

The Kinetics of Solution Copolymerization of Vinyl Chloroacetate with Vinyl Acetate in a CSTR

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Synopsis

The kinetics of isothermal, solution copolymerization of vinyl chloroacetate (VCLAC) with vinyl acetate (VAC) in methyl isobutyl ketone (MIBK) has been investigated using a continuous flow stirred-tank reactor (CSTR). The initiator used was 2,2'-azobis 2,4-dimethyl valeronitrile (ADVN). Polymerizations were carried out to moderately high conversions, necessitating the use of a modified parameter estimation method to determine the reactivity ratios. The copolymer composition conforms to terminal model kinetics. The values obtained for r_1 and r_2 are 1.18 and 0.80, respectively, with VCLAC as M_1 and VAC as M_2 . Both values are close to unity indicating random copolymerization. The cross termination factor ϕ strongly depends on the composition of the comonomer feed ratio, implying that the chain-termination step is possibly diffusion controlled. The variation of ϕ could also be caused by chain transfer to the solvent retarding the reaction rate. Such a possibility is consistent with the observed reduction in the molecular weight of the copolymer in the presence of the solvent. The approach to steady-state in the reactor was characterized. It was not possible to obtain good agreement between experiment and simulation with a single value of the ϕ factor.

INTRODUCTION

The use of continuous copolymerization methods to estimate rate parameters in copolymerization has not been extensively studied.¹ The majority of the investigations in copolymerization have been carried out at low conversions using batch reactors. However, since industrial processes are most economical when carried out to high conversions, kinetic studies conducted under such conditions are of prime importance. Solution polymerization in a CSTR offers an elegant method for producing chemically homogeneous copolymers at high conversions. Provided the solvent concentration is kept well above the "critical solvent concentration," the "gel effect" can be ignored.²

The kinetics and mechanism of solution polymerization are determined primarily by the type of initiation used and by the type of solvent employed. The solvent can influence the rate (except in the case of "regular" chain transfer) and the molecular weight. The extent of that influence is determined by the solvent chain transfer constant. Such chain transfer is not usually taken into consideration in copolymerization rate equations. Hence these equations can only be approximations in such cases, and the cross-termination factor ϕ thus loses its physical meaning. It becomes an adaptable correction factor.³

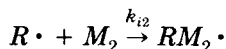
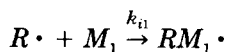
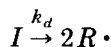
The two vinyl monomers selected for this work have similar general structures. The polymerization of vinyl acetate in various solvents has been reported.⁴ In contrast, few references are available on solution polymerization of vinyl chloroacetate.⁵ There are only two reported studies on the copolymerization of the two monomers.^{6,7} But, in these studies the emphasis was not on the kinetics of the copolymerization. Moreover, there is little agreement between the results of the two studies.

In the present work, the copolymerization kinetics for the VCLAC-VAC system was studied in a continuous stirred tank reactor. Methyl isobutyl ketone was selected among several solvents since it gave good yields for VCLAC polymerization. The validity of copolymerization models pertaining to free-radical copolymerization was tested against a set of experiments conducted at 70°C. These models do not take into account the "gel effect" since it is assumed that the presence of the solvent delays the onset of this effect to very high conversions in the reactor. Measurements included the rate of copolymerization, the copolymer composition, the average molecular weight of the copolymer, and its polydispersity. The transient behavior of the reactor was also characterized.

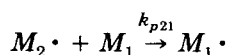
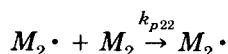
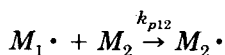
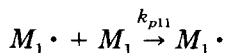
THEORY

The kinetic mechanism assumed in the reactor model is based on the classical terminal model, which asserts that only the terminal unit in a growing chain will affect the kinetics of the process. The scheme is shown here:

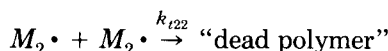
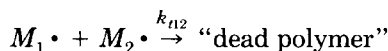
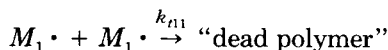
Initiation:



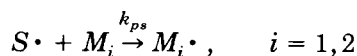
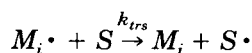
Propagation:



Termination:



Chain transfer to solvent:



Several simplifying assumptions have been made to make the kinetic equations tractable. The first assumption, the “long chain approximation” (LCA) asserts that the copolymer chains are long so that the monomer consumption occurs predominantly in the propagation step. A further consequence of this assumption is that the effect of kinetic randomness on the copolymer composition distribution is greatly reduced.

A second approximation which has been made is the “quasi-steady approximation” (QSSA), whereby the initiation and termination rates of active intermediates are virtually equal. Since the kinetic expressions in copolymerization have been derived by applying the QSSA to reactions carried out in closed systems, the validity of such expressions in describing relations in flow reactors is open to question. However, for free-radical polymerizations in which the lifetime of the active intermediate is sufficiently short as compared to the residence time of the reactor, the QSSA is a valid approximation. The mathematical details have been addressed in several papers.^{8,9}

Other assumptions made are the constant density approximation, the assumption of “regular” chain transfer through the solvent ($k_p \gg k_{tr}$, $k_{ps} = k_p$), and, finally the three partial steps during initiation are summarized in the rate of initiation, R_i . Some of these assumptions which have been included for mathematical convenience need to be tested by experiment.

The rate expression arrived at by incorporating the assumptions in the reaction scheme is¹⁰

$$R_p = \frac{(r_1 M_1^2 + 2M_1 M_2 + r_2 M_2^2) R_i^{0.5}}{\left[(r_1 \delta_1 M_1)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 M_1 M_2 + (r_2 \delta_2 M_2)^2 \right]^{0.5}} \quad (1)$$

where

$$r_1 = k_{p11}/k_{p12}, \quad r_2 = k_{p22}/k_{p21}$$

$$\delta_1 = (2k_{t11}/k_{p11}^2)^{0.5}, \quad \delta_2 = (2k_{t22}/k_{p22}^2)^{0.5}$$

$$\phi = k_{t12}/[2(k_{t11}k_{t22})^{0.5}]$$

$$R_i = 2fk_d I$$

The rate constants for propagation and termination have been replaced by the reactivity ratios, the δ terms which are typical ratios of constants used in the kinetics of homopolymerization, and the cross termination factor ϕ . The coefficient 2 in the denominator of ϕ takes into consideration that cross-termination is statistically favored over termination by like radicals by a factor of 2.¹¹

For steady-state copolymerization, the perfectly mixed CSTR model takes the form

$$M_{1f} - M_1 = R_1\theta \quad (2)$$

$$M_{2f} - M_2 = R_2\theta \quad (3)$$

where θ is the residence time in the reactor. The rates of polymerization, R_1 and R_2 , are defined as

$$R_1 = K_1 M_1 I^{0.5} \quad (4)$$

$$R_2 = K_2 M_2 I^{0.5} \quad (5)$$

and

$$I = I_f/(1 + k_d\theta) \quad (6)$$

The constants K_1 and K_2 are functions only of the monomer ratio and independent of the total concentration of monomers. From eqs. (1), (4), and (5) the definitions of K_1 and K_2 follow¹²:

$$K_1 = [(r_1 - 1)f_1 + 1]/T_1^{0.5} \quad (7)$$

$$K_2 = [(1 - r_2)f_1 + r_2]/T_1^{0.5} \quad (8)$$

$$f_1 = M_1/(M_1 + M_2) \quad (9)$$

$$T_1 = T/2fk_d \quad (10)$$

and

$$T = (r_1\delta_1 f_1)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 f_1(1 - f_1) + [r_2\delta_2(1 - f_1)^2] \quad (11)$$

where f is the efficiency of the initiator.

In the case of homopolymerization,

$$K_1 = (2fk_d)^{0.5}/\delta_1 \quad (12)$$

$$K_2 = (2fk_d)^{0.5}/\delta_2 \quad (13)$$

Combining eqs. (7) and (8), we obtain an expression which can be used to estimate the reactivity ratios

$$\frac{K_1}{K_2} = \frac{(r_1 - 1)f_1 + 1}{(1 - r_2)f_1 + r_2} \quad (14)$$

Equation (14) has been derived under steady-state conditions and is therefore applicable at different levels of conversion in the reactor.

A differential form of the copolymer composition equation derived by Mayo and Lewis¹³ has been widely used for estimating reactivity ratios in copolymer systems. The method assumes that the feed composition in the reactor does not change as the reaction proceeds. This is valid only at very low conversions. The equation they derived was

$$\frac{dM_1}{dM_2} = \left(\frac{M_1}{M_2} \right) \left(\frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \right) \quad (15)$$

which has been rearranged by Fineman-Ross¹⁴ in a linear form

$$\frac{f_1(1 - 2F_1)}{F_1(1 - f_1)} = r_2 + \left[\frac{f_1^2(F_1 - 1)}{F_1(1 - f_1)^2} \right] r_1 \quad (16)$$

where $F_1 = dM_1/d(M_1 + M_2)$.

The number-average degree of polymerization in a CSTR (if one assumes termination by coupling) is defined as

$$\bar{X}_n = (M_{1p} + M_{2p})/fI_p \quad (17)$$

where M_{1p} , M_{2p} , I_p represent the molar concentrations of monomers M_1 , M_2 , and the initiator I in the polymer.

Analogous to the equation obtained by assuming chain-transfer in the case of homopolymerization, the following equation predicts the average degree of polymerization:

$$\frac{1}{\bar{X}_n} = C_x + S_x \frac{S}{M_2} + T_x \frac{R_p}{M_2^2} \quad (18)$$

C_x and S_x represent chain transfer to monomer and solvent respectively. T_x is defined as

$$T_x = \frac{(r_1\delta_1x)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 x + (\delta_2 x)^2}{(r_1 x^2 + 2x + r_2)} \quad (19)$$

where $x = M_1/M_2$. As is obvious, C_x , S_x , and T_x are functions of the comonomer ratio in the reactor. The first term in eq. (18) can be neglected if we assume that chain transfer takes place predominantly with solvent. The chain transfer constant with the solvent S_x for a particular comonomer ratio is determined by plotting the reciprocal degree of polymerization as a function of the solvent concentration. To get a linear fit, it is necessary to keep the third term in eq. (18) constant by adjusting the initiator concentration such that R_p/M_2^2 is a constant. Equation (18) can be written as

$$\frac{1}{\bar{X}_n} = \left(\frac{1}{\bar{X}_n} \right)_0 + C_x \frac{S}{M_2} \quad (20)$$

where $(1/\bar{X}_n)_0$ is the reciprocal degree of polymerization in the absence of a solvent and represents the first and third terms of eq. (18).

EXPERIMENTAL

The vinyl chloroacetate (Polysciences) was purified by vacuum distillation (60°C/50 mm Hg). The vinyl acetate (Polysciences) was distilled at atmospheric pressure (b.p. = 71–73°C). The initiator 2-2'-azobis-2,4-dimethyl valeronitrile (Polysciences) and the solvent MIBK were reagent grade chemicals and were used as received without any further purification. The solvent and the monomers were dried with molecular sieves (10–16 mesh, effective bead size 4 Å). Nitrogen was bubbled through the reaction mixture for 30 min before starting the reactor to remove dissolved oxygen which acts as an inhibitor.

The CSTR used in this study is shown in Figure 1. A recirculating pump (with a heating coil and a thermostat) was used to maintain the bath temperature at 70°C. The monomer and the initiator mixture were withdrawn at constant flow rates using positive displacement pumps. The startup procedure was to fill the reactor initially with the desired ratio of the monomers in the solvent. The reactor was then purged with nitrogen for 20–30 min while

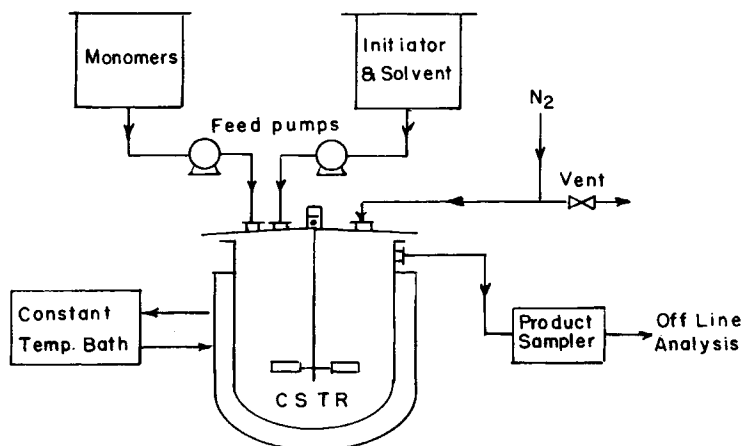


Fig. 1. Schematic of the experimental reactor system.

TABLE I
Experimental Conditions

Polymerization temp	70°C
Solvent	Methyl isobutyl ketone
Solvent/comonomer ratio	4:1 (v/v)
Initiator used	ADVN (azobis dimethylvaleronitrile)
Initiator conc	8.05 mmol/L
Residence time	7200 s
Reactor volume	0.24 L

the reactant mixture in the reactor was being heated to the desired temperature. The nitrogen was maintained in the reactor throughout the copolymerization. The initiator was added to the mixture in the reactor just before starting the pumps. The total flow rate was maintained at 2 mL/min. With the reactor volume being 0.24 L, the residence time was 2 h. The typical duration of a run was about four residence times, at which steady state was achieved.

Samples were withdrawn at intervals of half residence time to test for conversion, composition, and molecular weight distribution. The samples were dried to constant weight in a vacuum oven at 30°C for several days. The copolymer composition was determined by quantitative IR analyses.¹⁵ Since the homopolymers were found to be miscible, mixtures of varying compositions of the two homopolymers in MIBK were prepared and their spectra were obtained. The ratio of the absorbances at 1370 and 1180 cm^{-1} was determined, and a standard curve was obtained in each case by plotting the percent chloroacetate content against the ratio of the absorbances. The number- and weight-average molecular weights, M_n and M_w , were estimated by gel permeation chromatography (GPC) with the column system calibrated with polystyrene standards. HPLC grade tetrahydrofuran was used as the carrier solvent.

To reduce gel formation, the volume fraction of solvent in the reaction mixture was kept at 0.8. The initiator concentration was kept constant at 8.0 mmol/L for all the copolymerization runs. Polymerization conditions are given in Table I.

RESULTS AND DISCUSSION

Rate of Homopolymerization

The kinetics and mechanism of bulk and solution polymerization are quite similar. However, in many solvents the order of reaction is quite complex, changing constantly with the monomer concentration. In the present study, batch homopolymerizations were carried out in MIBK to test the bulk polymerization mechanism in solution. The polymerization conditions were identical to those used for the continuous runs (Table I). Polymerization runs were carried out at two different temperatures, 60 and 70°C. Samples were withdrawn periodically and analyzed by procedures outlined previously.

Figures 2 and 3 show the rate plots for vinyl acetate and vinyl chloroacetate respectively. The rate plots at 60°C are linear for both homopolymerizations,

TABLE II
Summary of Kinetic Parameters

$$k_d = 2.1 \times 10^{-4} \text{ s}^{-1}$$

$$f = 0.3$$

$$r_1 = 1.18$$

$$r_2 = 0.80$$

$$\delta_1 = 2.0 (\text{mol s/L})^{1/2}$$

$$\delta_2 = 3.1 (\text{mol s/L})^{1/2}$$

$$\phi \text{ varies between 75 and 400}$$

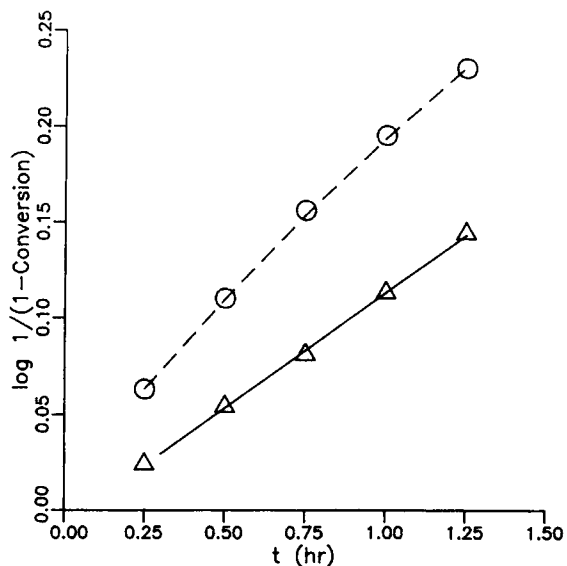


Fig. 2. First-order rate plots for batch polymerization of vinyl acetate in MIBK at two different temperatures: (Δ) 60°C; (○) 70°C. $M_{1f} = 2.16$ mol/L, $I_f = 8.05$ mmol/L.

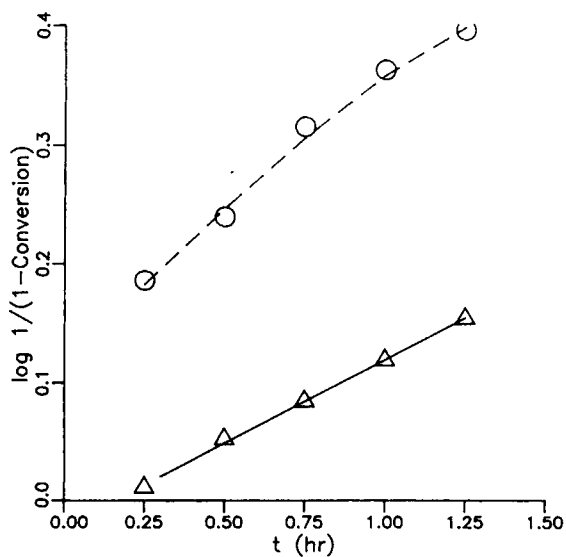


Fig. 3. First-order rate plots for batch polymerization of vinyl chloroacetate in MIBK at two different temperatures: (Δ) 60°C; (○) 70°C. $M_{1f} = 1.91$ mol/L, $I_f = 8.05$ mmol/L.

indicating that the rate has a first-order dependence on the monomer concentration. Both plots exhibit an inhibition period, although it is not appreciable and presumably results from the presence of trace impurities in the polymerization mixture. The half-life of the initiator is about 5 h so that the initiator concentration is almost constant. At 70°C the experimental points do not lie on a straight line. The half-life of the initiator is only about 1 h. Hence, the initiator concentration changes significantly within the time span of the polymerization and is reflected in the curvature of the rate plot. At this temperature, the monomer dependence on the rate cannot be determined independently owing to the depletion of the initiator. It would not be unreasonable to assume, however, a first-order dependence since the polymerization mechanism is not likely to change going from 60 to 70°C. Also, our experiments indicate that both vinyl acetate and vinyl chloroacetate do not undergo any thermal, self-initiated polymerization at 70°C.

Parameter Estimation Procedures

To compare our experimental results with model predictions, it was necessary to estimate most of the rate parameters, since they were not available in the literature. Some of these parameters have been measured from our own experimental results. In other cases, due to the complexity of the experiments and the large degree of imprecision inherent in measuring them, it was deemed necessary to adopt approximate estimation procedures. The parameter values are tabulated in Table II.

The time rate of decomposition of the initiator in MIBK at 70°C was monitored by UV absorbance measurements. The decomposition rate constant k_d was calculated assuming the decomposition process follows first-order kinetics (Fig. 4). In the case of azonitriles, this is a valid approximation since

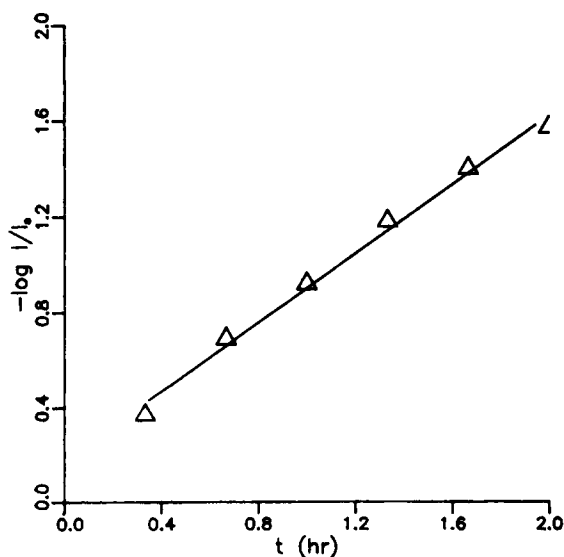


Fig. 4. Decomposition profile for 2,2'-azobis 2,4-dimethyl valeronitrile (ADV N) in MIBK at 70°C. The slope of the line will give the decomposition constant of the initiator, k_d .

these initiators are not susceptible to induced decomposition. Any deviation from first-order behavior may be attributed to experimental inaccuracies.

The efficiency of the initiator, azobis dimethyl valeronitrile, was estimated by comparing the polymerization rates for vinyl acetate, initiated by AIBN and ADVN, respectively. The efficiency of AIBN in vinyl acetate polymerization is known to be 0.6.¹⁶ All other factors remaining the same, the efficiency of ADVN was calculated to be 0.3. It is fairly well established that two sets of reactions contribute to the wastage of initiators leading to lower efficiencies in a polymerization process. One is the chain transfer to initiator which results from the induced decomposition of the initiator by attacking radicals. This reaction, as mentioned previously, is negligible for azonitriles. In the second reaction(s), the radicals formed in the initial decomposition step combine to form decomposition products instead of initiating the polymerization. In this case, the reactions occurring within the solvent cage are primarily responsible for lower efficiencies since once the radicals have diffused out of the cage, the reaction with monomer is more probable. The lifetime of the radicals within the cage depends on their structure as well as the viscosity of the reaction medium. The "cage effect" may be advanced as a plausible explanation for the low efficiency of the two initiators, especially for the larger ADVN molecule. The value of 0.3 for ADVN was also assumed in the copolymerization of VAC with VCLAC, since no information on the efficiencies of either AIBN or ADVN in VCLAC polymerization is available in the literature.

The literature on vinyl acetate polymerization quotes a wide range of values for the propagation and termination rate constants.¹⁷ For our purpose, the δ value [defined in eq. (1)] for VAC at 70°C was calculated as 3.1 from kinetic data provided by Odian.¹⁸ The δ value for VCLAC was estimated by a procedure similar to that used in determining the efficiency of the initiator. Batch homopolymerization rates of VAC and VCLAC for low-conversion runs were compared. All other conditions being identical, the δ value for VCLAC (monomer M_1) can be estimated. If one substitutes the δ values in the kinetic equation for homopolymerization [eq. (22)], the extent of "degradative" chain transfer retarding the rate of polymerization in continuous runs can be determined. This has been dealt with in a later section.

Copolymer Composition

The composition drift in the copolymerization of VCLAC with VAC is shown in Figure 5. The compositions have been estimated while the CSTR is operating at steady state and a uniform copolymer is obtained in the exit stream of the reactor. The apparent rate constants K_1 and K_2 are estimated from eqs. (4) and (5), once the concentrations and the polymerization rates of the individual monomers are determined from the conversion and the copolymer composition. Balaraman et al.¹² have discussed the full details of the method. The reactivity ratios have been calculated from the copolymer composition equation [eq. (12)] by a nonlinear least-squares technique, outlined in Appendix A. The optimum values are $r_1 = 1.18$ and $r_2 = 0.80$, implying that VCLAC is more reactive than VAC towards both propagating species. These values are close to literature values.¹⁸ To test the validity of terminal-model kinetics, the composition of the copolymer is calculated from r_1 and r_2

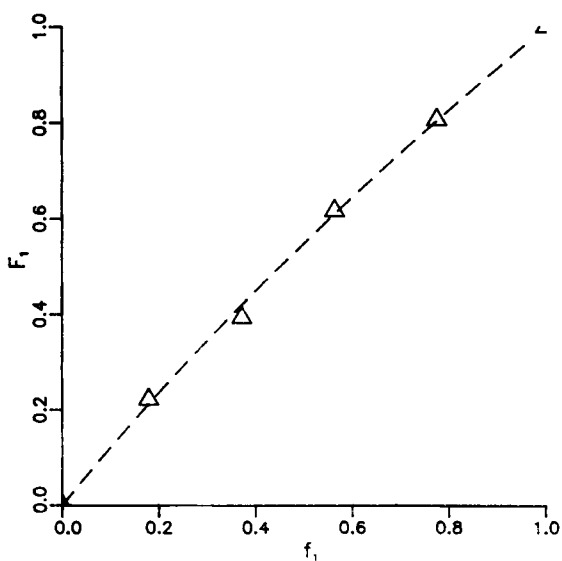


Fig. 5. Dependence of copolymer composition F_1 on the comonomer composition f_1 : (Δ) observed; (---) predicted from eq. (14) using $r_1 = 1.18$ and $r_2 = 0.80$ as the parameter values. Excellent agreement is obtained.

and compared with the experiment. Excellent agreement is obtained between the two sets of values, the deviations being no more than $\pm 3\%$.

The use of eq. (14) potentially overcomes the limitations of the methods based on differential forms of the copolymerization derived by Mayo and Lewis [eq. (15)]. However, it is necessary to operate the reactor far from the multiplicity region in order to achieve steady state. To minimize gel formation and prevent the reactor from "fouling up," a high fraction of solvent in the feed should be maintained. The reactivity ratios were also determined from eq. (16) by a linear least-squares fit. The values of 1.21 and 0.83 obtained for r_1 and r_2 , respectively, compare well with the values estimated from eq. (12). It appears that the nonlinearity of eq. (12) is not so pronounced at the moderate conversions we worked at so that the two methods gave good agreement.

Rate of Copolymerization

In Figure 6, the rate of copolymerization R_p (calculated from steady-state conversion data) is plotted against the comonomer feed composition in reactor f_1 . The rate rises with increasing proportion of VCLAC, going through a maximum in R_p close to monomer mixture with nearly pure VCLAC. It is difficult to ascertain the exact position of the maxima without more data points in that region. R_p has been normalized by $(M_1 + M_2)$ so that all the runs can be compared on the same basis. The experiments cannot be well described by a single value of the ϕ parameter. From Figure 7, it can be seen that ϕ [determined from eq. (1)] drops monotonically with decreasing VAC content in the feed, with the values ranged from 75 to 400. Such high composition-dependent values of ϕ are not unusual in free-radical polymerizations. Burnett and Gersmann¹⁹ reported ϕ values for VAC-MMA copolymer

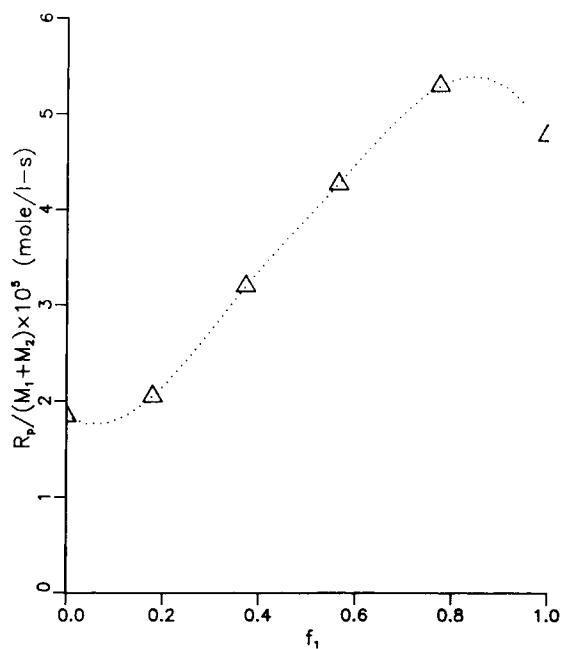


Fig. 6. Dependence of the rate of copolymerization on the comonomer feed composition. Model comparison was not possible since the experimental points cannot be well described by a single value of ϕ . The curve has been obtained by a cubic spline fit of all the data points and indicates the approximate position of the maximum in the rate curve.

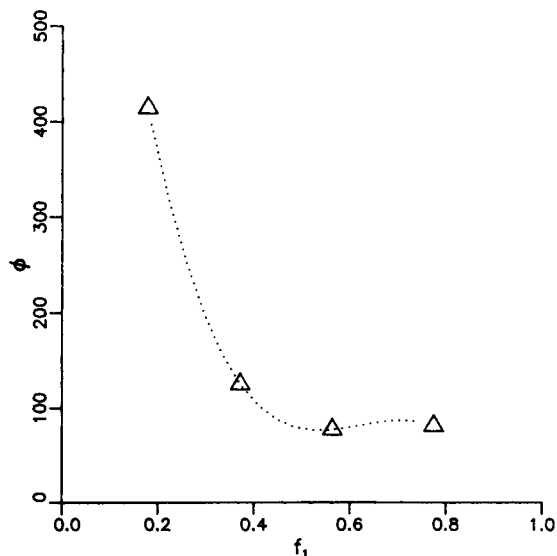


Fig. 7. Dependence of ϕ on the comonomer composition f_1 . Notice the strong dependence of ϕ in the case of a vinyl-acetate-rich comonomer feed.

system, which were widely scattered over the range 100–800. However, our results do indicate that if one assumes chemical-controlled termination, the usual reaction scheme does not adequately describe the copolymerization of VCLAC–VAC. The ϕ factor cannot be interpreted primarily in terms of the chemical effects on the radical ends since the termination rate may be dependent on the segmental and translational diffusion of the polymer chains. Such a dependence has been described by Atherton and North²⁰ in their rate equation:

$$R_p = \frac{(r_1 M_1^2 + 2M_1 M_2 + r_2 M_2^2) R_i^{0.5}}{k_{t(12)}^{0.5} (r_1 M_1 / k_{p11} + r_2 M_2 / k_{p22})} \quad (21)$$

where the termination rate constant $k_{t(12)}$ is a function of the copolymer composition. This equation is limited in its practical application since it requires the determination of the two homopropagation constants, k_{p11} and k_{p22} . Hence in our results it was not possible to show how $k_{t(12)}$ depends on the composition of the monomer mixture.

The kinetic equations for describing copolymerization rates [eqs. (1) and (21)] are derived assuming that the homopolymerization rates of the individual monomers follow the "classical" kinetic scheme:

$$R_p = \frac{R_i^{0.5}}{\delta} [M] \quad (22)$$

The measured rates of homopolymerization for both VAC and VCLAC are much lower than predicted by eq. (22). Ham⁴ has indicated that in the case of VAC, the chain transfer process retards the rate of polymerization. The kinetic analysis is quite different for this case. The rate equation derived for this case is

$$R_p = k_p (R_i / k_t)^{0.5} [M] \frac{(R_i k_t)^{0.5}}{k_{trs} [S] + (R_i k_t)^{0.5}} \quad (23)$$

which can be rearranged in the more useful form

$$R_p = \frac{R_i M}{C_s [S] + R_i^{0.5} \delta} \quad (24)$$

where C_s is the chain-transfer constant of the solvent. The main assumptions involved in deriving this equation are: (i) k_{ps} is much smaller than k_p ; (ii) k_p is much larger than k_{trs} . The chain-transfer constant of MIBK for VAC was obtained from the literature ($C_s = 0.003452$).¹⁸ There was good agreement between the measured rate and that predicted from eq. (24). In the absence of a value for the solvent chain transfer constant for VCLAC, it was not possible to compare experiment with prediction in the case of VCLAC.

In light of the discussion on homopolymerizations it is possible to explain, at least qualitatively, the copolymerization results. The large values of the ϕ factor could be explained by chain transfer to the solvent retarding the

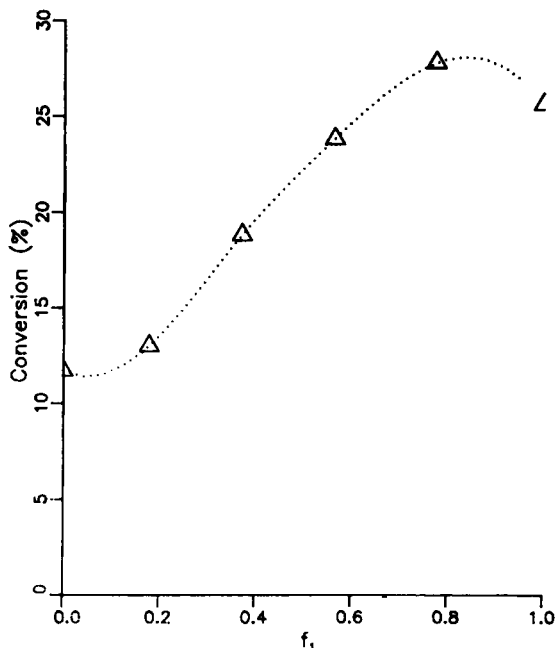


Fig. 8. Dependence of conversion on the comonomer composition.

reaction rate. Since the chain-transfer process is not taken into consideration in deriving eq. (1) and since, in general, the chain transfer constant of the solvent will be different for the two monomers, the factor ϕ will show a composition dependence if the copolymerization rate is retarded by chain-transfer processes.

The conversions obtained in the copolymerization experiments involving different comonomer feed compositions are shown in Figure 8. The values ranged from 11 to 28%.

Degree of Polymerization (DOP)

The number-average molecular weight of the copolymer, M_n , ranged between 5000 and 9000 with M_n increasing with increasing amount of VCLAC in the feed mixture. The polydispersity in all the runs was close to 2, indicating that auto-acceleration is not present. Figure 9 shows the dependence of the DOP on the comonomer composition of the reactor. The measured values are compared with the predictions from eq. (7), assuming termination wholly by coupling in one case and by disproportionation in the other case. The experimental values lie well below the predicted curves, as is expected in the case of a process involving chain transfer.

Approach to Steady State

The time-dependent behavior of the reactor, in particular the approach to steady state, has been characterized by both experiment and simulation. In Figure 10, the rate of copolymerization is shown as it approaches a steady state. The model is given in Appendix B. The model predictions are higher

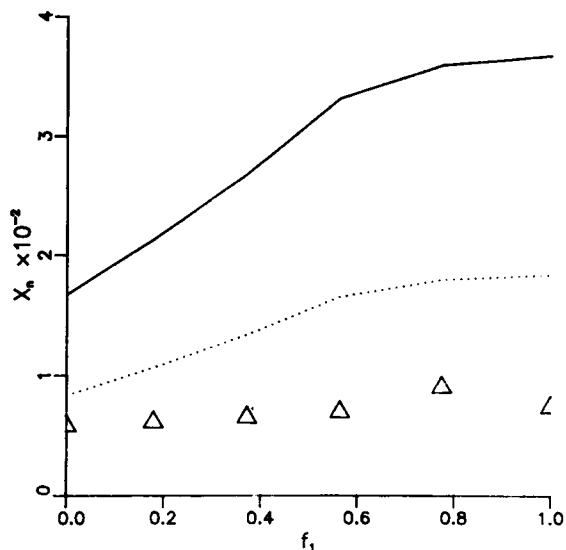


Fig. 9. Extent of chain transfer as a function of the comonomer composition. The curves represent the predictions from eq. (17) for the two cases: (—) coupling; (---) disproportionation; (Δ) molecular weight measurements using GPC. The number-average molecular weights have been converted to the corresponding average degrees of polymerization by dividing by the appropriate mer weight.

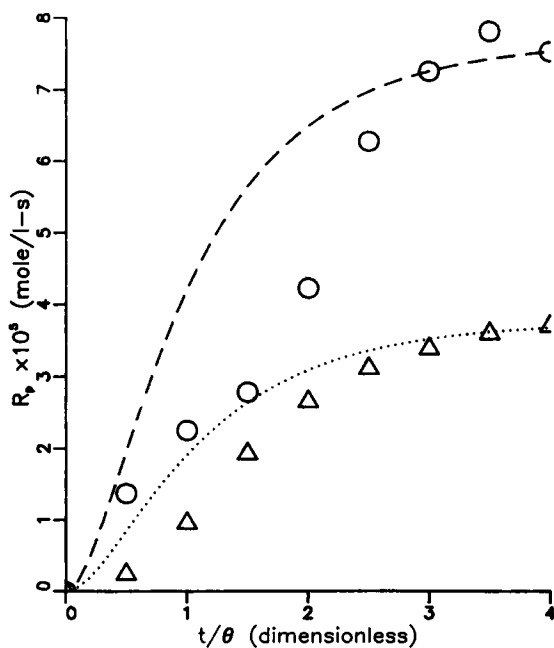


Fig. 10. Transient behavior in the CSTR. The two runs represent different comonomer feed compositions: (Δ) $f_1 = 0.175$; (\circ) $f_1 = 0.775$ with VCLAC as M_1 and VAC as M_2 . The lines represent the model predictions.

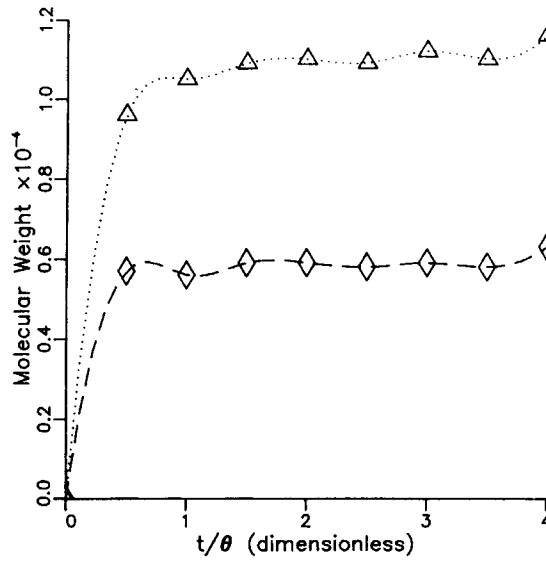


Fig. 11. Transient behavior in the CSTR. The number-average molecular weight M_n (\diamond) and the weight-average molecular weight M_w (Δ) are plotted against time; $f_1 = 0.175$. The polydispersity index is about 2.

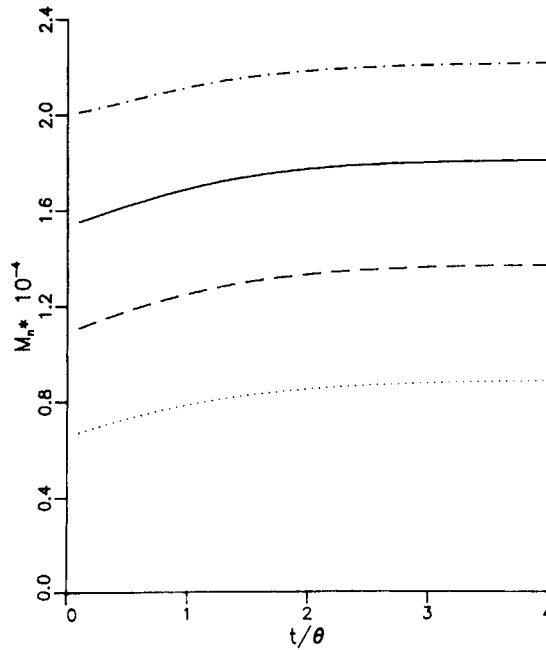


Fig. 12. Model predictions of the transient behavior. The four curves represent various comonomer ratios in the reactor: (\cdots) $f_1 = 0.179$; ($---$) $f_1 = 0.372$; ($—$) $f_1 = 0.564$; ($- \cdot -$) $f_1 = 0.775$.

than the experimental values, even though ϕ has been used as an adaptable parameter and presumably takes into account the chain transfer due to the solvent. The discrepancy could possibly have resulted from some impurity in the reaction mixture or due to induction effects.

In the case of free-radical polymerizations, the polymer chains grow in a very short period of time (s). As is evident from Figure 11, the value of M_n rapidly approaches a steady state. M_w behaves in similar fashion, implying that the polydispersity is constant after the initial brief period of rapid chain growth. Computer simulation results for the different comonomer feed ratios are shown in Figure 12. Qualitatively the same trend is noticed, although the actual values in the simulation are higher since chain transfer has not been considered in the model.

APPENDIX A

Consider the copolymer composition equation

$$\frac{K_1}{K_2} = \frac{(r_1 - 1)f_1 + 1}{(1 - r_2)f_1 + r_2}$$

which can be rearranged to give

$$f_1 - \left[r_1 f_1 + r_2 \frac{K_1}{K_2} (1 - f_1) + \left(f_1 \frac{K_1}{K_2} - 1 \right) \right] = 0$$

The objective function is to minimize

$$Z = \sum \left\{ f_1 - \left[r_1 f_1 + r_2 \frac{K_1}{K_2} (1 - f_1) + \left(f_1 \frac{K_1}{K_2} - 1 \right) \right] \right\}^2$$

The optimum values of the reactivity ratios are obtained by invoking the minimization criteria

$$\frac{\partial Z}{\partial r_1} = 0, \quad \frac{\partial Z}{\partial r_2} = 0$$

The resultant linear equations in r_1 and r_2 are

$$\begin{aligned} r_1 \sum f_1^2 - r_2 \left(\sum f_1 \frac{K_1}{K_2} - \sum f_1^2 \frac{K_1}{K_2} \right) &= \left(\sum f_1^2 \frac{K_1}{K_2} - \sum f_1 + \sum f_1^2 \right) \\ r_1 \left(\sum f_1 \frac{K_1}{K_2} - \sum f_1^2 \frac{K_1}{K_2} \right) + r_2 \left[- \sum \left(\frac{K_1}{K_2} \right)^2 + 2 \sum f_1 \left(\frac{K_1}{K_2} \right)^2 - \sum f_1^2 \left(\frac{K_1}{K_2} \right)^2 \right] \\ &= \left[\sum f_1 \left(\frac{K_1}{K_2} \right)^2 - \sum f_1^2 \frac{K_1}{K_2} - \sum f_1^2 \left(\frac{K_1}{K_2} \right)^2 - \sum \frac{K_1}{K_2} + 2 \sum f_1 \frac{K_1}{K_2} \right] \end{aligned}$$

The equations can be solved simultaneously to give r_1 and r_2 .

APPENDIX B

The copolymerization modeling equations are

$$V \frac{dM_1}{dt'} = (M_{1f} - M_1)q - R_1V$$

$$V \frac{dM_2}{dt'} = (M_{2f} - M_2)q - R_2V$$

$$V \frac{dI}{dt'} = (I_f - I)q = k_dIV$$

where

$$R_1 = K_1M_1I^{0.5}$$

$$R_2 = K_2M_2I^{0.5}$$

These sets of equations can be simplified by defining the following variables and parameters:

$$x_1 = \frac{M_{1f} - M_1}{M_{1f}}, \quad x_2 = \frac{M_{2f} - M_2}{M_{2f}}, \quad x_3 = \frac{I_f - I}{I_f}$$

$$t = \frac{t'}{\theta}, \quad \theta = \frac{V}{q}, \quad f' = \frac{M_{1f}}{M_{2f}}, \quad f'' = \frac{I_f}{M_{2f}}, \quad \beta = \frac{K_1}{K_2},$$

$$\gamma = \frac{k_d}{K_2I_f^{0.5}}, \quad Da = K_2I_f^{0.5}\theta$$

$$K_1 = \frac{r_1(1 - x_1)f' + (1 - x_2)}{T_1^{0.5}}$$

$$K_2 = \frac{(1 - x_1)f' + (1 - x_2)r_2}{T_1^{0.5}}$$

$$T_1 = \frac{T}{2fk_d}$$

$$T = [r_1\delta_1(1 - x_1)f']^2 + 2\phi r_1r_2\delta_1\delta_2(1 - x_1)(1 - x_2)f' + [r_2\delta_2(1 - x_2)]^2$$

Standard mathematical manipulations lead to the following dimensionless modeling equations:

$$\frac{dx_1}{dt} = -x_1 + (1 - x_1)(1 - x_3)^{0.5}Da\beta$$

$$\frac{dx_2}{dt} = -x_2 + (1 - x_2)(1 - x_3)^{0.5}Da$$

$$\frac{dx_3}{dt} = -x_3 + (1 - x_3)Da\gamma$$

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