Free-Radical Polymerization with Long-Chain Branching: Batch Polymerizations of Vinyl Acetate in t-Butanol

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Synopsis

Vinyl acetate was batch polymerized at 60°C in t-butanol solution. Conversion and molecular weights were measured as functions of time for several initiator and solvent concentrations. Although the overall rate constant depends somewhat on solvent concentration, the reaction is first order in monomer concentration up to at least 60% conversion and one-half order in the concentration of initiator. Molecular weights were independent of initiator concentration, confirming that the polymerization is transfer dominated. Measurements of $\bar{M}_w$ and $\bar{M}_n$ versus conversion were used to establish the individual transfer constants. All are independent of solvent concentration, except C_p, the polymer transfer constant, which decreases systematically with increasing solvent concentration.
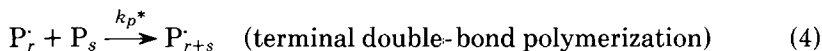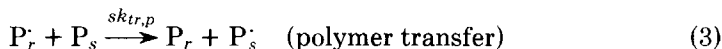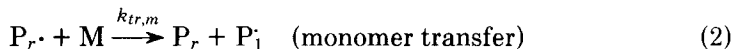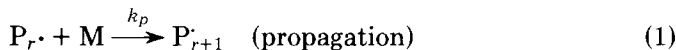
INTRODUCTION

Several years ago, we published a comparison of rates and molecular weights for the batch and continuous stirred tank reactor (CSTR) polymerization of vinyl acetate.[1,2] The purpose was to test in some detail the calculations of molecular weight distribution in continuous polymerizations with kinetic parameters obtained from batch studies. The reaction scheme was complex, involving long-chain branching as well as the usual initiation, propagation, and termination reactions. Batch studies in solution showed first-order kinetics with respect to conversion, but only after an initial inhibition period. Average molecular weights increased with conversion in accordance with calculations based on the kinetic parameters from bulk polymerization, supplemented by an experimental value for the solvent transfer constant. In CSTR polymerizations, the molecular weight increased with conversion more rapidly than in batch, as expected qualitatively from the mechanism. The conversion dependence of molecular weight agreed with predictions for a reactor which is perfectly macromixed but completely segregated. However, the rates were lower and the molecular weights at low conversions were smaller than those in the batch reactor, in direct conflict with the basic reaction scheme. Thus, the validity of the kinetic scheme in continuous reactors was placed in some doubt, and conclusions about the degree of local mixedness could not be drawn with confidence.

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The current work was undertaken to settle these unresolved questions. This paper describes several sets of batch studies dealing with the effects of monomer concentration, initiator concentration, and reactant impurities. The results of a new series of CSTR studies will be published elsewhere.[3]
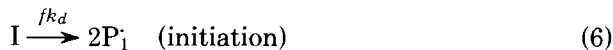
MECHANISM

Earlier studies on bulk free-radical polymerization led to the following set of elementary reactions for vinyl acetate:[4,5]

$$P_r\cdot + M \xrightarrow{k_p} P_{r+1}^{\cdot} \quad \text{(propagation)} \tag{1}$$

$$P_r\cdot + M \xrightarrow{k_{tr,m}} P_r + P_1^{\cdot} \quad \text{(monomer transfer)} \tag{2}$$

$$P_r^{\cdot} + P_s \xrightarrow{sk_{tr,p}} P_r + P_s^{\cdot} \quad \text{(polymer transfer)} \tag{3}$$

$$P_r^{\cdot} + P_s \xrightarrow{k_p^*} P_{r+s}^{\cdot} \quad \text{(terminal double-bond polymerization)} \tag{4}$$

In solution polymerization, one must consider radical transfer to solvent also:

$$P_r\cdot + S \xrightarrow{k_{tr,s}} P_r + P_1^{\cdot} \quad \text{(solvent transfer)} \tag{5}$$
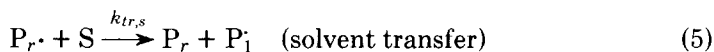
The overall rate of conversion of monomer to polymer depends on the total radical concentration, which in turn is governed by radical initiation and termination:

$$I \xrightarrow{fk_d} 2P_1^{\cdot} \quad \text{(initiation)} \tag{6}$$

$$P_r^{\cdot} + P_s^{\cdot} \xrightarrow{k_t} \text{nonradical products} \quad \text{(termination)} \tag{7}$$

The rate of conversion is related to initiator and monomer concentrations through the usual stationary state approximation for the total radical population:

$$-\frac{d[M]}{dt} = k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [M][I]^{1/2} \tag{8}$$

or

$$\frac{dx}{dt} = \lambda [I]^{1/2} (1 - x) \tag{9}$$

in which f is the initiator efficiency, λ is the combination $k_p(fk_d/k_t)^{1/2}$, and x is the fractional conversion of monomer at time t.

Differential equations for the moments of the molecular weight distribution can be derived from population balances on the individual radical and polymer species. When transfer reactions, eqs. (2), (3), and (5), are much more frequent than termination, the distribution of molecular weights becomes independent of initiator concentration and conversion rate, and the moments can be expressed

as functions of conversion alone.[1,6] For batch polymerization, the expressions for the first three moments are[1]

$$\frac{dQ_0}{dx} = C_m - \frac{KQ_0}{1-x} + \frac{C_s S}{1-x} \tag{10}$$

$$\frac{dQ_1}{dx} = 1 \qquad (Q_1 = x) \tag{11}$$

$$\frac{dQ_2}{dx} = \frac{2}{1-x} \frac{(1-x+KR)(1-x+KR+C_pQ_2)}{C_m(1-x) + C_px + C_sS} \tag{12}$$

in which R is given by

$$\frac{dR}{dx} = \frac{C_pR(1-x) + C_m(1-x)^2 - KR[C_sS + C_p(x-R)]}{(1-x)[C_m(1-x) + C_px + C_sS]} \tag{13}$$

In the above, Q_m is $\Sigma_{r=1}^{\infty} r^m[P_r]$, in which $[P_r]$ is the concentration of r-mers at conversion x (moles per initial mole of monomer) and S is the initial mole ratio of solvent to monomer $[S]_0/[M]_0$. The initial values of Q_m and R are all zero. The average molecular weights depend on the moments

$$\overline{M}_n = m_0 \frac{Q_1}{Q_0} = m_0 \overline{DP}_n \tag{14}$$

$$\overline{M}_w = m_0 \frac{Q_2}{Q_1} = m_0 \overline{DP}_w \tag{15}$$

in which m_0 is the mer molecular weight, 86 in the case of poly(vinyl acetate). The moment equations can be integrated numerically and compared with experimental data on $\overline{M}_n$ and $\overline{M}_w$ versus x to establish the four kinetic parameters: the monomer transfer constant $C_m = k_{tr,m}/k_p$; the polymer transfer constant $C_p = k_{tr,p}/k_p$; the solvent transfer constant $C_s = k_{tr,s}/k_p$; and the terminal double-bond reactivity $K = k_p^*/k_p$.

EXPERIMENTAL PROCEDURES

The polymerization system is shown in Figure 1. All surfaces in contact with monomer are either stainless steel, glass, or Teflon. The reaction vessel is a 1-liter glass resin flask, fitted with an exit line at the bottom for withdrawing samples. The top is a stainless steel plate clamped to the flange of the resin flask and fitted with lines for admitting the monomer–solvent–initiator mixture, water from a constant-temperature bath for the heating coils, a thermocouple, argon gas, and the stirrer shaft.

A 5-psi pressure relief value was mounted on the top plate. The standard operating pressure was only about 0.5 psig, however, maintained by a very slow inflow of argon and a controlled leakage out through the stirrer stuffing box.

Polymerization-grade vinyl acetate (Celanese Chemical Company) was distilled at reduced pressure under an atmosphere of argon (99.997% purity) in a packed column. A middle fraction was collected in a closed transfer bottle and stored under argon in a refrigerator.

The solvent was t-butyl alcohol (Baker, analyzed grade). Argon was bubbled through the t-butyl alcohol for about 15 min before mixing with monomer in order to remove oxygen. Comparative experiments on polymerization rates and
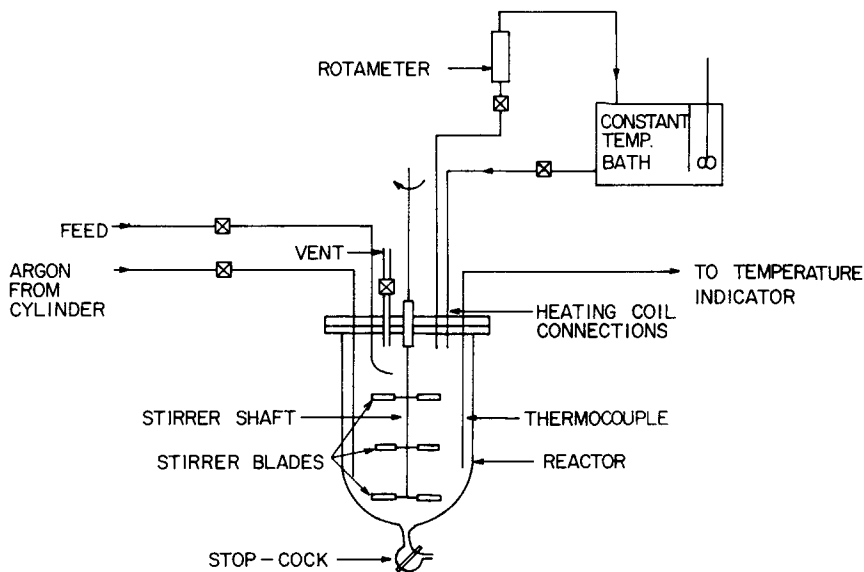
Fig. 1. Diagram of polymerization reactor.

on the molecular weights obtained showed that more elaborate solvent purification, such as distillation or freeze–thaw cycling and decantation, was unnecessary.

The initiator was azobisisobutyronitrile (AIBN) (Eastman Kodak Co.). Its decomposition rate constant k_d at 60°C in organic solvents[7] is approximately 9×10^{-6} sec^{-1}, corresponding to a half-life of approximately 21 hr. The desired amount of AIBN was weighed, placed in a closed transfer bottle, and dissolved in a few ml of t-butyl alcohol. The bottle was purged with argon and connected to the vessel containing the purified vinyl acetate via a short length of Teflon tubing. The desired volume of vinyl acetate was then transferred by pressure. The t-butyl alcohol was added similarly. The contents were mixèd and transferred by argon pressure into the argon-purged reactor. The reactor was first rinsed and then filled with about 800 ml of the mixture. A slow flow of argon into the reactor was maintained continuously to exclude atmospheric oxygen. Careful exclusion of oxygen at all stages of monomer preparation resulted in polymerization without an inhibition period, in contrast to results in the earlier studies.[2,8]

Stirring was begun, and the reactor was heated by hot water flowing through the coils. The temperature reached 60°C within 5–6 min, at which point timing was begun. Throughout the run, the temperature and flow rate of water through the coils were adjusted to keep the reactor temperature at 60° ± 0.5°C.

Samples were withdrawn periodically for determination of molecular weight and conversion. The stopcock at the bottom of the reactor was opened, and the first 5 ml were discarded. The next 10–30 ml were collected and the polymer recovered immediately by precipitation with a large excess of heptane for the molecular weight determinations. After vacuum drying at room temperature, the samples were taken up in benzene and freeze dried. A separate sample for conversion determination was then collected in a preweighed glass vial. The

TABLE I
Conversion and Molecular Weights of Batch Poly(Vinyl Acetates)

S	$[I]_0$, moles/liter	t, hr	$A*$	x	$\overline{M}_n$	$\overline{M}_w$
2.0	0.42×10^{-3}	.57	.995	.073	—	6.06×10^5
		1.07	.991	.148	2.77×10^5	6.34
		2.07	.983	.265	2.62	6.52
		3.07	.976	.395	—	7.15
		4.07	.968	.475	2.82	8.37
		5.07	.960	.558	—	8.79
		5.82	.954	.600	3.08	9.40
2.0	1.00×10^{-3}	0.25	.998	.058	2.58	—
		0.75	.994	.158	—	5.98
		1.25	.990	(.259)a	2.68	6.34
		1.75	.986	.326	—	6.58
		2.25	.982	.407	—	7.23
		2.75	.978	.487	—	8.39
		3.33	.974	.570	—	8.83
		3.58	.972	.584	—	9.64
2.0	1.60×10^{-3}	.66	.995	.188	2.68	6.31
		1.16	.991	.293	—	—
		1.66	.987	.369	2.79	6.91
		2.16	.983	.518	—	—
		2.66	.979	.560	2.92	8.95
		3.16	.975	.672	—	—
		3.66	.971	.797	—	—
3.0	1.00×10^{-3}	.25	.998	.041	—	—
		.50	.996	.085	2.53	—
		1.0	.992	.166	2.49	5.24
		1.5	.988	.245	2.78	—
		2.0	.984	.314	—	5.83
		2.5	.980	.401	—	—
		3.0	.976	.445	—	6.52
		3.5	.972	.502	—	—
		4.0	.968	.550	—	7.13
		4.5	.964	.604	—	—
		5.0	.961	.634	—	7.75
		5.5	.957	.670	—	—
		6.0	.953	.706	—	8.68
6.0	1.00×10^{-3}	0.25	.998	0.001	—	—
		2.25	.982	(.173)a	—	—
		3.75	.970	(.274)a	1.85	4.18
		5.25	.959	.361	1.93	4.21
		6.75	.947	.438	—	3.99
		8.25	.936	.505	—	4.02
		9.75	.925	.560	—	4.11

a Values of x in parentheses were obtained by interpolation for use in Figures 5 and 7.

amount of this sample varied from 5–15 ml at low conversions to 1–2 ml at high conversions. The vial was weighed immediately, heptane was added to precipitate the polymer, and the supernatant liquid was quickly evaporated in a vacuum oven at room temperature. After one day, the temperature was raised to 60 °C and evacuation was continued until a constant weight was attained. The fractional conversion was calculated from the sample weight, the weight of recovered polymer, and the original solvent–monomer ratio.

Number-average molecular weight $\overline{M}_n$ was determined by osmotic pressure measurements with the Mechrolab Model 501 High Speed Membrane Osmometer. Osmotic pressure was determined at 37°C for dilute solutions in toluene and analyzed as described elsewhere.[5] Values of $\overline{M}_n$ obtained are given in Table I.

Weight-average molecular weight $\overline{M}_w$ was determined by light-scattering measurements at room temperature with the FICA-50 Automatic Light Scattering Photometer. Unpolarized light of wavelength 546 nm was used; the solvent was methyl ethyl ketone. The data were analyzed as described elsewhere.[5,9] Values of $\overline{M}_w$ obtained are given in Table I.

Conversion and the molecular weights as functions of polymerization time were measured for three initiator concentrations and three initial solvent–monomer ratios.

ANALYSIS OF CONVERSION DATA

For the times of polymerization used here, the effect of initiator depletion is small but not altogether negligible. Initiator decomposition is a first-order process, so the initiator concentration varies with time according to

$$[I] = [I]_0 e^{-k_d t} \tag{16}$$

in which $[I]_0$ is the initial concentration. If λ is independent of conversion, eq. (9) can be integrated after substitution of eq. (16) for $[I]$:

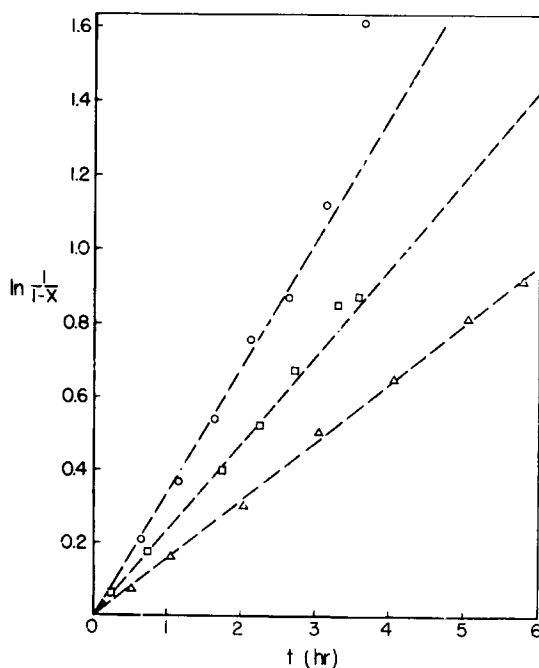$$\ln \frac{1}{1 - x} = \lambda [I]_0^{1/2} t A^* \tag{17}$$

Fig. 2. First-order plots of conversion–time data for various initiator concentrations. The solvent–monomer ratio S is 2. No correction has been applied for initiator depletion. Symbols indicate $[I]_0 = 0.42 \times 10^{-3}$ mole/liter ($\triangle$), 1.0×10^{-3} mole/liter ($\square$), and 1.6×10^{-3} mole/liter ($\bigcirc$).

in which A^* is an initiator depletion factor:

$$A^* = \frac{1 - e^{-k_d t/2}}{k_d t/2} \qquad (18)$$

With the approximate value given earlier, $k_d = 9 \times 10^{-6} \, \text{sec}^{-1}$, A^* varies practically linearly from a value of unity at $t = 0$ to a minimum value of 0.925 at $t = 9.75$ hr, the longest polymerization time used here. If no initiator depletion had occurred, A^* would be unity for all times and the usual first-order dependence on time would result:

$$\ln \frac{1}{1 - x} = \lambda [I]_0^{1/2} t \qquad (19)$$

Figure 2 shows the conversion–time data for three initial initiator concentrations with the same initial solvent–monomer ratio, plotted according to eq. (19). The appearance is practically the same if the data are corrected for initiator depletion by plotting as a function of $t^* = A^* t$. No inhibition period is observed, and straight lines are obtained up to 60% conversion. Beyond this point, the run with highest initiator concentration increases in rate. This autoacceleration is probably caused by a reduced termination rate, a common occurrence in free-radical polymerizations at high conversions. The conversion data reduce to the same curve when plotted as a function of either $[I]_0^{1/2} t$ or $[I]_0^{1/2} A^* t$. Figure 3 shows the result with $[I]_0^{1/2} A^* t$, using values of A^* calculated from eq. (18) and listed in Table I. The dashed lines in the figures indicate the original batch results of Nagasubramanian[2] and later results by Kathju[8] who used an improved system for oxygen elimination. Both had used a different source of vinyl acetate
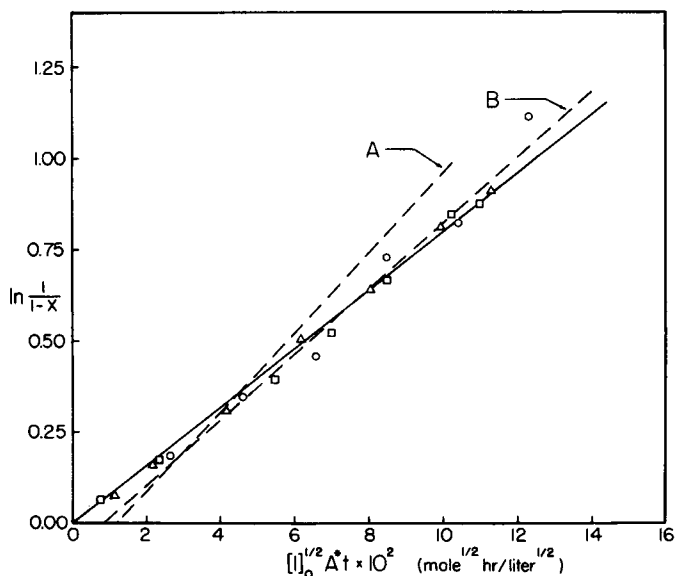

Fig. 3. Combined first-order plot for polymerizations with solvent–monomer ratio $S = 2$. Symbols have the same meanings as in Fig. 2. Dotted lines indicate earlier batch data from Nagasubramanian[2] for the same solvent–monomer ratio (line A) and Kathju[8] (line B).
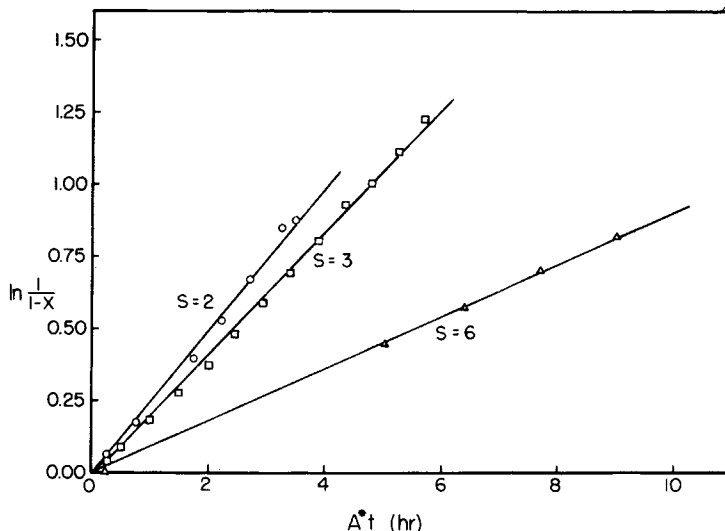
Fig. 4. First-order plots of conversion data for various solvent–monomer ratios. Initiator concentration is 1.0×10^{-3} mole/liter in all cases.

(Union Carbide) than that in the present work. The behavior at 60°C for $x <$ 0.6 and $S = 2$ is well described by

$$\ln \frac{1}{1 - x} = 8.00 \ [I]_0^{1/2} A^* t \tag{20}$$

in which the AIBN concentration and polymerization time are expressed in moles/liter and hours, respectively.

Figure 4 shows the conversion data for polymerizations with different solvent–monomer ratios but the same initiator concentration. The straight lines indicate that the reaction is essentially first order in monomer concentration in each case, so it seems likely that the lack of coincidence is due to variations in one or more factors in λ (rate constants or catalyst efficiency) with t-butanol concentration. The values of λ obtained from the slopes in Figures 3 and 4 are shown in Table II. A value for undiluted vinyl acetate is also included. An expression for initial rates obtained by Matsumato and Maeda[10] for undiluted polymerization at 60°C, initiated by AIBN,

$$-\frac{d[M]}{dt} = 1.25 \times 10^{-2} [I]^{1/2} \text{ moles/liter-sec} \tag{21}$$

gives $\lambda = 4.21$ liter$^{1/2}$/mole$^{1/2}$-hr. Analysis of recent data by Moze et al.[11] gives a similar value, $\lambda = 4.32$, under the same conditions.

ANALYSIS OF MOLECULAR WEIGHT DATA

Figure 5 shows $\overline{M}_n$ and $\overline{M}_w$ as functions of conversion for $S = 2$. Unlike the rate results, agreement in molecular weights here and in earlier batch studies[2] is reasonably good, with perhaps slightly higher (~5%) values in the current work. Samples obtained with different initiator concentrations fall along the same line. The same result had been obtained earlier in undiluted polymerizations[5] and by others[12] for similarly slow rates of initiation. This merely confirms that the
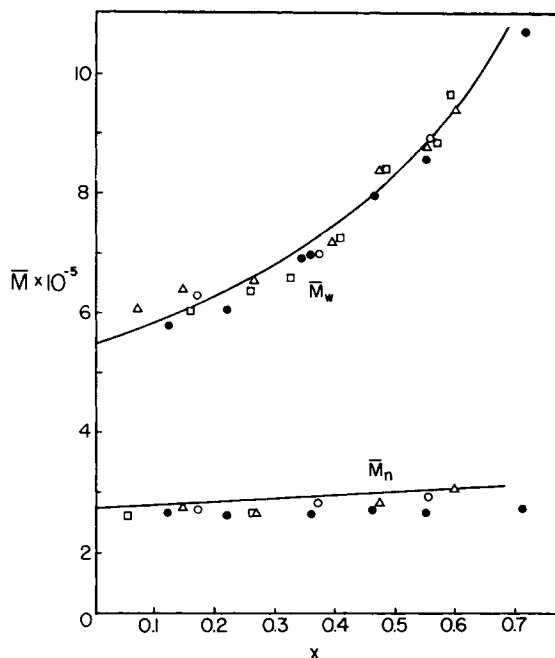
Fig. 5. Dependence of molecular weights on conversion for a solvent–monomer ratio S of 2. Symbols indicating various initiator concentrations have the same meaning as in Fig. 2. The filled circles (●) are data obtained in the earlier study.[2] The lines were calculated from eqs. (10)–(15) as described in the text.

polymerization is transfer dominated. The structure according to eqs. (10)–(13) depends only on conversion, solvent concentration, and the kinetic parameters C_m, C_s, C_p, and K.

The molecular weights at sufficiently low conversions depend only on monomer and solvent transfer rates:

$$1/(\overline{DP}_n)_0 = C_m + C_s S \tag{22}$$

Also the distribution of molecular weights should be exponential, so that

$$\overline{DP}_w/\overline{DP}_n = 2 \tag{23}$$

Values of $(\overline{M}_n)_0$ and $(\overline{M}_w)_0$ were obtained by extrapolating the experimental molecular weights to $x = 0$ for each solvent–monomer ratio and also for undiluted polymerization with data reported earlier.[5] The results are given in Table II.

TABLE II
Variation of Rate and Structural Parameters with t-Butanol Concentration

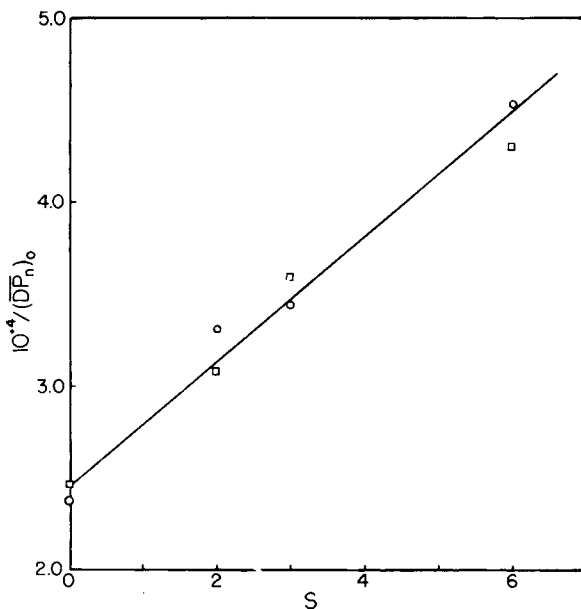| S	λ, liter$^{1/2}$mole$^{-1/2}$hr^{-1}	$(\overline{M}_n)_0$	$(\overline{M}_w)_0$	C_p
0	4.26	3.6×10^5	7.0×10^5	$2.3_6 \times 10^{-4}$
2.0	8.00	2.6	5.6	1.3
3.0	6.59	2.5	4.7_5	1.2
6.0	2.85	1.9	4.0	0.6

Fig. 6. Reciprocal of initial degree of polymerization vs. solvent–monomer ratio. Values of $(\overline{DP}_n)_0$ were calculated from $(\overline{M}_n)_0$ (○) and were estimated independently from $(\overline{M}_w)_0$, assuming $\overline{M}_w/\overline{M}_n$ = 2 at zero conversion (□).

Values of $(\overline{DP}_n)_0$ were calculated from both $(\overline{M}_n)_0$ and $(\overline{M}_w)_0$, the latter with eq. (23), and plotted according to eq. (22) (Fig. 6). Values of $C_m = 2.46 \times 10^{-4}$ and $C_s = 0.34 \times 10^{-4}$ were obtained from the intercept and slope in Figure 6.

With values of C_m and C_s inserted in the moment equations, the conversion dependence of molecular weight involves only the parameters C_p and K. According to eqs. (10)–(14), $\overline{M}_n$ versus x depends on K alone, while $\overline{M}_w$ versus x depends on both K and C_p. It became apparent that data at all solvent–monomer ratios could not be fitted with the same values of C_p and K. The predicted increase in $\overline{M}_w$ with conversion, based on C_p and K from undiluted polymerizations,[5] is greater than that observed. On the other hand, the conversion dependence of $\overline{M}_n$ calculated with $K = 0.66$, the value for undiluted polymerization, is in reasonable agreement with observations at all solvent–monomer ratios. That is, the predicted values of $\overline{M}_n$ are practically independent of conversion in the solution polymerizations, which is the behavior observed experimentally (see Table I). If K rather than C_p were taken to decrease with increasing t-butanol concentration, then $\overline{M}_w$ versus x could be fitted, but $\overline{M}_n$ would be predicted to decrease appreciably with conversion, contrary to observations. We found no alternative other than to assume that the polymer transfer constant C_p varies with the concentration of t-butanol. Values of C_p which give the best visual fit to the $\overline{M}_w$ data at each solvent concentration were determined by trial and error. The values so obtained are given in Table II; comparison of calculated and observed $\overline{M}_w$ behavior is shown in Figure 7.

The unexpected variation in C_p with solvent concentration clearly raises some questions about the postulated mechanism. However, we have been unable to develop a satisfactory alternative. The modified mechanism suggested earlier[5] requires similar variations in C_p with solvent concentration.
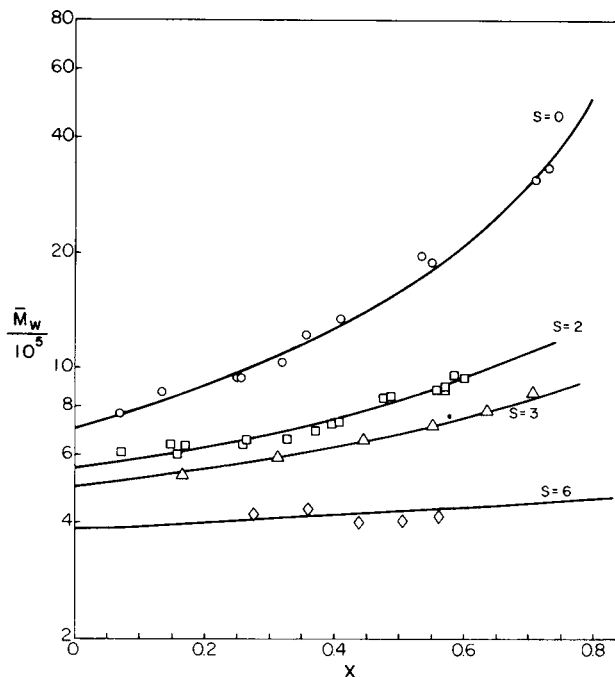
Fig. 7. Weight-average molecular weight vs. conversion for various solvent–monomer ratios. The lines were calculated from eqs. (10)–(15) as described in the text.

DISCUSSION

The batch studies confirm that vinyl acetate polymerization at 60°C in t-butanol is transfer dominated at low rates of initiation. The polymerization rate is first-order with respect to monomer up to 60% conversion and half-order with respect to AIBN concentration. There is no significant induction period. The overall rate constant λ decreases with increasing t-butanol concentration, as appears also to be the case for the polymer transfer constant C_p.

Elimination of the induction period is due in part to improvements in monomer purification and in exclusion of oxygen from the reactor. However, another important factor is the source of vinyl acetate. The monomer used in the earlier studies was derived from acetylene. Certain trace by-products of the acetylene process are very difficult to remove and may behave as inhibitors or transfer, agents.[13] We found some success with prepolymerization; but with careful distillation and exclusion of oxygen alone, we were not able to eliminate the induction period entirely.

The vinyl acetate used here is derived from ethylene. With this material, the induction period is avoidable by distillation and oxygen exclusion alone. We believe the earlier disagreement in molecular weights between batch and continuous reactor products[2] is directly related to the presence of such impurities. Their elimination or avoidance was, therefore, crucial to our further study of CSTR polymerization.

The apparent dependence of the overall rate constant λ and the polymer transfer constant C_p on the solvent concentration is puzzling. It is possible that λ changes because of variations in initiator efficiency f, although changes in the elementary rate constants with t-butanol concentration may also be responsible.

Whatever the explanation, in this transfer-dominated polymerization, the polymer structure is independent of rate. Therefore, peculiarities in λ should have no effect on the structure of CSTR products.

The apparent variation in C_p with solvent concentration is not in itself a serious matter, since all CSTR studies[3] were conducted with the same solvent concentration. It does, however, suggest complexities in the polymer transfer reaction which would be of concern in the population balance calculations. For example, an apparent reduction in C_p with dilution might reflect systematic changes in the shielding of interior segments from free-radical attack.[14] If shielding were important, the rate of polymer transfer would be less than directly proportional to molecular weight, thus violating eq. (3) even under conditions of constant solvent concentration. Such an effect should have much less influence on K, since the reactive site in this case lies out on an end of the molecule, and very little influence on C_m and C_s, as is observed. On the other hand, the recent studies of Nozakura and coworkers[15] indicate that polymer transfer occurs mainly with protons attached to the backbone carbons, while monomer transfer involves protons on the acetate group. Thus, it is conceivable that specific solvent effects could change C_p without also changing C_m, C_s, or K, thereby leaving the population balance equations unimpaired.

At present, we are inclined toward the latter explanation. Shielding must vary with polymer concentration in order to explain the variation of C_p with solvent concentration, so its effect should also vary with conversion at fixed solvent concentration. Under such conditions, it seems unlikely that good fits of $\overline{M}_w$ versus x at each solvent–monomer ratio would have been obtained with a conversion-independent value of C_p.

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