

Diffusion-Controlled Kinetics for the Solution Copolymerization of 2-Ethylhexyl Acrylate with Vinyl Chloroacetate in a CSTR

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Synopsis

The solution copolymerization of the comonomer pair 2-ethylhexyl acrylate–vinyl chloroacetate (in ethyl acetate) has been studied in a continuous stirred tank reactor (CSTR). The initiator used in this study, 2,2'-azobis-2,4-dimethyl valeronitrile was selected on the basis of its high decomposition rate constant. Measurements included the rate of copolymerization, the copolymer composition by infrared spectrophotometric analysis, the molecular weight distribution by gel permeation chromatography, and the viscosity of the reaction mixture by capillary viscometry. The reactivity ratios for the EHA–VCLAC pair were markedly different so that both propagating chains preferentially add EHA. Both the ϕ factor and the penultimate effect models were inadequate for describing the termination reaction. By defining an appropriate expression, based on physicochemical considerations, for the overall termination rate constant, it was possible to model the steady state rates by the diffusion model of Atherton and North. An attempt to model the transient behavior of the reactor by using the ϕ value as an adaptable correction factor was unsuccessful due to the rapid composition drift during approach to steady state. The measured conversions were lower than the model predictions for all feed ratios.

INTRODUCTION

The solution polymerization (or copolymerization) of esters of acrylic monomers is important in the production of low molecular weight resins. These polymers and copolymers are used as adhesives, plasticizers, protective coatings, and paints. The higher acrylates (polymers of 2-ethylbutyl acrylate and 2-ethylhexyl acrylate) are also important as viscosity index improvers. In general, the acrylates are added to impart film-forming characteristics to copolymers while hardness is imparted by vinyl ester monomers. As compared to the vinyl ester polymers, the polymer of 2-ethylhexyl acrylate tends to give films having soft and tacky surfaces. This makes it suitable as a plasticizing comonomer. Depending on the type and quality of solvent and initiator used, as well as the temperature and chain-transfer agents, it is possible to produce polymers of varying molecular weights.

In a previous publication, the copolymerization of vinyl chloroacetate with vinyl acetate was investigated.¹ The present study is concerned with the solution copolymerization of 2-ethylhexyl acrylate with vinyl chloroacetate.^{2,3} The motivation for this study was prompted by the rather sparse literature in the area of continuous copolymerization processes. Moreover, as pointed out in several articles,^{4,5} continuous processes offer the advantages of improved

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polymer properties and economies of scale. However, it is also true that the design of continuous systems requires far more understanding than is required in the design of batch processes. At moderate to high conversions, the kinetics of a polymerization process is complicated by transport effects. Also as several studies have indicated,⁶⁻¹¹ continuous polymerization reactors can exhibit complex dynamic behavior such as multiple steady states even under isothermal conditions. The influence of transport effects on the copolymer composition and the molecular weight distribution has been discussed in numerous papers.¹²⁻¹⁹ In the present study, the "gel effect" was not included in the copolymerization model since it was assumed that the presence of the solvent would delay the onset of this effect to very high conversions in the reactor.

EXPERIMENTAL

Vinyl chloroacetate (VCLAC) and 2-ethylhexyl acrylate (EHA) were obtained from PolySciences. The vinyl chloroacetate was purified by vacuum distillation (60°C/50 mm Hg). The color of the predistilled monomer varies from lot to lot, ranging from pale yellow to dark brown. The purified monomer, on the other hand, is a colorless liquid, so that any contamination while distilling is easily detectable. The ethylhexyl acrylate is a very high boiling monomer (bp 229°C approx.). An ion-exchange resin (Dehibit 100) was used to remove the inhibitor, methyl hydroquinone, from the monomer. The inhibitor level can be reduced to concentrations below 1 ppm by this procedure. Dehibit-100 was obtained from PolySciences. It is supplied as water-saturated chloride beads and can be regenerated and reused. The initiator used in the study, 2,2'-azobis-2,4-dimethyl valeronitrile (PolySciences) was of analytical reagent grade and was used as received without any further purification. The solvent used in the polymerization experiments was ethyl acetate (Aldrich). This was reagent grade and was also used as received without any further purification. Both the solvents and the monomers were dried before use with molecular sieves (10-16 mesh, effective pore size 4 Å).

The polymerization reactor and start-up procedures were the same as those used previously, as is the procedure for sample isolation and analysis.¹ The polymerization conditions are summarized in Table I. The copolymer composition was determined by quantitative IR analyses. The homopolymers of ethylhexyl acrylate and vinyl chloroacetate were not miscible in any of the solvents tested; hence the IR calibration standards could not be prepared by simply mixing the two homopolymers. A series of polymerizations in which

TABLE I
Experimental Conditions

Polymerization temperature	70°C
Solvent	Ethyl acetate
Solvent/comonomer ratio	4 : 1 (v/v)
Initiator used	ADVN(azobis dimethyl valeronitrile)
Initiator concentration	8.05 mmol/L
Residence time	7200 s
Reactor volume	0.24 L

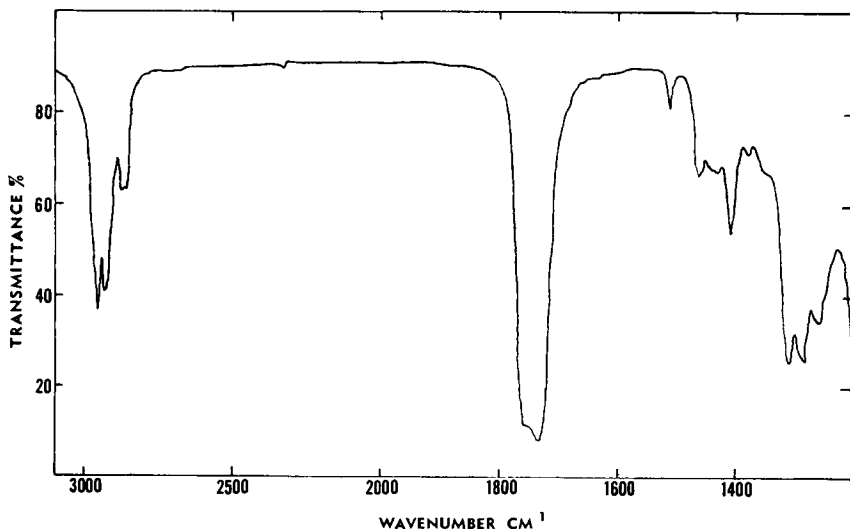


Fig. 1. Infrared spectra of copolymer film of poly(ethylhexyl acrylate-vinyl chloroacetate).

the feed ratio was varied of EHA to VCLAC in ethyl acetate yielded copolymers over a wide range of compositions. The composition of the copolymer samples was determined by elemental analysis (based on the chlorine content in the copolymer) and correlated with respective IR spectra to give a calibration curve. The wavenumbers corresponding to strongly absorbing VCLAC and EHA were determined as 1310 and 2960 cm^{-1} , representing the CH_2 wagging vibration for the CH_2Cl group and the CH_3 symmetrical stretching vibration for EHA respectively. Figure 1 shows a typical IR spectra of the copolymer.

RESULTS AND DISCUSSION

Rate of Homopolymerization

Batch polymerizations were carried out in ethyl acetate to test the homopolymerization mechanism in solution. The polymerization conditions were similar to that used for the continuously run experiments (Table I). Polymerization runs were carried out at 70°C. Samples were withdrawn at intervals of 15 min and their conversions determined by procedures outlined previously.

Figures 2 and 3 show the first-order rate plots for 2-ethylhexyl acrylate (M_1) and vinyl chloroacetate (M_2). The half-life of the initiator is about 1 h so that initiator depletion will affect the monomer dependence on the rate. The problem of simultaneous depletion of the monomer and the initiator can be minimized by using the initial slope of the concentration-time plot to estimate the rate parameters. Since the δ value ($\delta = k_i^{0.5}/k_p$) for the VCLAC is already known from studies on the VCLAC-VAC system,¹ the δ value for the EHA can be determined by comparing the slopes of the concentration-time plots for the vinyl-chloroacetate and 2-ethylhexyl acrylate.

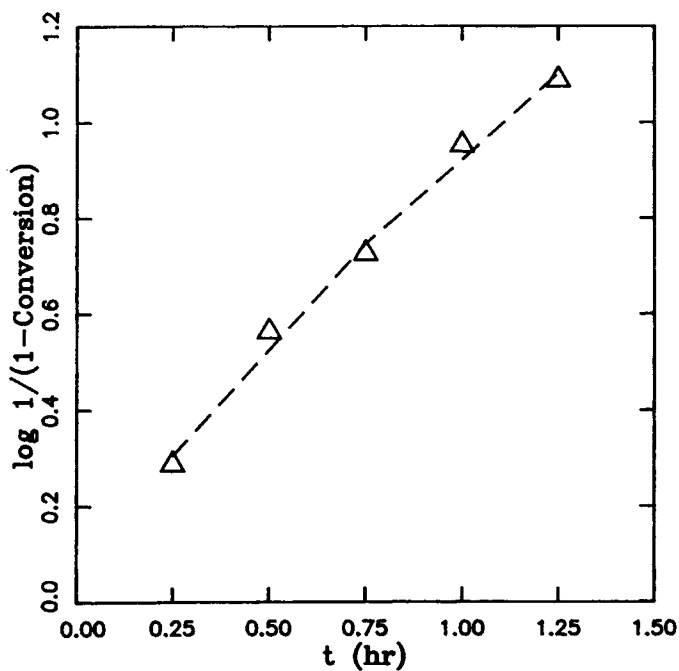


Fig. 2. First-order rate plots for batch polymerization of ethylhexyl acrylate at 70°C. $M_{1f} = 0.957$ mol/L; $I_f = 8.05$ mmol/L.

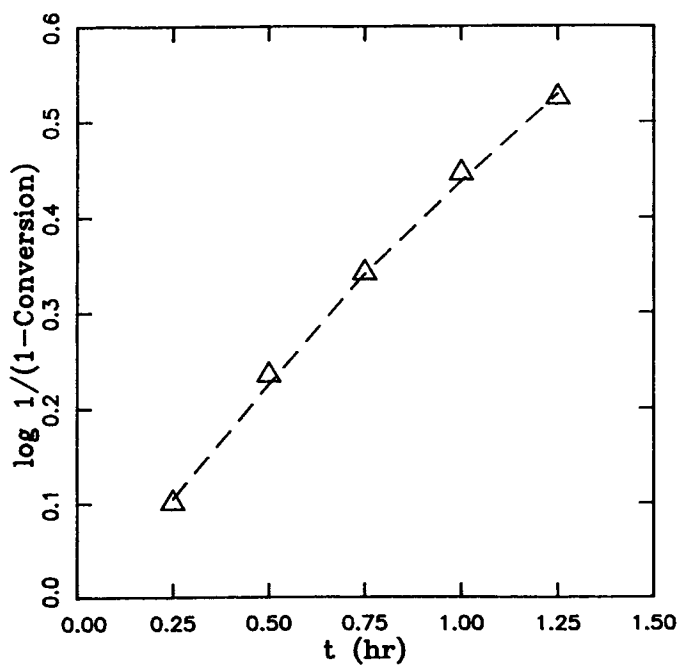


Fig. 3. First-order rate plots for batch polymerization of vinyl chloroacetate in ethyl acetate at 70°C. $M_{1f} = 1.96$ mmol/L; $I_f = 8.05$ mmol/L.

The value for EHA determined by this procedure is 0.95. The literature on acrylate polymerization did not yield any information to confirm our findings. The δ value for methyl acrylate is about 1.2, which is close to 0.95. The comparison, while not strictly valid since esters within a particular homologous series could vary widely in their reactivities, does indicate that the estimated value is reasonable.

Copolymer Composition

Copolymerization experiments at various initial comonomer feed compositions were carried out in order to estimate the reactivity ratios. The composition drift in the copolymerization of EHA with VCLAC is quite significant (Fig. 4). The copolymerization appears to be more selective since the compositions of the copolymers are quite different from those of the comonomer feed. The copolymer compositions represent steady-state values since they were obtained by operating the reactor under steady-state conditions. The reactivity ratios have been determined by the equation of Balaraman et al.^{20,21} A detailed description of the parameter extraction steps and the nonlinear least-squares procedure used to determine the optimum values of the reactiv-

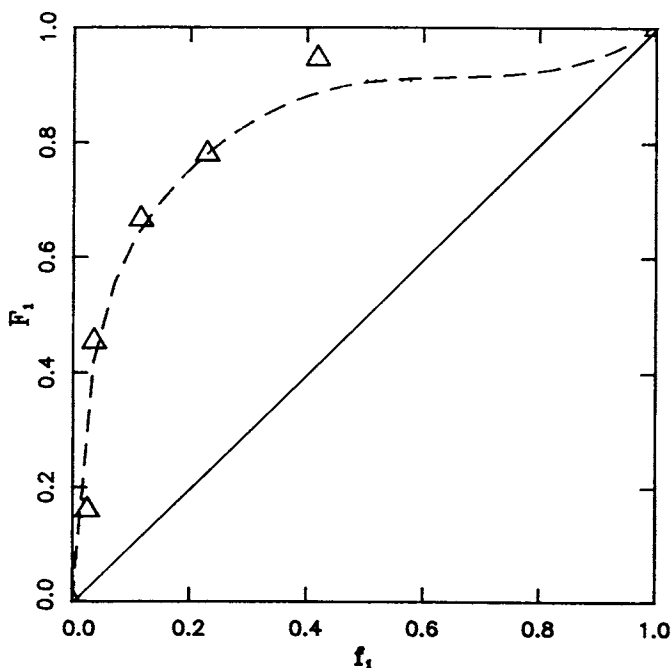


Fig. 4. Dependence of copolymer composition F_1 on the comonomer composition f_1 for the EHA/VCLAC pair: (Δ) observed; (---) predicted from the Balaraman equation

$$\frac{K_1}{K_2} = \frac{(r_1 - 1)f_1 + 1}{(1 - r_2)f_1 + r_2} = \frac{F_1 M_2}{F_2 M_1}$$

where $r_1 = 10.0$ and $r_2 = 0.033$. K_1 and K_2 are defined in Table II.

ity ratios is provided in our earlier paper.¹ The superiority of this technique over the Fineman–Ross equation²² has been described in the literature.²³

The reactivity ratios for r_1 and r_2 were estimated to be 10.0 ± 0.2 and 0.033 ± 0.005 , respectively. Each data point in Figure 4 is an average of two to three measurements and the curve has been constructed using the values of r_1 and r_2 . The calculated copolymer compositions appear to give good agreement with the experimentally determined values over the whole range of comonomer compositions.

Our results indicate that the wide difference in reactivities of the two monomers would make it difficult to produce copolymers containing appreciable amounts of vinyl chloroacetate in the copolymer. Only at very high proportions of VCLAC in the comonomer feed ratios are significant amounts of VCLAC in the copolymer obtained. However, this results in an accompanying decrease in the rate of polymerization so that from the practical standpoint, the process might become uneconomical to operate.

Rate of Copolymerization

The copolymerization of 2-ethylhexyl acrylate with vinyl chloroacetate exhibits quite unusual behavior. As shown in Figure 5, the rate of copolymerization exhibits a minimum corresponding to a comonomer feed which is mostly VCLAC. Such behavior is not unusual in free-radical copolymerizations where the two monomers often exert a mutual depressing effect on the rate of copolymerization. As a result, the rate of copolymerization over a range of monomer feed compositions is well below the rate of polymerization of either of the pure monomers under similar experimental conditions. The theory has been discussed by Palit²⁴. Palit has investigated the conditions under which the minimum occurs in the rate of copolymerization curve. According to him, the necessary condition for the minimum to occur is $M_1/M_2 < (r_1/r_2)^{0.5}$. If $r_1 \gg r_2$, the minimum occurs close to a monomer mixture of pure M_2 .

This is indeed the case for the EHA–VCLAC system where the reactivity ratios are vastly different ($r_1 = 10.0$, $r_2 = 0.033$). It was necessary to limit most of the experiments to a region close to pure VCLAC monomer in the feed mixture in order to ascertain the exact position of the minimum. Also the region between 0.5 mole fraction EHA and pure EHA in the feed mixture is not of interest since the rate of copolymerization remains almost constant over this region. This is because the proportion of VCLAC in the feed mixture is not sufficient to exert a depressing effect on the polymerization rate which therefore remains almost constant. From the experimental data, one can roughly estimate the point of the minimum as corresponding to a feed composition of 0.05–0.1 mole fraction of EHA ($M_1/M_2 = 0.05$ –0.1). From Palit's condition, the minimum is expected to occur at 0.057, which seems to be compatible with the observed range mentioned above. The rate of copolymerization, R_p , has been normalized by $(M_1 + M_2)$ in order to compare all the runs on the same basis.

As in the case of the VCLAC–VAC system, the experimental data do not conform to the copolymerization rate equation if one assumes chemical con-

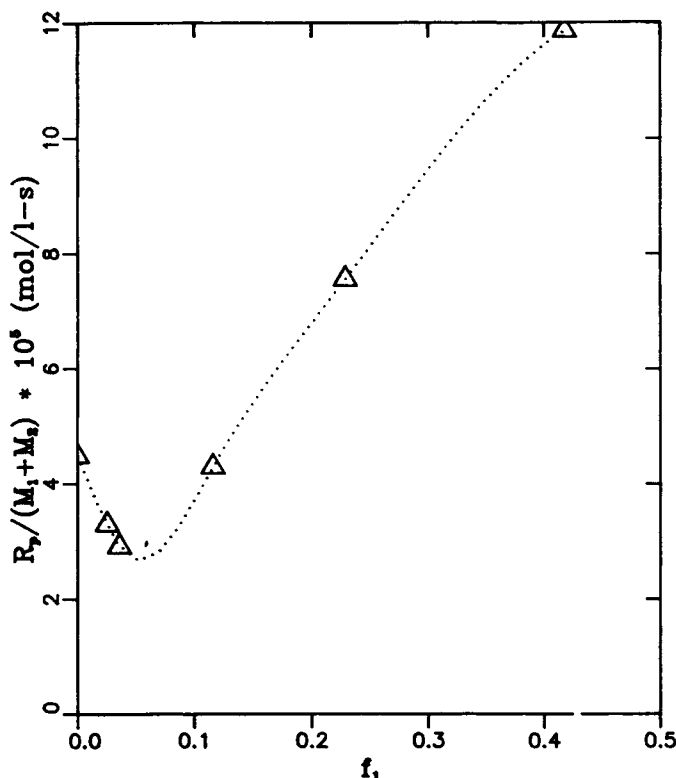


Fig. 5. Dependence of the rate of copolymerization on the comonomer feed composition for EHA/VCLAC pair. The curve has been obtained by a cubic spline fit through all the data points and indicates the position of the minimum in the rate curve.

trolled termination, i.e.,

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

The cross-termination parameter ϕ was determined from the copolymerization data. As is evident from Figure 6, the ϕ factor shows a strong dependence on the comonomer feed compositions. The factor increases with increasing amount of the EHA monomer in the comonomer feed mixture, and the values ranged from roughly 100 to 400. Uncertainties in the values of δ_1 and δ_2 from the respective homopolymerizations would alter the ϕ values. However, our analyses indicates that it was not possible to reconcile the rate data with a single ϕ value even when δ_1 and δ_2 were determined from eq. (1) by least squares analysis rather than from their individual homopolymerization reactions.

While in the VCLAC-VAC copolymer system the ϕ factor decreases as one increases the composition of the more reactive monomer, VCLAC in the feed,

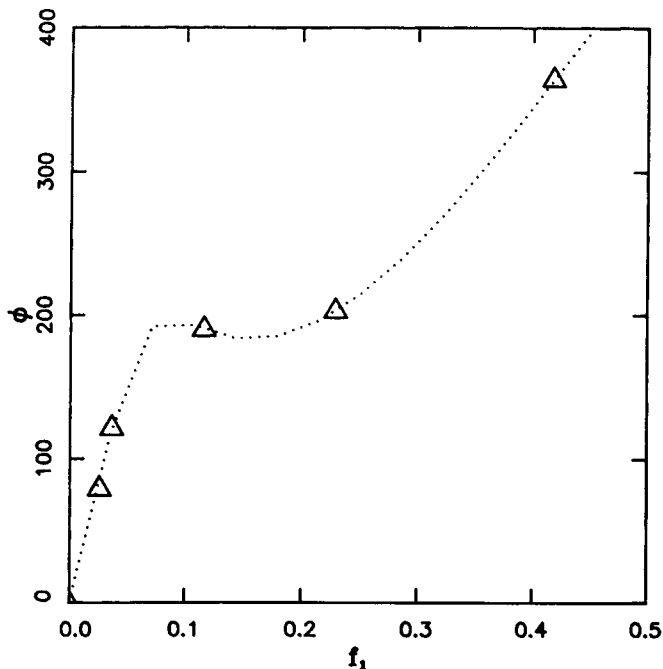


Fig. 6. Dependence of ϕ on the comonomer feed composition f_1 for EHA/VCLAC pair.

in the case of the EHA-VCLAC system, the opposite appears to be true. The ϕ factor increases with increase in the more reactive monomer EHA in the feed. Hence the termination mechanism for this system must be quite different. The penultimate effect model²⁵ cannot describe the present system, since one of the parameters δ_{21} , is negative.

It has been observed in several copolymer systems that ϕ rises with increasing size of the side group. This is especially true in cases where styrene is one of the comonomers. In the present system, the pendant group of ethylhexyl acrylate is bulkier than that of vinyl chloroacetate. Hence the results obtained are consistent with earlier observations. It appears that the ϕ factor is related to the flexibility of the chain. In the analysis of the copolymerization data for the VCLAC-VAC system, it was assumed that the termination constant varies inversely as the solution viscosity. However, this approach is valid only when the polymer backbone chain is very flexible, so that backbone rotational motions are very efficient. When these rotational motions are constrained by large pendant groups, the termination rate constant ceases to be dependent on the solution viscosity.

To get back to the original hypothesis that the termination process in free-radical copolymerization is diffusion-controlled, we assume that in the present copolymer system, since the reactivity ratios are widely different, the monomer with the larger reactivity ratio (in this case ethyl-hexyl acrylate) is polymerized favorably. Therefore, the terminal units in the growing polymer chains are likely to consist of units of EHA. Thus, the termination of the chain takes place mainly between EHA units. Again, starting with the rate

equation of Atherton and North,²⁶

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

the termination rate constant $k_{t(12)}$ is expected to be a function of the termination constants for the two homopolymerizations:

$$k_{t(12)} = k_{t11} F_1 + k_{t22} F_2 \quad (3)$$

where F_1 and F_2 are the molar fractions of the two monomers in the copolymer. This dependence is highly idealized and does not hold in all cases studied. However, it has been found quite reliable at higher temperatures above 60°C. Assuming that eq. (2) holds in the present case, since termination takes place mainly between growing radicals with EHA as the terminal unit,

$$k_{t(12)} = k_{t11} F_1 \quad (4)$$

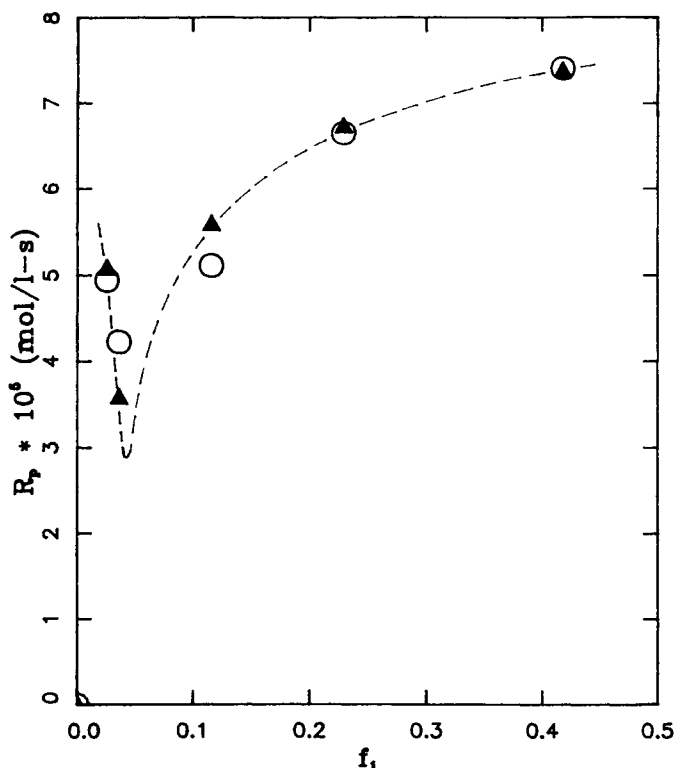


Fig. 7. Comparison of model prediction and experimental observations for the rate of copolymerization of EHA/VCLAC pair: (O) experimental; (▲), predicted from eq. (5). The curve has been obtained by a cubic spline fit through the points representing the model predictions.

and substituting in the rate equation,

$$R_p = \frac{(r_1 M_1^2 + 2M_1 M_2 + r_2 M_2^2) R_i^{0.5}}{(F_1 k_{t1})^{0.5} (r_1 M_1 / k_{p11} + r_2 M_2 / k_{p22})} \quad (5)$$

The above equation can be linearized to the form

$$y = b_1 x + b_2 \quad (6)$$

where

$$b_1 = (k_{t1})^{0.5} r_1 / k_{p11} = k_{t1}^{0.5} / k_{p12} \quad (7)$$

$$b_2 = (k_{t1})^{0.5} r_2 / k_{p22} = k_{t1}^{0.5} / k_{p21} \quad (8)$$

Using a least-squares procedure, one obtains

$$b_1 = 23.14$$

$$b_2 = 3.39$$

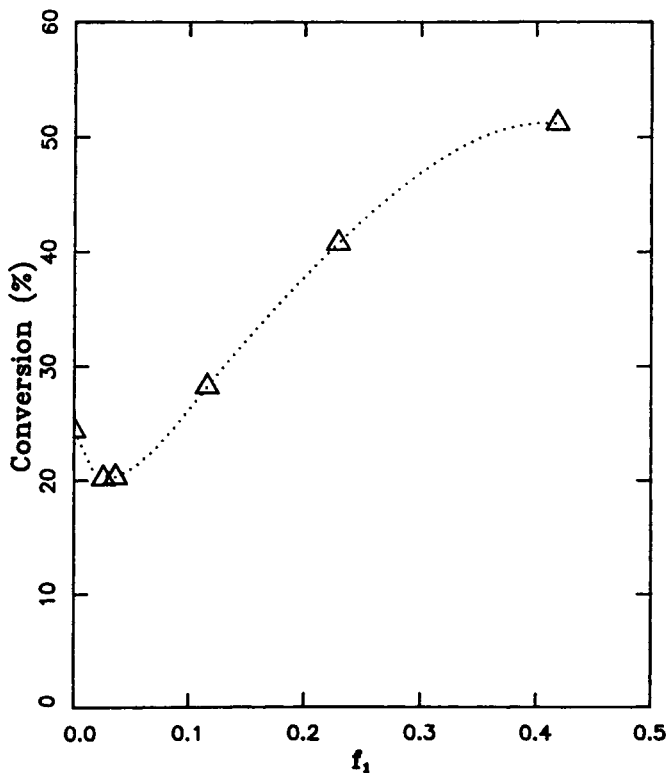


Fig. 8. Dependence of conversion on the comonomer composition f_1 for EHA/VCLAC pair. The curve has been obtained by a cubic spline fit through all the data points.

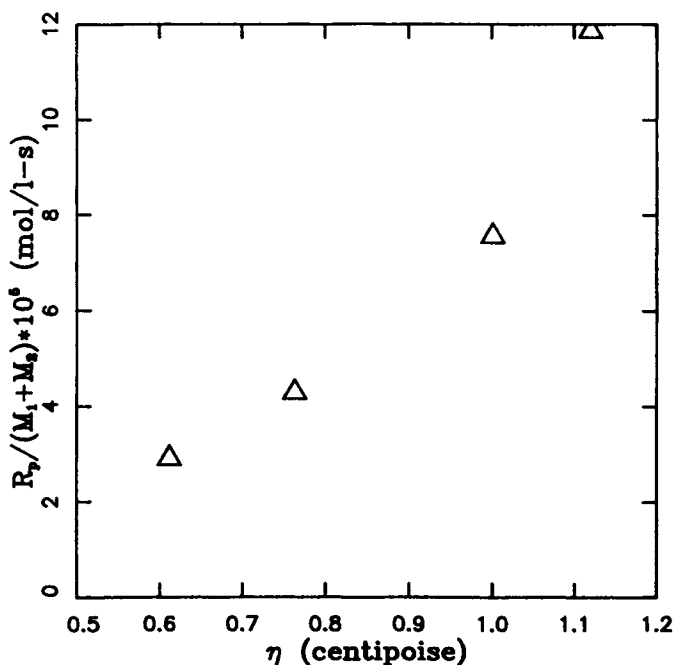


Fig. 9. Dependence on viscosity of copolymerization rates for EHA/VCLAC pair.

As can be seen from Figure 7, the copolymerization results can be well described by this model. The depth of the minimum is somewhat exaggerated by the model. The minimum corresponds to 0.04 mole fraction of EHA in the comonomer feed mixture. This is in agreement with the condition for the minimum determined earlier (< 0.057).

The conversion and the viscosity of the reaction mixture are shown in Figures 8 and 9 as a function of comonomer composition. The conversions ranged from 20 to 50% while the measured viscosities ranged from 0.6 to 1.1 cP. Although these values are moderate, postulating a diffusion-controlled termination mechanism is not totally unreasonable. Such behavior has been observed in systems of normal viscosity, e.g., radical-radical, ion-ion, and triplet-state reactions (involving species which have much higher diffusivity than polymer radicals) demonstrate diffusion-controlled kinetics.^{26,27}

Approach to Steady State

The dynamic behavior of the CSTR was modeled for a particular feed ratio by using the ϕ value from Figure 6. Although this approximation neglects the transient change in the ϕ value in the case of rapid composition drift, it provides some qualitative insight into the dynamics. In cases where the composition changes from the initial feed composition are minimal, this approximation is expected to give good agreement with experiment. The copolymerization modeling equations and the simulation parameters are given in Table II. Deviations from experimental data are shown in Figure 10. In general, the agreement is poor, with the measured rates being lower than that predicted by simulation. The present system differs from the VCLAC/VAC

TABLE II
Copolymerization Modelling Equations and Simulation Parameters

Numerical values of parameters

$$r_1 = 10.0$$

$$r_2 = 0.033$$

$$\delta_1 = 0.95 \text{ (mol/L s)}^{-0.5}$$

$$\delta_2 = 2.0 \text{ (mol/L s)}^{-0.5}$$

$$k_d = 1.55 \times 10^{-4} \text{ (s}^{-1}\text{)}$$

$$f = 0.3$$

ϕ varies from 79 to 364

Dimensionless modeling equations

$$dx_1/dt = -x_1 + (1 - x_1)(1 - x_3)^{0.5}Da\beta \quad (\text{II.1})$$

$$dx_2/dt = -x_2 + (1 - x_2)(1 - x_3)^{0.5}Da \quad (\text{II.2})$$

$$dx_3/dt = -x_3 + (1 - x_3)Da\gamma \quad (\text{II.3})$$

where

$$x_1 = (M_{1f} - M_1)/M_{1f}, x_2 = (M_{2f} - M_2)/M_{2f}, x_3 = (I_f - I)/I_f$$

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

$$\gamma = k_d/K_2 I_f^{0.5}, Da = K_2 I_f^{0.5} q$$

$$K_1 = [r_1(1 - x_1)f' + (1 - x_2)]/T_1^{0.5}$$

$$K_2 = [(1 - x_1)f' + (1 - x_2)r_2]/T_1^{0.5}$$

$$T_1 = T/2fk_d$$

$$T = [r_1\delta_1(1 - x_1)f']^2 + 2\phi r_1 r_2 \delta_1 \delta_2 (1 - x_1)(1 - x_2)f' + [r_2\delta_2(1 - x_2)]^2 \quad (\text{II.4})$$

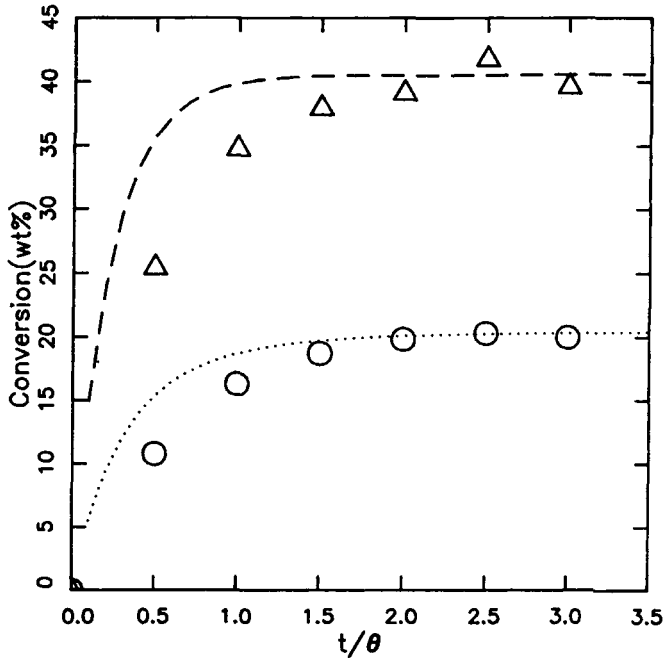


Fig. 10. Transient behavior of the CSTR for EHA/VCLAC pair: conversion. The two runs represent different comonomer feed compositions: (O) $f_1 = 0.0365$ and (Δ) $f_2 = 0.229$, with EHA as M_1 and VCLAC as M_2 . The lines represent the model predictions.

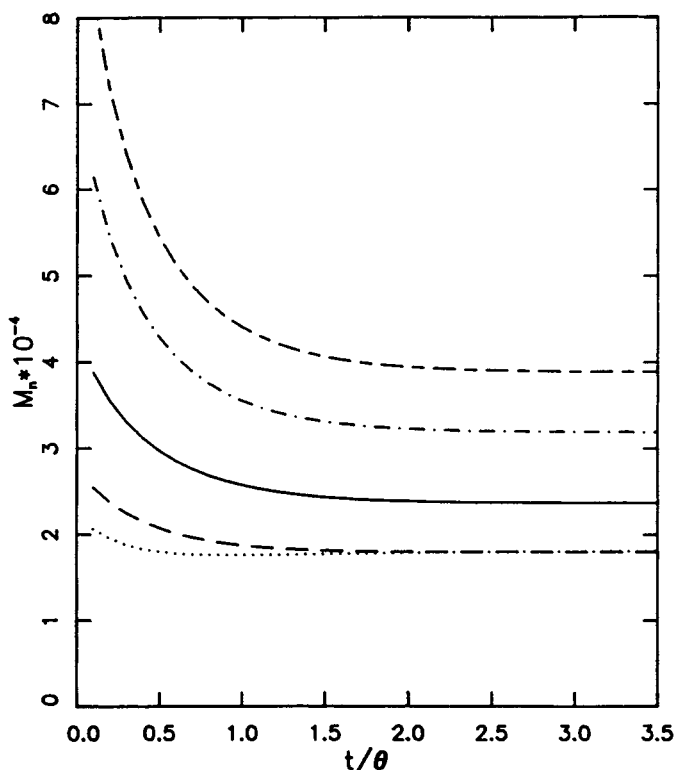


Fig. 11. Transient behavior of the CSTR for EHA/VCLAC pair: molecular weight. The five curves represent the model predictions for the number average molecular weight corresponding to various comonomer ratios in the reactor: (\cdots) $f_1 = 0.0259$; ($- - -$) $f_1 = 0.0365$; ($-$) $f_1 = 0.116$; ($- \cdot - \cdot$) $f_1 = 0.229$; ($- \cdot - \cdot$) $f_1 = 0.418$.

system in that the steady state predicted by the simulation is attained in approximately one residence time compared to two or three residence times for VCLAC/VAC.¹ It is possible that the high reactivity of the acrylate radicals contributes to the faster dynamics.

Figure 11 shows simulation runs to determine the number-average molecular weights for various feed ratios. In all cases, the molecular weight shoots to a maximum value almost instantaneously and then approaches a steady state. The fast growth of the chains is typical in radical polymerizations. The size of the overshoot increases with increasing amount of EHA in the feed mixture. It appears that the growth of the polymer chains occurs in two phases. In the first phase, the high reactivity of the acrylate radicals leads to rapid chain growth and the resulting overshoot. In the second phase, the proportion of acrylate radicals decreases and the inhibiting influence of vinyl chloroacetate dominates. This is manifested in a slow decrease to the steady state value of the molecular weight. Experimentally, it was difficult to observe any definite trends due to the random fluctuations of the GPC measurements. In most cases the molecular weight did not change significantly after the initial growth period.

The change in copolymer composition with start-up in the present system can be quite significant. Figure 12 are simulation runs showing the predicted

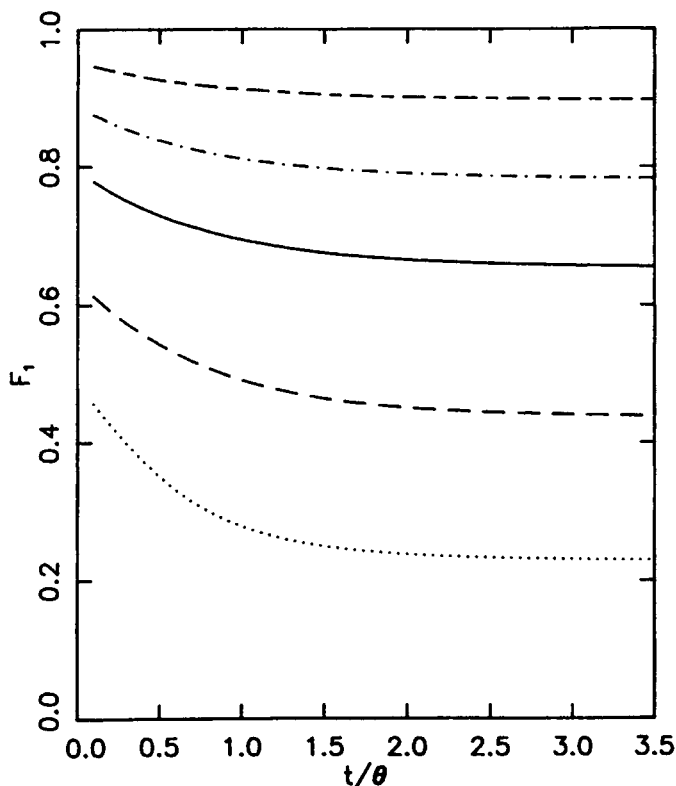


Fig. 12. Transient behavior of the CSTR for EHA/VCLAC pair: copolymer composition. The five curves represent the model predictions for the copolymer composition corresponding to various comonomer ratios in the reactor: (\cdots) $f_1 = 0.0259$; ($--$) $f_1 = 0.0365$; ($-$) $f_1 = 0.116$; ($- \cdot -$) $f_1 = 0.229$; ($- - -$) $f_1 = 0.418$.

variation in copolymer composition with time, the change increasing with increasing proportionation of VCLAC in the feed. Due to its greater reactivity, EHA is incorporated preferentially at the start of the polymerization. As the polymerization proceeds, the acrylate depletes and the copolymer becomes increasingly richer in vinyl chloroacetate, approaching a limiting composition at the steady state.

CONCLUSION

The free-radical, solution copolymerization of 2-ethylhexyl acrylate with vinyl chloroacetate has been successfully modeled by an appropriate extension of the previously developed diffusion-controlled termination model of Atherton and North. Both the ϕ factor and the penultimate effect model were unsuitable for describing the termination reaction for this system. The cross-termination factor ϕ showed a strong composition dependence. The inverse dependence of the termination rate constant on the solution viscosity applicable for flexible chains was not observed in this case, suggesting that the pendant group in ethylhexyl acrylate makes backbone rotational motions very inefficient, so that rearrangement diffusion is likely to be an important rate determining process in the termination mechanism.

The reactivity ratios for the EHA/VCLAC pair were determined as 10.0 and 0.033, respectively, indicating that both propagating species preferentially add EHA. There may also be a tendency towards consecutive homopolymerization of the two monomers, since EHA will homopolymerize until it is depleted followed by subsequent homopolymerization of VCLAC. However, in a continuous reactor, there is a moderation of this tendency due to the continuous flow of feed.

Qualitative behavior of the reactor dynamics was modeled for a particular feed ratio by using the appropriate ϕ value. In general, agreement with experiment was unsatisfactory. The measured conversions were lower than the model predictions, possibly due to impurities which result in continuous inhibition in the system. The chain growth is rapid as is expected in radical polymerizations. The rapid chain growth leads to an overshoot, which is followed by a gradual decline to the steady state value. The copolymer composition drift is quite significant in the approach to steady-state.

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