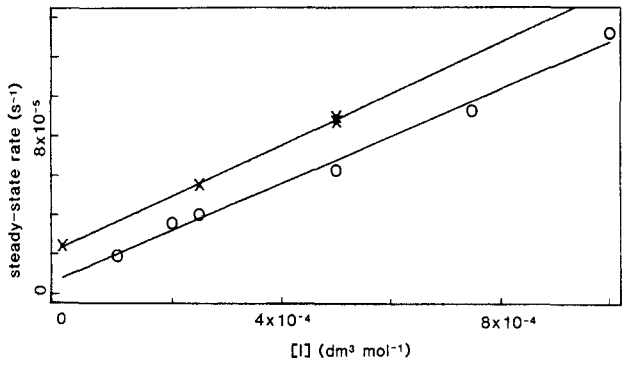

Figure 3. Steady-state polymerization rate, as $-\mathrm{d} \ln (1 - x)/\mathrm{d}t$, as a function of initiator concentration for all chemically initiated runs. Upper data for seed A; lower data for seed B; N_c values given in Table I.

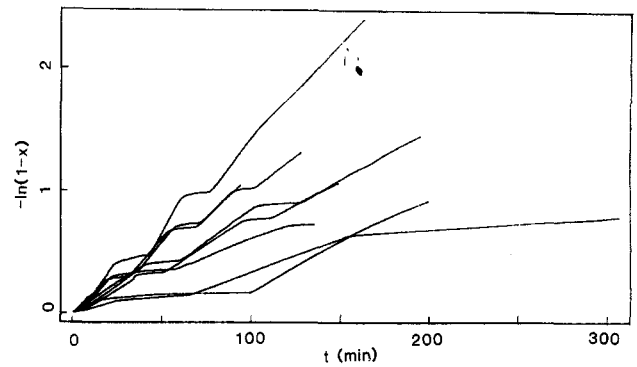

Figure 4. Fractional conversion/time results for γ-radiolysis relaxation runs given in Table II plotted as $-\ln (1 - x)$ against t; each run involves a number of successive insertions into and removal from the radiation source. Seed used was seed B; initial concentration of monomer was 0.78 mol dm^{-3}.

cordingly the component of $\bar{n}_{SS}$ arising from chemical initiation over this range is also proportional to [I].

These results imply that the system is characterized by $c \simeq 0$, $\alpha < 1$, and 100% capture efficiency. This conclusion arises as follows: (i) The calculations of $\bar{n}_{SS}$ as a function of ρ_A, k, c, and α discussed in the Methodology section show that the steady-state value of $\bar{n}$ is proportional to ρ_A if and only if $c \simeq 0$ and $\alpha < +1$; (ii) ρ_A is the sum of a component arising directly from initiator decomposition (ρ_I) and a component from background thermal initiation (ρ_T);[16,17] i.e., $\rho_A = \rho_I + \rho_T$; and (iii) ρ_I (the component of the free radical attachment rate coefficient arising entirely from initiator decomposition) can only be proportional to [I] if there is negligible aqueous-phase homotermination of free radicals arising directly from initiator.[16]

Given the above general conclusion, the data for chemical initiation enable us to determine the quantity $2k_p q k_d/k(1 - \alpha)$, from eq 4 and 9, the observed slope, and the relation $\rho_I = 2k_d[I]N_A/N_c$ (applicable to 100% capture efficiency). No additional information can be obtained from these results alone, since we are unable to obtain meaningful data on the rate of approach to steady state (see above).

Radiolytic Initiation. Figure 4 shows the results of γ-initiated runs, including successive insertions into and removals from the source.

As intimated above, all retarders are scavenged during the initial insertion (a comparatively slow approach to steady state). Upon removal from the source, there is a relatively rapid relaxation to a low background thermal steady state; subsequent insertions show a much more rapid approach to steady state. This steady state lasts until ca. 60% conversion, whereafter there is a decrease in rate. At higher dose rates, the duration of this steady state declines appreciably. This could be ascribed to the emergence of a second-order loss process.

In the light of the conclusions given above under Chemical Initiation, the relaxation results for both insertion into and after removal from the radiation source can be quantitatively interpreted as follows. By integration of eq 4 and 8, one obtains

$$-\ln (1 - x) = A\kappa^{-1}(\rho_A[t - \kappa^{-1}(1 - e^{-\kappa t})] + \bar{n}_i(1 - e^{-\kappa t})) \quad (10)$$

where $\kappa = k(1 - \alpha)$, $A = k_p q N_c/N_A$, and $\bar{n}_i$ is the value of $\bar{n}_{SS}$ at $t = 0$; for convenience in eq 10 we have chosen the origin (i.e., $x = 0$) to be at $t = 0$, which is here the instant of insertion into, or removal from, the source.

In eq 10, for relaxation after removal from the source, $\rho_I = 0$; otherwise, ρ_I depends on the γ intensity. Equation 10 can therefore be written in two alternative forms (given below) suitable for least-squares fitting, depending on whether relaxation or insertion is being considered. These forms allow for uncertainty in the initial time and initial x (since removal from or insertion into the source takes a brief but finite time). In the fitting, one must also take into account that after the initial insertion, $\bar{n}_i$ is known from the slope just prior to insertion or removal. The forms of eq 10 suitable for least-squares fitting which take these effects into account are

$$\text{relaxation:} \quad -\ln (1 - x) = Q_T t + \kappa_R^{-1} Q_R(1 - \exp[-\kappa_R t]) + C_R \quad (11)$$

$$\text{insertion:} \quad -\ln (1 - x) = Q_A t - \kappa_I^{-1} Q_I(1 - \exp[-\kappa_I t]) + C_I \quad (12)$$

Here the subscripts R and I refer to relaxation or insertion values, $Q_T = A\rho_T/\kappa_R$, $Q_I = A\rho_I/\kappa_I$, $Q_A = Q_I + Q_T$, and Q_R is the value of Q_A from the previous insertion. The quantities C_R and C_I are to allow for the small uncertainties in the starting time and starting x. For each removal or insertion, the Q's are known from the previous insertion or removal, respectively. Thus each least-squares fitting is to two variables ($\kappa_R = k(1 - \alpha_R)$ and C_R for relaxation; $\kappa_I = k(1 - \alpha_I)$ and C_I for insertion). Note that in principle the value of $(1 - \alpha)$ may well vary depending on the γ flux, insertion or relaxation mode, etc., since first-order loss (and hence α) may be influenced by the aqueous-phase generation of free radicals. Moreover, k may vary with fractional conversion; i.e., it may depend inter alia on the particle size. Initial insertion into the source cannot be meaningfully fitted by eq 12 since the time evolution is masked by inhibition and/or retardation effects.

Table II shows the results for various fitted quantities for each relaxation/insertion cycle from each run. In Figure 5, the calculated and observed rates (i.e., the differential of the experimental data) are compared; this highlights insignificant noise in the data caused by (for example) small fluctuations in bath temperature, etc., and provides a particularly sensitive comparison between theory and experiment. There is good agreement between the observed and calculated differentials; the raw data (as conversion/time curves) are indistinguishable from those calculated. This confirms that the kinetics are in actuality governed by a relationship of the type shown in eq 10, i.e., that $\bar{n}(t)$ relaxes with single-exponential decay. This shows that loss of free radicals is indeed first order of $\bar{n}$ (as in eq 8).

Table II shows that, for the relaxation results, the value of the effective overall first-order loss rate coefficient $k(1 - \alpha)$ shows no systematic variation from cycle to cycle nor

Table II
γ-Radiolysis Results: Quantities Obtained from Fitting Eq 11 and 12[a]

Relaxation Mode

run	x_0	γ flux, krad h^{-1}	Q_R, 10^{-4} s^{-1}	Q_T, 10^{-5} s^{-1}	κ_R, 10^{-3} s^{-1}
19/12b	0.31	17.6	3.9	1.8	5.9
	0.60	17.6	4.5	0.6	7.1
12/12	0.24	10.1	2.8	2.2	7.4
	0.49	10.1	2.9	1.6	7.5
	0.62	10.1	2.5	0.0	6.9
13/12	0.21	10.1	2.8	2.3	8.0
	0.47	10.1	2.9	1.4	6.9
15/12	0.23	4.9	1.4	1.7	5.8
	0.52	4.9	1.6	1.2	6.9
16/12	0.31	4.9	1.8	2.2	7.3
	0.57	4.9	1.7	1.6	7.1
20/12	0.09	4.9	1.2	3.4	6.2
18/12	0.26	4.9	1.7	1.4	7.2
	0.51	2.5	0.80	0.4	7.5
19/12a	0.08	0.84	0.82	1.0	6.4
	0.46	0.84	0.91	0.4	5.9

Insertion Mode

run	x_0	γ flux, krad h^{-1}	Q_A, 10^{-4} s^{-1}	Q_T, 10^{-5} s^{-1}	κ_I, 10^{-3} s^{-1}
12/12	0.27	10.1	2.9	2.2	10.4
13/12	0.24	10.1	2.9	2.3	9
15/12	0.28	4.9	1.6	1.7	13
	0.53	4.9	1.6	1.7	10
16/12	0.34	4.9	1.8	2.2	9.3
18/12	0.30	2.5	1.2	1.0	12
	0.53	2.5	0.70	0.4	10
19/12a	0.13	0.84	0.91	1.8	6.8

[a] Each run (except 20/12 involves successive insertions and removals; x_0 denotes the conversion at the start of each removal or insertion.

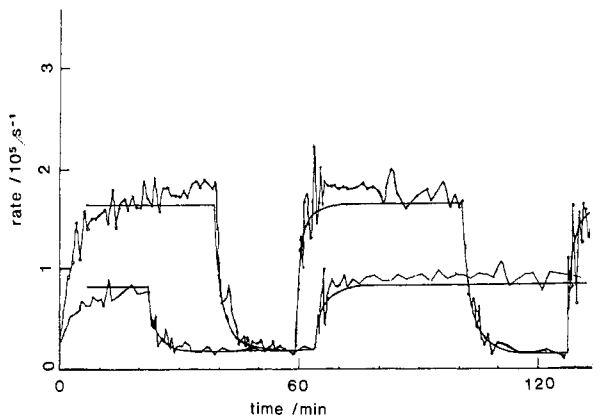

Figure 5. Comparison of experimental and calculated values of rate $-d \ln (1 - x)/dt$ as a function of time for typical γ-radiolysis runs: 16/12 and 19/12a (Table II).

with dose rate. This provides strong evidence for the correctness of our mechanistic interpretation. The value of $k(1 - \alpha_R)$ from all relaxation results is $(7 \pm 1) \times 10^{-3}$ s^{-1}.

Note that the value of $k(1 - \alpha_R)$ appears independent of fractional conversion x. This implies that $k(1 - \alpha_R)$ is independent of the particle size, since this changes substantially during the course of the run: typically the radius changes by a factor of 2 and thus the surface area by a factor of 4 and the volume by a factor of 8.

The observed behavior of $k(1 - \alpha)$ in the insertion mode can be used to make inferences about α and k, as follows. (i) Suppose first that the first-order loss process consists of true desorption of free radicals into the aqueous phase. Under such circumstances, there are convincing experimental and deductive indications[3,5,15] that α_R would be +1 for any monomer: in the absence of any significant source of free radicals in the aqueous phase, any desorbed free radicals must eventually reenter a latex particle. Now, as explained in the Methodology section, if α_R were to be +1, eq 10 would not hold. However, this contradicts experiment, since the data fit eq 10 (i.e., the only radical loss process is first order). (ii) Hence the first-order loss process in the relaxation mode must involve first-order disappearance of the free radicals without desorption into the aqueous phase. There are a number of plausible mechanisms for this, which will be discussed in the succeeding section. If the first-order loss does not involve desorption, then $\alpha_R = 0$. (iii) Since $\alpha_R = 0$, the observed value of $k(1 - \alpha_R)$ must be the value of k: thus $k = 7 \times 10^{-3}$ s^{-1}. (iv) The relaxation data thus show that k is independent of particle size (since, as stated above, the size changes by a large amount during the runs, yet k is observed to remain constant).

Combination of all these data yields a value for the quantity $k_p q$ (recall q is the partition coefficient for monomer between the aqueous phase and the locus of polymerization). One thus obtains $k_p q = 6 \times 10^2$ dm^3 mol^{-1} s^{-1}. An independent measurement of q would thus yield k_p.

We briefly consider the behavior in the source. Q_A (and hence ρ_I) shows a definite trend with γ flux and (within the uncertainty engendered by the small range of this quantity) is linear therein. This is entirely consistent with 100% capture efficiency as observed with chemical initiation. The mean values of the background thermal rate [$(1.5 \pm 1) \times 10^{-5}$ s^{-1} from the relaxation results and $(1.7 \pm 1) \times 10^{-5}$ s^{-1} from the in-source results] are in agreement with that from extrapolation of the chemically initiated results (ca. 1.5×10^{-5} s^{-1}). One notes that the in-source thermal rate will differ by a factor of $(1 - \alpha_I)$ from the others; the data suggest that α_I must be close to zero. The scatter in κ_I values is too great to enable any statement about the dependence of this quantity on γ flux to be made. However, we note that κ_R [$(10 \pm 2) \times 10^{-3}$ s^{-1}] may be greater than κ_I [$(7 \pm 3) \times 10^{-3}$ s^{-1}]; this could be due to some termination with OH· from the γ radiolysis (i.e., α_I is slightly less than zero). These arguments are however suggestive rather than indicative.

We make no attempt in the present work to fit runs where no steady state is observed. Lack of a steady state was sometimes seen with very high [I] and can be ascribed to a number of causes: for example, (i) ρ_A (or equivalently capture efficiency) may vary with monomer concentration in the aqueous phase, or (ii) at high ionic strength or free radical flux, k may vary with monomer concentration, particle surface area, etc., or (iii) second-order loss (i.e., termination) starts to become important, and c may vary with monomer concentration, etc.; or (iv) the linearity between $[M_L]$ and $[M_{aq}]$ may no longer hold (due to nonlinearity in the adsorption isotherm). Elucidation of these possibilities must await further work.

Mechanistic Conclusions

(i) Free Radical Concentration. The results for α_I ($0 \gtrsim \alpha_I > -1$) and α_R ($\simeq 0$) given above imply that for chemical initiation, the value of α (which we denote α_C) is likely to lie between 0 and −1. For simplicity, we shall assume here that $\alpha_C = 0$; this will at worst introduce an error of a factor of 2 in the resulting deductions. Assuming $\alpha_C = 0$, we have $k(1 - \alpha_C) = k$. From our data, we can then estimate the steady-state average number of free radicals per polymerization locus, from $\bar{n}_{SS} = \rho_A/k = 2k_d[I]N_A/kN_c$. For a typical initiator concentration of 10^{-3} mol dm^{-3} and $k_d = 1.3 \times 10^{-6}$ s^{-1} at 50 °C,[20] this yields $\bar{n}_{SS} \simeq 250$. This

is a very high value, which is only possible if the locus of polymerization is of very high viscosity. This is consistent with the supposition that the locus of polymerization is an isolated macroradical on the surface of a glassy polymer latex particle.

(ii) Propagation Rate Coefficient. From the results for the quantity $2k_pqk_d/k(1 - \alpha_C)$ obtained from chemical initiation data, we may estimate k_p assuming that $\alpha_C = 0$ together with estimates of k_d (see above) and the partition coefficient q (the ratio of the equilibrium concentration of monomer on the surface to that in the aqueous phase). No independent measures of q are yet available, and arguments for virtually any value could be put forward. If we assume q lies in the range 0.5–2, we find $k_p = 6 \times 10^2/q$ lies between 12×10^2 and 3×10^2 dm^3 mol^{-1} s^{-1}. This is similar to the value of k_p of many other monomers at 50 °C. This value of k_p obtained by assuming $q \simeq 1$ is however in disagreement with the high values often reported for acrylonitrile in solution. However, k_p would be expected to be strongly solvent dependent for such a polar monomer and also to depend strongly on whether the propagation process is heterogeneous (as is the present case) or homogeneous (in solution). Clearly, further work is required.

(iii) Radical Capture Efficiency. It has been shown that capture efficiency is 100%. This is as predicted by theory[21] for a monomer which is as water-soluble as acrylonitrile.

(iv) First-Order Loss. We have established that over a substantial range of fractional conversion, free radical loss is by a pseudo-first-order process, except at the highest free radical fluxes used here. Moreover, it was established that in this system (except possibly at the highest free radical fluxes), first-order loss cannot be by complete desorption of free radicals into the aqueous phase. A precise value is given for the first-order loss rate coefficient, which can in the future be compared with quantitative theory.

Coincidentally, the value deduced for k (7×10^{-3} s^{-1}) is of similar magnitude to that in styrene emulsion polymerization systems with latex particles of similar sizes.[3,17,19,22] In the styrene system, the observed value of k and its (comparatively large) variation with particle size,[3,18] temperature,[3,19] added chain-transfer agent,[22] and agents to make monomer more soluble in the aqueous phase[22] are all in excellent quantitative accord with the Nomura–Harada transfer/diffusion theory for desorption.[23]

We now consider possible mechanisms for the first-order loss process in acrylonitrile. Any postulated mechanism must be consistent with our deductions that (i) k is independent of particle size and (ii) k does not involve complete desorption of the free radicals into the aqueous phase. This second deduction implies that first-order loss must take place entirely on, or very close to, the surface of the particles. Now, it has been shown[3,17,19,22] that first-order loss in emulsion polymerization systems is through transfer to monomer (or to chain-transfer agent) followed by complete diffusion away from the particles. Such cannot be the case here.

(1) One mechanism that has been suggested for first-order loss is free radical burial:[7,10] In this mechanism, it is supposed that a growing free radical becomes buried in the glassy matrix of the polymer particle, thereby being unable to propagate; thereafter the buried free radical may undergo termination with another free radical, this second step not being rate determining as far as polymerization is concerned, since propagation has already ceased. It has been suggested on the basis of ESR studies in bulk systems[8] that this mechanism is unlikely in a bulk medium; the relevance of such arguments to the present aqueous systems is difficult to assess.

In the present system, burial could not be through oligomeric free radicals attaching themselves to the particle, since in the relaxation studies, there are no such oligomeric units in the aqueous phase. Moreover, burial by such entities would imply a rate that depends on the surface area of the particle; this is in contradiction to our experimental result that k is independent of particle size.

(2) A plausible mechanism for first-order loss is through the propagating end of the macroradical becoming inaccessible to monomer. This can readily be envisaged to occur, for example, by a growing chain following a path (by accreting monomer) that is a "blind alley": the free radical may grow so that it becomes surrounded by a glassy polymer matrix through which no further monomer can diffuse. Alternatively, propagation may place the free radical chain ends in such close proximity to the surface that further monomer addition is precluded on steric grounds: the absence of backbone rotations in the glassy state would freeze the stunted chains in these hindered, nonpropagating conformations. Termination with another free radical (a second-order process) might eventually take place, but this would be on a much slower time scale, and thus the loss of free radical activity (now that the free radical in question can no longer propagate) would appear kinetically first order. Note that such mechanims are only possible for the case of a monomer that is insoluble in its own polymer and/or exists in the glassy state.

(3) Another mechanism that has been suggested[12] for first-order loss is geminate free radical recombination: here, it is postulated that free radicals from the aqueous phase may undergo attachment to the particles in pairs, their recombination being slow because they are immobilized in a glassy precursor particle formed by aqueous-phase propagation (such an attachment mechanism would still yield ρ_A proportional to [I], except that now the efficiency need not be 100%). These "siamese twin" free radicals could undergo termination once they reach the surface of the particle, which is likely to be less glassy than the precursor. However, the rate for this process would depend on the surface area of the particles, in contradiction to our data. The geminate recombination mechanism can thus be excluded for the systems studied here.

(4) Another possibility is a transfer mechanism[23] confined to or near the particle surface. One could suppose that transfer of free radical activity to a monomer unit is a rate-determining step, which would imply first-order kinetics; this monomeric free radical could then undergo rapid (non-rate-determining) termination on the surface of the particle, without undergoing desorption. Such a possibility can be excluded by the following analysis. The suggested mechanism implies that the termination event must take place before the free radical arising from transfer can undergo significant propagation. Thus this mechanism involves the following events: transfer ($R_L\cdot + M_L \rightarrow M\cdot$), termination ($M\cdot + R_L\cdot \rightarrow$ inert product), and propagation ($M\cdot + M_L \rightarrow$ new macroradical). The pseudo-first-order loss rate coefficient would then be given by

$$k = k_{tr}[M_L] + (k_t k_{tr}[M_L][R_L\cdot]/(k_t[R_L\cdot] + k_p[M_L]))$$

Here k_t is the termination rate coefficient. It can be seen that this cannot yield a k that is independent both of $[M_L]$ and of $[R_L\cdot]$, in contradiction to our experimental observations that the first-order loss is independent of monomer concentration and is a true first-order process; i.e., k is independent of $[R_L\cdot]$.

Our present data appear to be consistent only with first-order loss occurring through the growing free radical

becoming inactive by growing so that it can no longer have access to fresh monomer: mechanism 2 above. A slower bimolecular termination may subsequently take place. This conclusion could be tested by quantitative ESR.[24]

The observed increase in $(1 - \alpha_I)k$ with high radiation flux could easily be ascribed to a number of mechanisms, including some eliminated above for first-order loss in the relaxation mode: for example, burial by entering colloidal free radicals. A likely alternative mechanism is that some aqueous-phase heterotermination may become operative at high dose rate. The present data are insufficient to properly distinguish between the various possibilities.

Rationalization of Earlier Results. (i) We have shown unambiguously that there is a first-order loss present in these systems. This presence is in accord with the interpretation given to data of a number of other workers[10,12] in bulk systems; there is no need to explain such results in terms of a varying k_p.[25] (ii) We have also shown that the rate coefficient for propagation for acrylonitrile in our systems may fall in the same range as that of most other monomers at the temperature studied, without any need to invoke an anomalously high k_p value.[9] We note that some workers have reported a very high k_p in aqueous systems based on the assumption that $\bar{n}$ is $^1/_2$; it is clear that this apparently high k_p arises simply because the true $\bar{n}$ is much greater than $^1/_2$. (iii) Our results strongly suggest that the locus of polymerization is entirely on or near the particle surface. This is in accord with bulk results that suggest a high free radical concentration.[7,8,11,12] Thus the present aqueous systems behave similarly to diluted bulk systems, and no special mechanisms for the former need be invoked (contrary to some claims in the past[9]).

We finally conclude that the application of the methodology hitherto well established[3] for the elucidation of growth mechanisms in emulsion polymerization systems can be successfully applied to aqueous-phase heterogeneous polymerizations and that the mechanistic interpretations resulting therefrom are both physically reasonable and in accord with those in many other systems.

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Glossary of Symbols

A	$k_p q N_c / N_A$
c	pseudo-first-order rate coefficient for second-order loss of free radical activity by termination
C_R, C_I	fitted quantities in eq 11 and 12 allowing for experimental uncertainties in removal time, etc.
[I]	initiator concentration
k	rate coefficient for first-order loss of free radical activity
k_d	initiator decomposition rate coefficient
k_p	propagation rate coefficient
$[M_{aq}]$	monomer concentration in aqueous phase
$[M_L]$	monomer concentration in polymerization locus
N_A	Avogadro's constant
N_c	particle number density
N_i	number of polymerization loci with i free radicals associated with them
$\bar{n}$	average number of free radicals per polymerization locus
$\bar{n}_{SS}$	value of $\bar{n}$ in steady state
q	monomer partition coefficient between polymerization locus and aqueous phase
Q_A	$Q_I + Q_T$
Q_I	$A\rho_I/\kappa_I$
Q_R	value of Q_A^* from previous insertion
Q_T	$A\rho_T/\kappa_R$
$[R_L\cdot]$	radical concentration in polymerization locus
V_L	volume of individual polymerization locus
V_s	swollen volume of particle in emulsion polymerization
x	fractional conversion to polymer
α	"fate parameter" given relative importance of reentry, heterotermination, etc., if free radicals desorb (α_C, value with chemical initiator; α_I, value in γ source; α_R, value in relaxation mode)
κ	$(1 - \alpha)k$ [$\kappa_I = (1 - \alpha_I)k$; $\kappa_R = (1 - \alpha_R)k$]
ρ	overall entry rate coefficient into polymerization locus ($\rho = \rho_A + \alpha k\bar{n}$)
ρ_A	component of ρ from initiator and background thermal free radical sources ($\rho_A = \rho_I + \rho_T$)
ρ_I	component of ρ_A arising from initiator decomposition
ρ_T	background thermal component of ρ_A

Registry No. $H_2C{=}CHCN$, 107-13-1.

References and Notes

(1) Parts, A. G.; Elbing, E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1975**, *16*, 211. Parts, A. G.; Elbing, E. *ACS Symp. Ser.* **1976**, *No. 24*, 133.
(2) Lyons, C. J.; Elbing, E. *J. Macromol. Sci., Chem.* **1982**, *A17*, 113. Elbing, E.; McCarthy, S. J.; Snowdon, S.; Coller, B. A. W.; Wilson, I. R. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 943.
(3) Gilbert, R. G.; Napper, D. H. *J. Macromol. Sci., Rev. Macromol. Chem.* **1983**, *C23*, 127.
(4) Lichti, G.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 269. Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1984**, *17*, 2520.
(5) Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3225. Halnan, L. F.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2851.
(6) Chapiro, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1950**, *47*, 747, 764.
(7) Bamford, C. H.; Jenkins, A. D. *Proc. R. Soc. London, Ser. A* **1953**, *216*, 515; **1955**, *228*, 220. Bamford, C. H.; Jenkins, A. D.; Johnson, R. *Ibid.* **1957**, *241*, 364.
(8) Bamford, C. H.; Jenkins, A. D.; Ingram, D. J. E.; Symons, M. C. R. *Nature (London)* **1955**, *175*, 894. Bamford, C. H.; Jenkins, A. D. *J. Polym. Sci.* **1954**, *14*, 511; **1956**, *20*, 405.
(9) Dainton, F. S.; Seaman, P. H.; James, D. G. L.; Eaton, R. S. *J. Polym. Sci.* **1959**, *34*, 209. Dainton, F. S.; Seaman, P. H. *J. Polym. Sci.* **1959**, *39*, 279. Dainton, F. S.; James, D. G. L. *J. Polym. Sci.* **1959**, *39*, 299. Dainton, F. S.; Eaton, R. S. *J. Polym. Sci.* **1959**, *39*, 313.
(10) Thomas, W. M. *Adv. Polym. Sci.* **1961**, *2*, 401. Thomas, W. M.; Pellon, J. J. *J. Polym. Sci.* **1954**, *13*, 329. Thomas, W. M.; Gleason, E. H.; Mino, G. *J. Polym. Sci.* **1957**, *24*, 43.
(11) Peebles, L. H. In *High Polym.* **1964**, *18*, Chapter 9.
(12) Lewis, O. G.; King, R. M. *Adv. Chem. Ser.* **1969**, *No. 91*, 25.
(13) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.
(14) Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol.* **1976**, *49*, 536.
(15) Whang, B. C. Y.; Napper, D. H.; Ballard, J. M.; Gilbert, R. G.; Lichti, G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1117.
(16) Penboss, I. A.; Gilbert, R. G.; Napper, D. H. *J. Chem. Soc., Faraday Trans. 1*, in press.
(17) Hawkett, B. H.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1323.
(18) Ballard, M. J.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 533.
(19) Lansdowne, S. W.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1344.
(20) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055, 5118.
(21) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 3173.
(22) Lichti, G.; Sangster, D. F.; Whang, B. C. Y.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2129. Adams, M.; Sangster, D. F.; Napper, D. H.; Gilbert, R. G. *J.*

Chem. Soc., Faraday Trans. 1, in press.
(23) Nomura, M. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic: New York, 1982.
(24) Ballard, M. J.; Gilbert, R. G.; Napper, D. H.; Pomery, P. J.; O'Donnell, J. H. *Macromolecules* **1984**, *17*, 504; *Ibid.* **1986**, *19*, 1291.
(25) Burillo, G.; Chapiro, A.; Mankowski, Z. *Eur. Polym. J.* **1984**, *20*, 653.

Notes

Synthesis of Poly[1-(trimethylsilyl)-1-propyne] with Extremely High Molecular Weight by Using $TaCl_5$–Ph_3Bi (1:1) Catalyst[1]

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Recently, not only the polymerization of acetylene but also that of substituted acetylenes has been intensively studied.[3] We have succeeded in the synthesis of various substituted polyacetylenes.[4] 1-(Trimethylsilyl)-1-propyne [$CH_3C{\equiv}CSi(CH_3)_3$] polymerizes with the pentahalides of tantalum and niobium ($TaCl_5$ and $NbCl_5$) alone [2b,5] to give a new polymer having weight-average molecular weights ($\bar{M}_w$'s) of 1×10^5–1×10^6. Poly[1-(trimethylsilyl)-1-propyne] is white, soluble, air-stable, and electrically insulating, which gives a striking contrast to the properties of polyacetylene. Further, this polymer has proved to exhibit the highest oxygen permeability among all the existing polymers.[5,6]

Organometallics of group 4 and 5 main-group metals (e.g., Ph_4Sn, Et_3SiH, Ph_3Bi) work as weak reducing agents and eventually play important roles as cocatalysts in the polymerization of substituted acetylenes by group 5 and 6 transition-metal catalysts. For instance, the polymerization of disubstituted acetylenes (e.g., 1-phenyl-1-propyne, 2-octyne, 1-chloro-2-phenylacetylene) by WCl_6 or $MoCl_5$ yields polymers only in the presence of these cocatalysts.[4] As another example, polymer degradation occurs in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$, whereas it is restrained in the presence of the cocatalysts, resulting in the formation of high molecular weight poly(1-phenyl-1-propyne).[7]

Here we report the synthesis of high molecular weight poly[1-(trimethylsilyl)-1-propyne] with a catalyst system composed of a equimolar mixture of $TaCl_5$ and Ph_3Bi [1:1 $TaCl_5$–Ph_3Bi]. In the course of our study on the cocatalyst effect, it was found that the $TaCl_5$–Ph_3Bi catalyst achieves extremely high $\bar{M}_w$, up to 4×10^6. This molecular weight is the highest among those of the substituted polyacetylenes ever known.[3,4] The influences of various cocatalysts and polymerization conditions are also discussed.

Results and Discussion

Table I shows the effect of various cocatalysts on the polymerization of 1-(trimethylsilyl)-1-propyne by $TaCl_5$ and $NbCl_5$. Polymerizations were run in toluene at 80 °C for 24 h. $TaCl_5$ alone yielded quantitatively poly[1-(trimethylsilyl)-1-propyne] having a $\bar{M}_w$ somewhat lower than 1×10^6 [$\bar{M}_w$'s and number-average molecular weights ($\bar{M}_n$'s) were determined by gel permeation chromatography (GPC)]. It is of great interest that an equimolar mixture of $TaCl_5$ and Ph_3Bi afforded the polymer with $\bar{M}_w$ as high as 4×10^6 without reducing the polymer yield. Organoantimony, -tin, and -silicon cocatalysts also increased the $\bar{M}_w$ of the polymer to ca. 1.5×10^6–3.5×10^6 but reduced somewhat the polymer yield.

Table I
Polymerization of 1-(Trimethylsilyl)-1-propyne by Various $TaCl_5$- and $NbCl_5$-Based Catalysts[a]

catalyst	polymer[b] yield, %	$\bar{M}_w \times 10^{-4}$ [c]	$\bar{M}_n \times 10^{-4}$ [c]
$TaCl_5$	100	84	19
$TaCl_5$–Ph_3Bi	100	400	180
$TaCl_5$–Ph_3Sb	86	360	150
$TaCl_5$–Ph_4Sn	88	240	100
$TaCl_5$–n-Bu_4Sn	51	280	77
$TaCl_5$–Ph_3SiH	83	170	72
$TaCl_5$–Et_3SiH	65	260	100
$NbCl_5$	100	32	22
$NbCl_5$–Ph_3Bi	84[d]		
$NbCl_5$–Ph_4Sn	22[d]		
$NbCl_5$–Ph_3SiH	35[d]		

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [cat] = [cocat] = 10 mM. [b] Methanol-insoluble products; the polymer yields agreed with the monomer conversions. [c] Determined by GPC. [d] Virtually insoluble in toluene.

The polymer produced with 1:1 $TaCl_5$–Ph_3Bi under the conditions given in Table I completely dissolved in such solvents as toluene and chloroform. The GPC curve of this polymer was unimodal, and its dispersity ratio ($\bar{M}_w/\bar{M}_n$) was ca. 2. These mean that the molecular weight distribution is the most probable distribution and that the polymerization proceeds in a homogeneous system.

In the case of the $NbCl_5$ catalyst by itself, the polymer formed was totally soluble in toluene. In general, however, the polymers obtained in the presence of cocatalysts were virtually insoluble (Table I). This insolubility might be based on a difference in the geometric structure of the main chain.

Use of Ph_3Bi as a cocatalyst appreciably accelerates the polymerization by $TaCl_5$ to achieve 100% yield within 30 min under the conditions shown in Figure 1.[8] Unlike the case of 1-phenyl-1-propyne,[7] polymer degradation is not observed, irrespective of the presence or absence of Ph_3Bi. The addition of the cocatalyst increases the $\bar{M}_w$ of polymer by about 5 times. This result indicates that a more active propagating species forms in a smaller quantity in the polymerization by the $TaCl_5$–Ph_3Bi catalyst than that in the polymerization by $TaCl_5$ alone. Though the active species formed from the $TaCl_5$–Ph_3Bi catalyst has not been identified, probably Ph_3Bi will reduce $TaCl_5$ to form an active species which contains a moiety of Ph_3Bi, propagates quickly, and hardly undergoes the transfer and termination reactions.

Solvent effects on the polymerization were examined by using $TaCl_5$–Ph_3Bi, which had achieved the highest $\bar{M}_w$. Polymer yield reached 100% in the hydrocarbon and halogenated hydrocarbon solvents shown in Table II. The polymers obtained in cyclohexane and 1,2-dichloroethane, however, were partly insoluble, and the $\bar{M}_w$ of the polymer formed in chlorobenzene was lower than that in toluene.

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