Experimental investigation of vinyl chloride polymerization at high conversion: semi-batch reactor modelling

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(Received 20 April 1990; accepted 30 June 1990)

A comprehensive semi-batch reactor model for suspension polymerization of vinyl chloride at high conversions has been developed. A series of kinetic experiments covering different pressure levels was carried out in a semi-batch process. The present model is in excellent agreement with the experimental data including monomer consumption, conversion history and accumulated number- and weight-average molecular weights and molecular weight distribution. The present model combined with our previous batch reactor model can be used to predict monomer feed rate, accumulated monomer consumption, polymerization rate, conversion history, reactor pressure, instantaneous and accumulated molecular weight averages and distribution and other kinetic features. The advantages of a semi-batch process operated at the vapour pressure of vinyl chloride include increased productivity, narrower molecular weight distributions and increased thermal stability of poly(vinyl chloride) (PVC) compared with a batch process taken to high conversions.

(Keywords: vinyl chloride; PVC; semi-batch polymerization and reactor modelling)

INTRODUCTION

In previous publications[1,2], the kinetic behaviour of vinyl chloride (VCM) polymerization in a batch reactor was described quantitatively over the entire conversion range. During the two-phase polymerization period, the kinetic properties of the system are essentially constant because the composition of each phase is almost unchanged for conversions up to X_f, at which the liquid monomer phase is consumed and the reactor pressure begins to fall. The total reaction rate and accumulated molecular weight averages and distribution change with conversion during this period because the relative contribution of each phase changes with conversion. However, at high conversions (conversion $> X_f$), the kinetic behaviour of VCM polymerization changes with conversion dramatically, and this includes changes in reactor pressure, monomer concentration, reaction rate, instantaneous and accumulated molecular weight averages. Kinetic parameters, such as termination and propagation rate constants, initiator efficiency and decomposition rate constant fall while the radical concentration and CM values and polydispersity increase with conversion. Consequently, properties of poly(vinyl chloride) (PVC), such as thermal stability, deteriorate with increasing conversion. All the kinetic features which change at high conversions can be attributed to the decrease in monomer concentration. Therefore, these changes should be minimized if a constant monomer concentration was maintained at high conversions by semi-batch operation, for example.

A semi-batch process is applied commercially in emulsion polymerization of VCM[3], but has not been used commercially in bulk and suspension polymerizations. However, semi-batch or equivalent processes have been carried out, experimentally, in bulk[4,5], suspension[6–8] and emulsion[9–13] polymerizations under subsaturation pressure in order to study the kinetics, PVC microstructure and thermal stability of PVC produced at low monomer concentrations. In the literature[4–13], the presynthetic PVC powder or latex were often used as seed and monomer was fed as vapour by controlling the temperature of the monomer reservoir. Hence, the properties of PVC product are relative to the seed used, i.e. conversion history of PVC seed will affect properties of final product. In the present investigation, suspension polymerization was carried out in a batch process up to a certain conversion level, then the process was switched to semi-batch with VCM fed to the reactor. A comprehensive model for such a system has not yet been published. Therefore, the objectives of the present work were to develop a comprehensive semi-batch reactor model which can be used with different pressure levels and to study reactor dynamics and PVC properties made under different pressure levels.

MODEL DEVELOPMENT

In general, semi-batch operation for VCM polymerization at high conversions involves feeding fresh monomer to the reactor over time to maintain a desired monomer concentration–time profile. Therefore, it is essential to know the feed rate of monomer required for the desired semi-batch operation.

A possible constraint condition for the semi-batch polymerization is that the concentration of monomer in the polymer phase is maintained constant, i.e.:

$$\frac{d[M]_p}{dt} = 0 \tag{1}$$

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0032-3861/91/112087-09

Both the number of moles of monomer and the volume of the polymer phase are a function of time, hence equation (1) gives:

$$\frac{dN_{mp}}{dt}=[M]_p\frac{dV_p}{dt} \tag{2}$$

Equation (2) shows the relationship between the number of moles of monomer and the volume of the polymer phase as a function of time.

Monomer charging rate to the reactor is governed by the mass balance in the polymer phase as follows:

$$\frac{dN_{mp}}{dt}=-R_pV_p+F_{in}-\frac{dN_{mv}}{dt} \tag{3}$$

where dN_{mv}/dt is the rate of change of moles of monomer in the vapour phase, and this change is due to the net change of the volume in the vapour phase as a result of the monomer feed and the reaction volume shrinkage in the polymer phase. If the volume of monomer fed is greater than that of the reaction volume shrinkage, dN_{mp}/dt is negative.

Volume change in the polymer phase can be expressed as:

$$\frac{dV_p}{dt}=\frac{M_m}{D_m}\left(F_{in}+\frac{D_mR_pV_p}{D_p}-R_pV_p-\frac{dN_{mv}}{dt}\right) \tag{4}$$

The volume of the vapour phase also varies with time due to the semi-batch feeding of monomer and due to shrinkage as monomer is converted to polymer. The rate of volume change in the vapour phase can be expressed as:

$$\frac{dV_g}{dt}=R_pV_pM_m\left(\frac{1}{D_m}-\frac{1}{D_p}\right)+\frac{M_m}{D_m}\left(\frac{dN_{mv}}{dt}-F_{in}\right) \tag{5}$$

The relationship between monomer mole number and volume change in the vapour phase can be expressed as:

$$\frac{dN_{mv}}{dt}=\frac{P_m}{RT}\left(\frac{dV_g}{dt}\right) \tag{6}$$

when the ideal gas law is assumed to be valid.

Substituting equation (5) into (6), one obtains:

$$\frac{dN_{mv}}{dt}=\frac{D_gR_pV_p(1/D_m-1/D_p)-D_gF_{in}/D_m}{1.0-D_g/D_m} \tag{7}$$

where $D_g=P_mM_m/RT$.

Equations (2)–(4) and (7) allow one to solve for the semi-batch monomer feed rate as:

$$F_{in}=\frac{R_pV_p[(1/D_m-1/D_p)([M]_pM_m-D_g)+D_g/D_m-1.0]}{[M]_pM_m/D_m-1.0} \tag{8}$$

Equation (8) is a general one for monomer feed rate for the semi-batch process at high conversions. In other words, equation (8) is valid for the conversion range $X \geqslant X_f$. However, R_p, V_p and $[M]_p$ are different for the semi-batch process operated at different pressure levels. These can be classified into two cases.

Case 1. The batch process proceeds up to conversion X_f, where the reactor pressure is still at VCM saturation vapour pressure and then the process is switched to semi-batch operation to keep the monomer in the polymer phase the same as that at conversion X_f. Therefore, D_g, V_p, $[M]_p$ and R_p in equation (8) can be expressed as:

$$D_g=D_{go}=\frac{P_{mo}M_m}{RT} \tag{9}$$

The concentration of monomer in this case is the same as that at conversion X_f, i.e.:

$$[M]_p=[M]_{pxf}=\frac{M_o(1-X_f)-M_{gxf}-M_{wxf}}{M_m\left[M_o\left(\frac{X_f}{D_p}-\frac{1-X_f}{D_m}\right)-\left(\frac{M_{gxf}+M_{wxf}}{D_m}\right)\right]} \tag{10}$$

where

$$M_{gxf}=D_{go}\left[(1.0-W_i)V_r+\frac{X_fM_o(1/D_m-1/D_p)D_m}{D_m-D_{go}}\right]$$

and

$$M_{wxf}=KW_w$$

Although the total volume of the polymer phase increases with conversion, the ratio of monomer to polymer in the polymer phase is constant at any conversion level as long as the vapour pressure is maintained and is the same as that at conversion X_f, so that:

$$A=\frac{M_o(1-X_f)-M_{gxf}-M_{wxf}}{M_oX_f} \tag{11}$$

Hence,

$$V_p=M_oX\left[\frac{1}{D_p}+\frac{M_o(1-X_f)-M_{gxf}-M_{wxf}}{D_mM_oX_f}\right] \tag{12}$$

where conversion X is defined based on the initial monomer charged.

The polymerization rate under semi-batch conditions can be written as:

$$R_p=K_{p2}[M]_p\left\{\frac{2fK_dI_{xf}\exp[-K_d(t-t_{xf})]}{V_pK_{t2}}\right\}^{1/2} \tag{13}$$

where I_{xf}, K_{p2}, K_{t2}, f and K_d are the same as those at conversion X_f. In other words, the kinetic parameters under semi-batch conditions are not a function of conversion. Equation (13) can be rewritten in terms of monomer conversion per unit time as:

$$\frac{dX}{dt}=\frac{M_mK_{p2}}{M_o}[M]_p\left(\frac{2fK_dI_{xf}}{K_{t2}}\right)^{1/2}V_p^{1/2}\exp[-K_d(t-t_{xf})/2] \tag{14}$$

Substituting equation (12) into (14), one has:

$$\frac{dX}{dt}=CX^{1/2}\exp[-K_d(t-t_{xf})/2] \tag{15}$$

where

$$C=K_{p2}[M]_pM_m\left[\left(\frac{2fK_dI_{xf}}{M_oK_{t2}}\right)\times\left(\frac{1}{D_p}+\frac{M_o(1-X_f)-M_{gxf}-M_{wxf}}{D_mM_oX_f}\right)\right]^{1/2}$$

a constant during semi-batch polymerization. Therefore, equation (15) can be integrated from interval X_f to X corresponding to t_{xf} to t and becomes

$$X=\left\{\frac{C}{K_{\mathrm{d}}}\left[1.0-\exp(-K_{\mathrm{d}}(t-t_{xf})/2)\right]+X_f^{1/2}\right\}^2 \qquad (t\geqslant t_{xf}) \tag{16}$$

Equation (16) is the conversion history for the semi-batch process at vapour pressure.

Substituting equations (12), (13) and (16) into (8), one obtains:

$$F_{\mathrm{in}}=\frac{\mathrm{d}N_{\mathrm{F}}}{\mathrm{d}t}=DX^{1/2}\exp[-K_{\mathrm{d}}(t-t_{xf})/2] \tag{17}$$

where

$$D=\frac{CM_{\mathrm{o}}}{M_{\mathrm{m}}}\left[\frac{(1/D_{\mathrm{m}}-1/D_{\mathrm{p}})([M]_{\mathrm{p}}M_{\mathrm{m}}-D_{\mathrm{go}})+D_{\mathrm{go}}/D_{\mathrm{m}}-1.0}{[M]_{\mathrm{p}}M_{\mathrm{m}}/D_{\mathrm{m}}-1.0}\right]$$

Hence, accumulated moles of monomer fed to the reactor can be found by integrating equation (17) from t_{xf} to t, i.e.:

$$N_{\mathrm{F}}=D\left(\frac{C}{K_{\mathrm{d}}}+2X_{\mathrm{f}}^{1/2}\right)\{1-\exp[-K_{\mathrm{d}}(t-t_{\mathrm{xf}})/2]\}/K_{\mathrm{d}} \tag{18}$$

Equations (8), (14), (16) and (18) allow one to solve for monomer feed and polymerization rates, conversion history and accumulated monomer consumption as a function of time in a semi-batch process operating at a pressure equal to the vapour pressure of VCM.

Case 2. The batch process proceeds to a conversion X_{p} ($X_{\mathrm{p}}>X_{\mathrm{f}}$), at which time the reactor pressure is lower than the saturation pressure, the process is then switched to semi-batch VCM feed to maintain the monomer concentration constant at that pressure. Then, $[M]_{\mathrm{p}}$, V_{p}, R_{p}, X and N_{F}, analogous to case 1, can be expressed as:

$$[M]_{\mathrm{p}}=\frac{M_{\mathrm{o}}(1-X_{\mathrm{p}})-M_{\mathrm{gxp}}-M_{\mathrm{wxp}}}{M_{\mathrm{m}}\left[M_{\mathrm{o}}\left(\frac{X_{\mathrm{p}}}{D_{\mathrm{p}}}+\frac{1-X_{\mathrm{p}}}{D_{\mathrm{m}}}\right)-\frac{M_{\mathrm{gxp}}+M_{\mathrm{wxp}}}{D_{\mathrm{m}}}\right]} \tag{19}$$

$$V_{\mathrm{p}}=M_{\mathrm{o}}X\left[\frac{1}{D_{\mathrm{p}}}+\frac{M_{\mathrm{o}}(1-X_{\mathrm{p}})-M_{\mathrm{gxp}}-M_{\mathrm{wxp}}}{D_{\mathrm{m}}M_{\mathrm{o}}X_{\mathrm{p}}}\right] \tag{20}$$

where

$$M_{\mathrm{gxp}}=D_{\mathrm{g}}\left[(1-W_{\mathrm{i}})V_{\mathrm{r}}+M_{\mathrm{o}}(1/D_{\mathrm{m}}-1/D_{\mathrm{p}})\times\left(X_{\mathrm{p}}+X_{\mathrm{f}}\frac{D_{\mathrm{go}}}{D_{\mathrm{m}}-D_{\mathrm{go}}}\right)\right]$$

$$M_{\mathrm{wxp}}=KM_{\mathrm{w}}P_{\mathrm{m}}/P_{\mathrm{mo}}$$

$$R_{\mathrm{p}}=K_{\mathrm{p2}}[M]_{\mathrm{p}}\left(\frac{2fK_{\mathrm{d}}I_{\mathrm{xp}}}{V_{\mathrm{p}}K_{\mathrm{t2}}}\right)^{1/2}\exp[-K_{\mathrm{d}}(t-t_{\mathrm{xp}})/2] \tag{21}$$

where K_{p2}, K_{t2}, f and K_{d} are calculated at pressure P_{m} based on the equations in a previous publication[1].

$$X=\{C'[1-\exp(-K_{\mathrm{d}}(t-t_{\mathrm{xp}})/2)]/K_{\mathrm{d}}+X_{\mathrm{p}}^{1/2}\}^2 \tag{22}$$

where

$$C'=K_{\mathrm{p2}}[M]_{\mathrm{p}}M_{\mathrm{m}}\left(\frac{2fK_{\mathrm{d}}I_{\mathrm{xp}}}{M_{\mathrm{o}}K_{\mathrm{t2}}}\right)^{1/2}\times\left(\frac{1}{D_{\mathrm{p}}}+\frac{M_{\mathrm{o}}(1-X_{\mathrm{p}})-M_{\mathrm{gxp}}-M_{\mathrm{wxp}}}{D_{\mathrm{m}}M_{\mathrm{o}}X_{\mathrm{p}}}\right)^{1/2}$$

$$N_{\mathrm{F}}=D'\left(\frac{C'}{K_{\mathrm{d}}}+2X_{\mathrm{p}}^{1/2}\right)\{1-\exp[-K_{\mathrm{d}}(t-t_{\mathrm{xp}})/2]\}/K_{\mathrm{d}} \tag{23}$$

where

$$D'=\frac{C'M_{\mathrm{o}}}{M_{\mathrm{m}}}\left[\frac{(1/D_{\mathrm{m}}-1/D_{\mathrm{p}})([M]_{\mathrm{p}}M_{\mathrm{m}}-D_{\mathrm{g}})+D_{\mathrm{g}}/D_{\mathrm{m}}-1.0}{[M]_{\mathrm{p}}M_{\mathrm{m}}/D_{\mathrm{m}}-1.0}\right]$$

Equations (8) and (21)–(23) allow one to solve for monomer feed and polymerization rates, conversion history and accumulated monomer consumption during semi-batch operation with subsaturation pressure.

Using the same strategy shown above, one can easily derive an equation for initiator feed rate for the semi-batch process, such as

$$F_{\mathrm{I}}=[I]_{\mathrm{p}}V_{\mathrm{p}}R_{\mathrm{p}}\times\left\{K_{\mathrm{d}}+M_{\mathrm{o}}\left[\frac{1}{D_{\mathrm{p}}}+\frac{M_{\mathrm{o}}(1-X_{\mathrm{f}})-M_{\mathrm{gxf}}-M_{\mathrm{wxf}}}{D_{\mathrm{m}}M_{\mathrm{o}}X_{\mathrm{f}}}\right]\right\}M_{\mathrm{m}}/M_{\mathrm{o}} \tag{24}$$

where

$$R_{\mathrm{p}}=K_{\mathrm{p2}}[M]_{\mathrm{p}}\left(\frac{2fK_{\mathrm{d}}[I]_{\mathrm{p}}}{K_{\mathrm{t2}}}\right)^{1/2}$$

$$[I]_{\mathrm{p}}=[I]_{\mathrm{pxf}}=\frac{I_0\exp(-K_{\mathrm{d}}t_{\mathrm{xf}})}{M_{\mathrm{o}}\left(\frac{X_{\mathrm{f}}}{D_{\mathrm{p}}}+\frac{1-X_{\mathrm{f}}}{D_{\mathrm{m}}}\right)-\frac{M_{\mathrm{gxf}}+M_{\mathrm{wxf}}}{D_{\mathrm{m}}}}$$

It should be mentioned that the polymerization and monomer feed rates have to be modified corresponding to the initiator concentration.

Molecular weight development of PVC for the semi-batch process can be obtained by appropriately modifying the batch reactor model.

EXPERIMENTAL

To evaluate the present model, a series of experiments for suspension polymerization of VCM using batch and semi-batch operation was carried out.

The equipment used for the experiments and reactor operational procedures have been given in a previous publication[1]. The basic polymerization conditions are as follows: monomer 1116 g, distilled and deionized water 2232 g, stabilizer [poly(vinyl alcohol), KP-08] 0.08 wt% (based on water), initiator [bis(4-tert-butylcyclohexyl) peroxydicarbonate, Perkadox 16-W40] 0.175 wt% (based on monomer). When polymerization in the batch process proceeds up to a pressure drop or beyond a certain pressure level, fresh monomer from a monomer cell, for which the weight has been calibrated, was fed into the reactor under nitrogen pressure. The monomer flow rate was controlled by a manually operated valve. The accumulated amount of monomer fed to the reactor was weighed on-line. Conversion was measured by an on-line tracer method which has been described in detail in a previous publication[14].

Accumulated molecular weight averages and distribution were measured using a low-angle laser light scattering photometer and gel permeation chromatography as described earlier[2]. The rate of dehydrochlorination was measured by the conductimetric method[14a].

RESULTS AND DISCUSSION

The present model can be solved either numerically or analytically. However, both methods require initial conditions for semi-batch operation. According to the polymerization course described above, the initial conditions for the semi-batch process are the terminal conditions for the batch process. Therefore, solution of the semi-batch model equations follows solution of the batch reactor model equations with kinetic parameters and monomer concentration appropriately adjusted.

Monomer feed rate

Figures 1 and *2* show accumulated moles of fresh monomer fed to the reactor. One can see that the model predictions are in good agreement with the experimental data. Accumulated moles of monomer increase with time almost linearly (not a linear function). This is not surprising since the kinetic parameters and monomer concentration are constant; only the initiator concentration decreases with time due to its decomposition and increase of reaction mixture volume, so that the polymerization rate under these conditions is almost linear. The monomer fed is consumed by polymerization and the remainder swells the new PVC produced. It is obvious that monomer consumption rate decreases with decreasing pressure level. For seed polymerizations, monomer consumption increases with time more significantly at the beginning of the process[8,9], because extra monomer is required to swell the PVC seed. In fact, the present model is in agreement with the experimental results of Sorvik and Hjertberg[8,9].

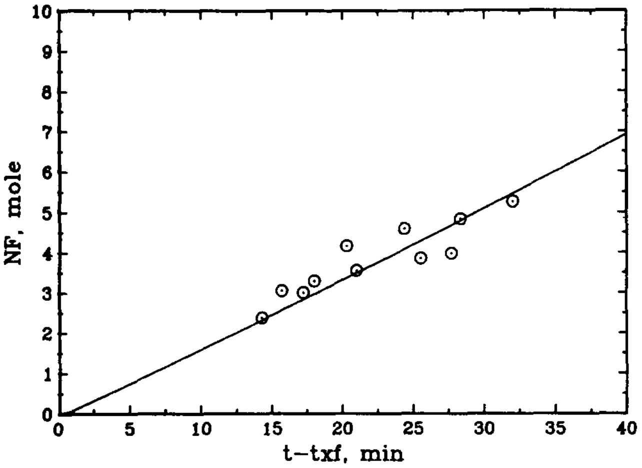

Figure 1 Monomer consumption of semi-batch polymerization with vapour pressure at 50°C: ⊙, experimental data; ——, model

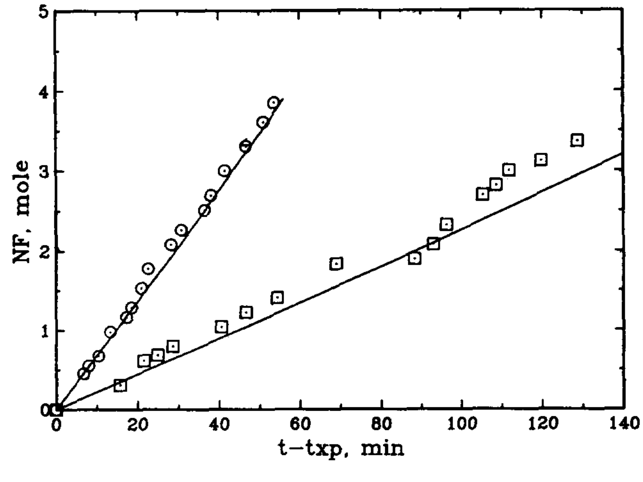

Figure 2 Monomer consumption of semi-batch polymerization with subsaturation pressure at 50°C: ⊙, at 90% P_{mo}; □, at 78% P_{mo}; ——, model

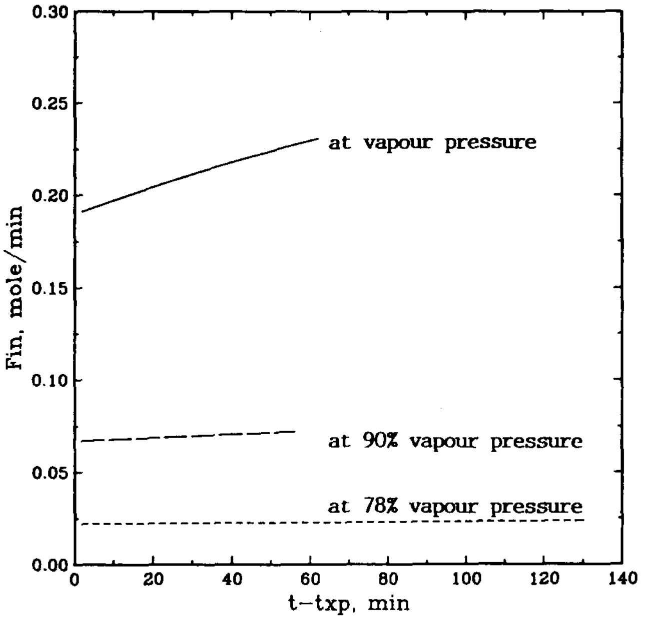

Figure 3 Instantaneous feed rate of VCM during semi-batch polymerization with different pressures at 50°C

The model prediction of the monomer feed rate is shown in *Figure 3*. It is difficult to obtain the instantaneous feed rate experimentally. As expected, the model predictions show that the required monomer feed rate decreases with decreasing pressure level. However, it increases with reaction time at a certain pressure level. This can be attributed to increasing reaction consumption and swelling produced PVC due to increasing reaction volume. Monomer feed rate is a key variable for semi-batch operation. Hence, the present model should be useful for commercial semi-batch reactor design and control.

Reactor dynamics

Conversion histories for seed or semi-batch polymerization depending on initiator concentration[5,12] and pressure level[6,10,12] are reported in the literature. However, a quantitative description of conversion history has not been reported. Both experimental data and model predictions of conversion histories for the semi-batch process at different pressure levels are shown in *Figures 4–6*. One can see that the present model predictions are in excellent agreement with the experimental data over the different pressure levels. Polymerization rates are almost linear with present polymerization conditions as expected. If the semi-batch process is operated at the vapour pressure of VCM, the polymerization rate is a maximum. Increase of productivity is very significant if the semi-batch process is operated at above 90% vapour pressure levels as shown in *Table 1*. The semi-batch process requires only 52% of the batch polymerization time to obtain 91% conversion (based on initial monomer charged) at 50°C. The reason is that the polymerization rate in the batch process falls significantly after 85% conversion. *Figures 4–6* also show the significant effect of monomer concentration on polymerization rate.

Reactor pressures corresponding to *Figures 4–6* are shown in *Figure 7*. The model for the pressure and

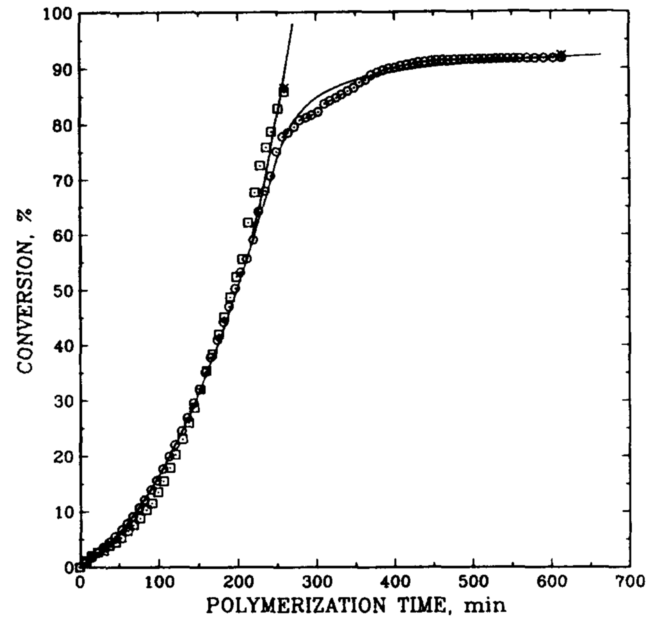

Figure 4 Comparison of conversion history between batch and semi-batch processes at 50°C: ⊙, batch; □, semi-batch at P_{mo}; ——, model; ✱, gravimetry

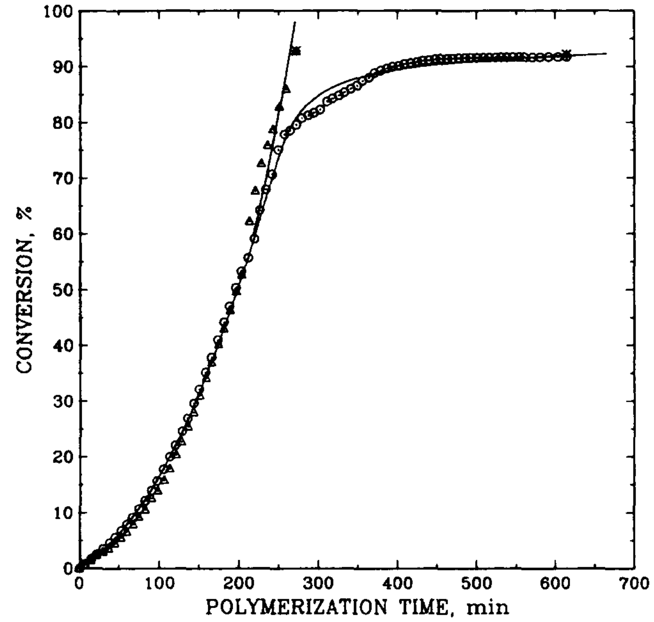

Figure 5 Comparison of conversion history between batch and semi-batch processes at 50°C: ⊙, batch; △, semi-batch at P_{mo}; ——, model; ✱, gravimetry

conversion relationship is given in previous publications[15,15a]. *Figure 7* clearly shows pressure histories for semi-batch operations. It should be mentioned that the reactor pressure drops slowly before the critical conversion X_f (see ref. 15a for details). Therefore, the semi-batch operation at vapour pressure commences before X_f as shown in *Figure 7*.

Molecular properties

Instantaneous and accumulated molecular weight averages of PVC made in a batch process decrease with conversion after X_f due to the significant increase in CM, the ratio of chain transfer to monomer rate constant to propagation rate constant. However, for the semi-batch process, CM should remain constant because of the constant monomer concentration and constant kinetic parameters. The model predictions for CM values corresponding to semi-batch operations discussed above are shown in *Figure 8*. One can see that CM increases with decreasing pressure level but remains constant at a given pressure. Hence, the instantaneous molecular weight averages should be almost constant for the semi-batch process. If the semi-batch process is operated at vapour pressure, the molecular weight averages should be the same as those in the polymer phase at conversion X_f. *Figure 9* shows a comparison of accumulated molecular weight averages for batch and semi-batch polymerizations. The model predictions for $\bar{M}_w$ and $\bar{M}_n$ increase slightly with conversion for semi-batch operated at vapour pressure. The experimental data are slightly lower than the model predictions. However, $\bar{M}_w$ and $\bar{M}_n$ of PVC made by the semi-batch process at vapour pressure seem higher than those by the batch process at the same conversion levels.

Accumulated molecular weight distribution (*MWD*) shown in *Figure 10* also indicates the difference between batch and semi-batch processes at the same conversion. Accumulated *MWD* for the batch process shifts to lower molecular weights compared with the *MWD* for the semi-batch process at vapour pressure. *Figures 11* and *12* show accumulated *MWD* for the semi-batch operation at pressure levels 90% and 78% P_{mo} (case 2), respectively.

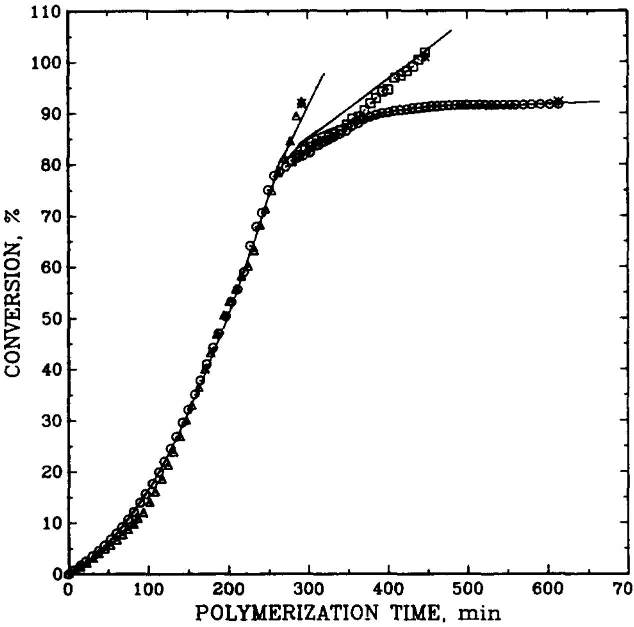

Figure 6 Comparison of conversion history between batch and semi-batch processes with subsaturation pressure at 50°C: ⊙, batch; △, semi-batch at 90% P_{mo}; □, semi-batch at 78% P_{mo}; ——, model; ✱, gravimetry

Table 1 Comparison of productivity between batch and semi-batch processes

Process type	Terminal conversion (%)	Terminal time (min)	Pressure level	Time fraction
Batch	91	500	52% P_{mo}	1.00
Semi-batch	91	262	P_{mo}	0.52
Semi-batch	91	300	90% P_{mo}	0.60
Semi-batch	91	350	78% P_{mo}	0.70

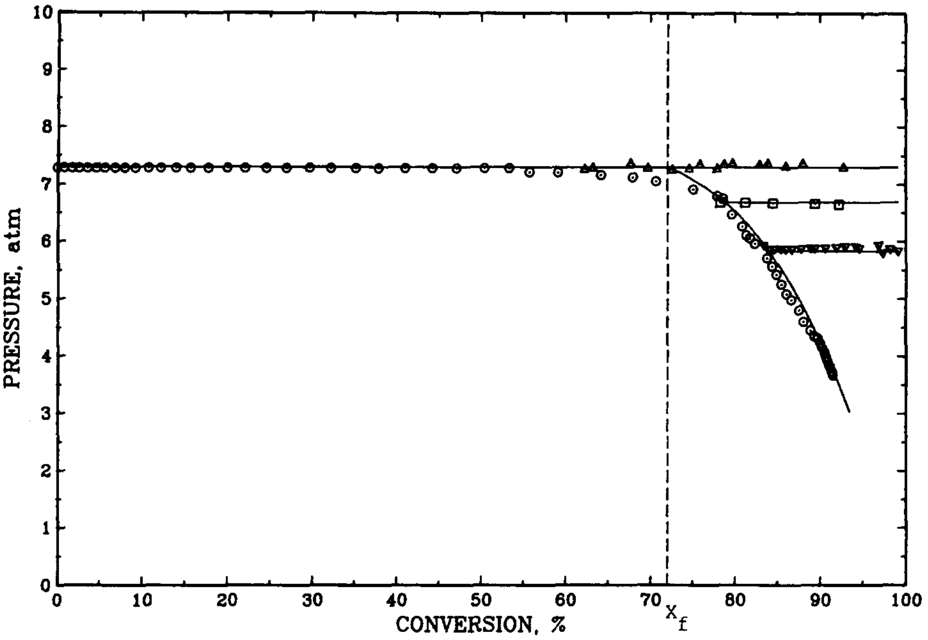

Figure 7 Conversion dependence of reactor pressure for batch and semi-batch polymerizations at 50°C: ⊙, batch; △, semi-batch at P_{mo}; □, semi-batch at 90% P_{mo}; ▽, semi-batch at 78% P_{mo}; ——, model

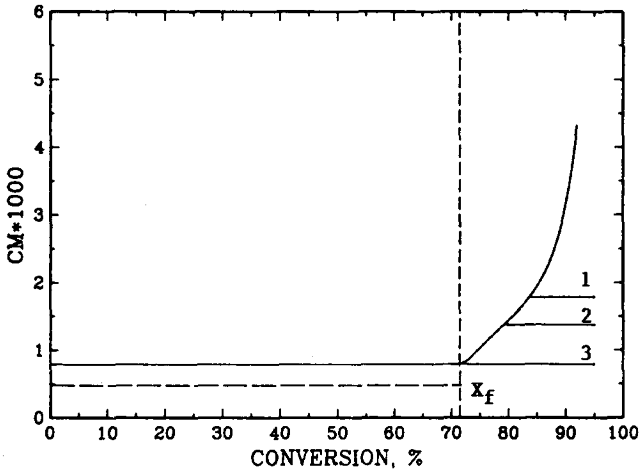

Figure 8 Conversion dependence of CM for batch and semi-batch polymerizations at 50°C: 1, at 78% P_{mo}; 2, at 90% P_{mo}; 3, at P_{mo}

These results demonstrate that the model in a previous publication[2] is in excellent agreement with the experimental data for the semi-batch process when kinetic parameters are adjusted accordingly.

The effect of the pressure level on accumulated *MWD* is shown in *Figure 13*. One can see that the accumulated *MWD* shifts towards lower molecular weight with decreasing reactor pressure. These results are in agreement with the experimental data of Hjertberg *et al.* using seed polymerizations[9]. Although $\bar{M}_w$ and $\bar{M}_n$ and accumulated *MWD* vary with pressure level, these changes are not significant because the amount of PVC produced in the semi-batch process in the present experiments is relatively small compared with the total amount of PVC produced. However, instantaneous *MWD* corresponding to *Figures 10* and *13* varies with polymerization pressure dramatically as shown in *Figure 14*. The instantaneous *MWD* of PVC

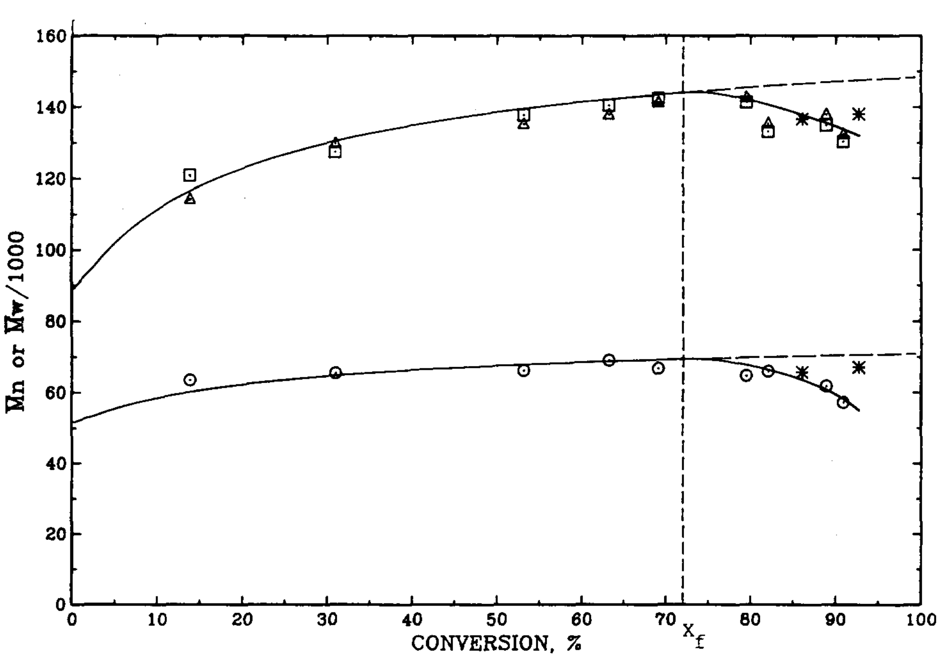

Figure 9 Conversion dependence of accumulated molecular weight averages for batch and semi-batch processes at 50°C: △, □, $\bar{M}_w$, batch; ⊙, $\bar{M}_n$, batch; ∗, semi-batch; ——, batch model; — — —, semi-batch model

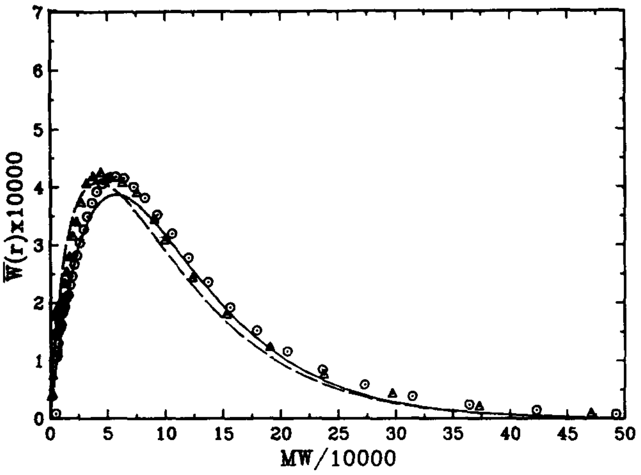

Figure 10 Comparison of accumulated *MWD* between batch and semi-batch polymerizations at 50°C ($M_w=62.5r$): △, batch with conversion 92.2%; ⊙, semi-batch with conversion 92.7%; ---, batch model; ——, semi-batch model

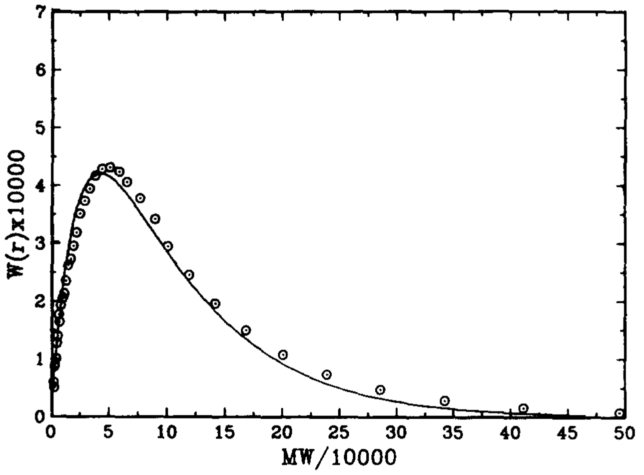

Figure 11 Accumulated *MWD* of PVC for semi-batch polymerization at 90% P_{mo} at 50°C ($M_w=62.5r$): ⊙, experimental data; ——, model

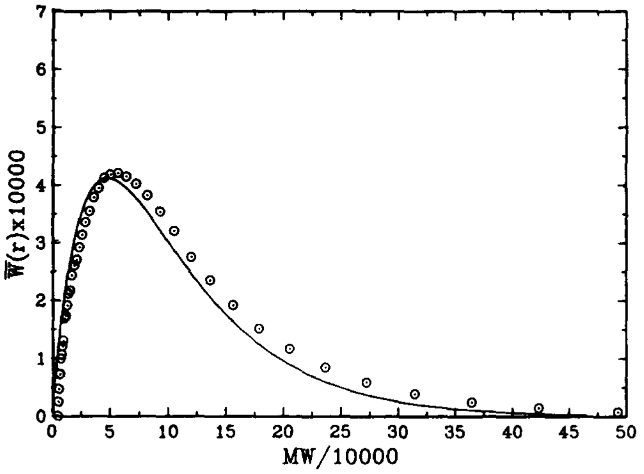

Figure 12 Accumulated *MWD* of PVC for semi-batch polymerization at 78% P_{mo} at 50°C ($M_w=62.5r$): ⊙, experimental data; ——, model

made by semi-batch at vapour pressure, even at high conversions, is similar to the accumulated *MWD* at conversion X_f. *Figures 15* and *16* further show that the instantaneous number- and weight-average molecular weights change with pressure level. If the semi-batch process is operated at vapour pressure, the instantaneous M_n and M_w are similar to those at conversion X_f and increase slightly due to chain transfer to polymer. Decreasing pressure level always leads to decrease of molecular weight. *Figure 17* shows how instantaneous *MWD* shifts toward lower molecular weight as pressure decreases at the same conversion level. Obviously, a lower polydispersity for PVC should result for the semi-batch process operated at vapour pressure.

Based on experimental data and model predictions above, one can conclude that the instantaneous molecular weight averages and *MWD* can be controlled by the semi-batch process. In other words, the instantaneous terminal groups and other defect structures of PVC can be controlled by pressure level or monomer concentration. Therefore, dehydrochlorination measurements of PVC should reflect the effect of pressure level on thermal

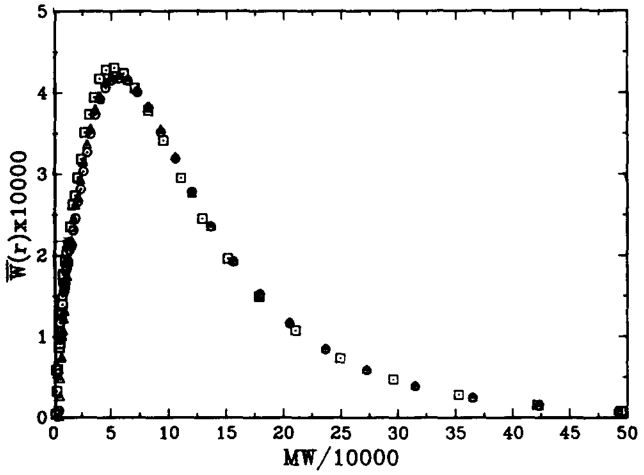

Figure 13 Effect of pressure level on accumulated *MWD* of PVC produced by semi-batch processes at 50°C ($M_w=62.5r$): ⊙, at P_{mo}, conversion 92.7%; △, at 90% P_{mo}, conversion 91.8%; □, at 78% P_{mo}, conversion 101%

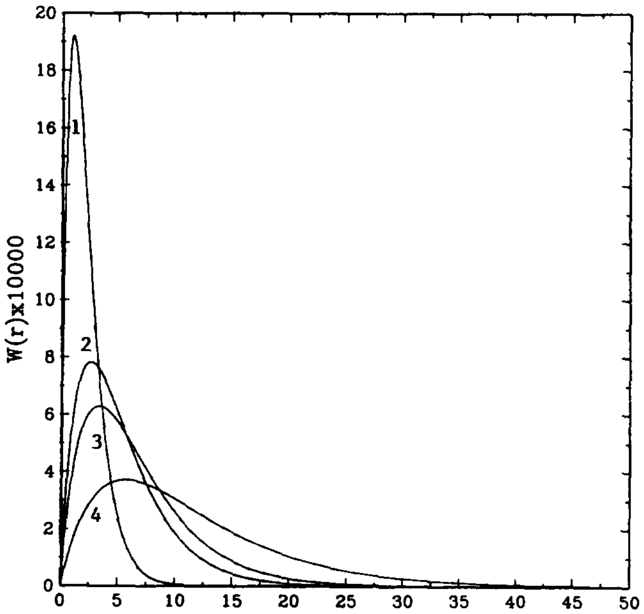

Figure 14 Effect of pressure level on instantaneous *MWD* for batch and semi-batch polymerizations at 50°C ($M_w=62.5r$): 1, batch with terminal pressure 45% P_{mo}; 2, semi-batch at 78% P_{mo}; 3, semi-batch at 90% P_{mo}; 4, semi-batch at P_{mo}

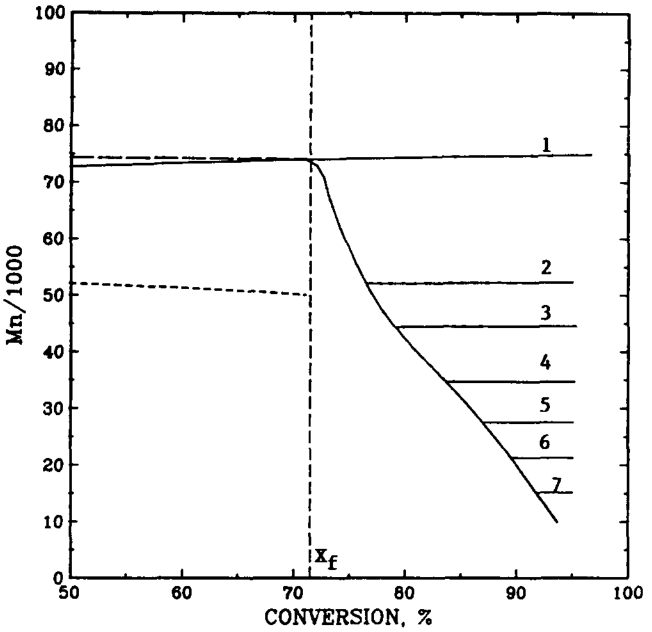

Figure 15 Effect of pressure level on instantaneous number-average molecular weight for batch and semi-batch polymerizations at 50°C: 1, at P_{mo}; 2, 95%; 3, 90%; 4, 80%; 5, 70%; 6, 60%; 7, 50% P_{mo}, respectively

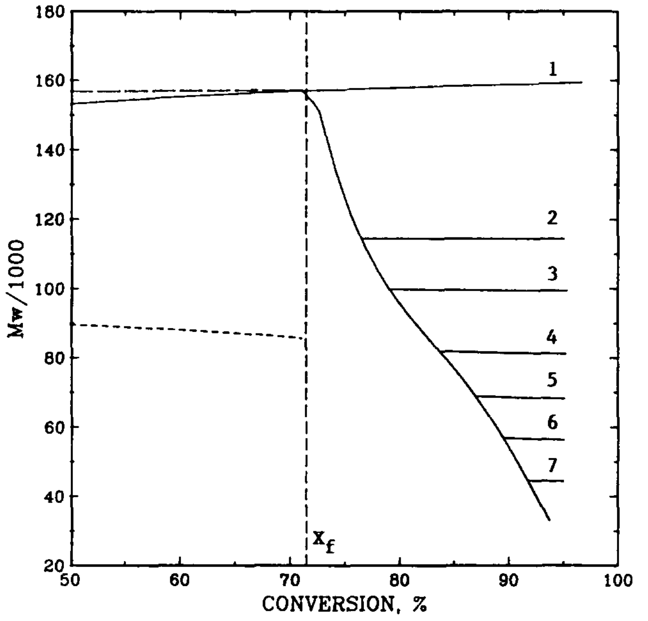

Figure 16 Effect of pressure level on instantaneous weight-average molecular weight for batch and semi-batch polymerizations at 50°C: 1, at P_{mo}; 2, 95%; 3, 90%; 4, 80%; 5, 70%; 6, 60%; 7, 50% P_{mo}, respectively

stability of PVC. The results of dehydroclorination rates are shown in *Table 2*. For the batch process, thermal stability of PVC decreases significantly with conversion after the pressure drop. However, for the semi-batch process at vapour pressure, the dehydrochlorination rate is the same as that for the batch process before pressure drop (see *Table 2*). For the same conversion level, the dehydrochlorination rate for the semi-batch process at vapour pressure is much lower than that for the batch process. Dehydrochlorination rate increases with decreasing pressure level for the semi-batch process. These results are in agreement with the experimental results of Sorvik and Hjertberg using seed polymerizations[7–10].

The dehydrochlorination rate measurements in the present work are based on accumulated PVC samples. One can predict from these results that the dehydrochlorination rate of instantaneous PVC produced at subsaturation pressure must increase with decreasing pressure level dramatically. These results indicate that the defect structures which are responsible for the decrease in thermal stability of PVC increase dramatically with decreasing monomer concentration. At subsaturation pressure, the terminal structure of 1-chloro-2-alkene which results in chain transfer to monomer reactions increases as a result of decrease in monomer concentration. Meanwhile, the concentration of long chain branches, 2,4-dichloro-n-butyl and 2-chloroethyl branches, also ought to increase with decreasing monomer concentration. All these branches contain tertiary chloride[16]. The experimental results of Hjertberg *et al.*[17–19] and Van den Heuvel *et al.*[20] show that the terminal structure of 1-chloro-2-alkene is not significantly involved in the degradation of PVC. Therefore, tertiary chloride seems to be responsible for the decrease in thermal stability of PVC with decreasing monomer concentration. Detailed microstructure measurements for these PVC samples are required to confirm the effect of the defect structures on the thermal stability of PVC.

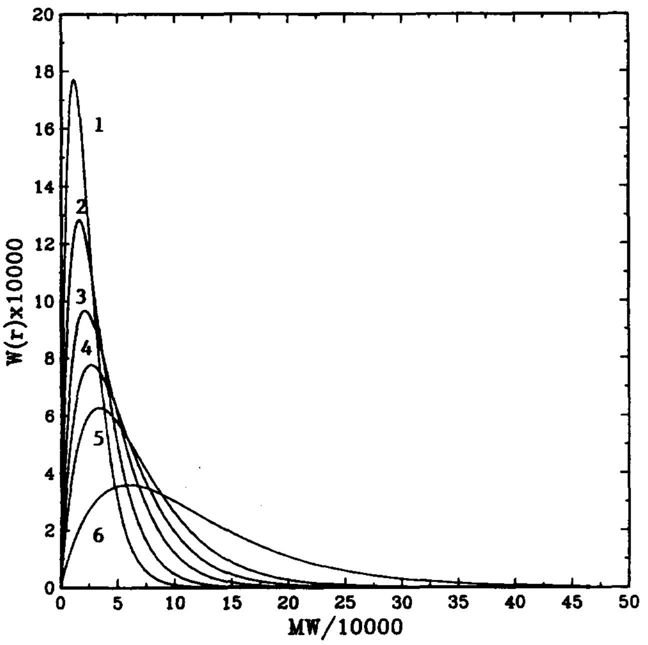

Figure 17 Pressure dependence of instantaneous *MWD* for semi-batch polymerization at 50°C, conversion 95% ($M_w = 62.5r$): 1, at 50% P_{mo}; 2, 60% P_{mo}; 3, 70% P_{mo}; 4, 80% P_{mo}; 5, 90% P_{mo}; 6, at P_{mo}, respectively

Table 2 Effect of semi-batch process on dehydrochlorination rate of PVC

Process type	Terminal conversion[a] (%)	Pressure level	$10^3 \times$ (dHCl/dt) (% min^{-1})
Batch	$<X_f$	P_{mo}	16.5
Batch	92.2	45% P_{mo}	19.5
Semi-batch	86.1	P_{mo}	16.5
Semi-batch	92.7	P_{mo}	16.5
Semi-batch	91.8	90% P_{mo}	16.8
Semi-batch	101	78% P_{mo}	23.4

[a] Conversion was calculated based on the initial monomer charged

However, the present experimental results show that the semi-batch operation at vapour pressure can provide an effective way to limit the defect structures and to obtain high productivity at a given polymerization temperature.

The effect of the semi-batch process on other properties of PVC, such as porosity, particle size, bulk density and molecular structure, is currently being studied. Details will be reported in a subsequent publication.

CONCLUSIONS

In the present investigation, a comprehensive model for the semi-batch process has been developed. The present model combined with the batch reactor model can be used to predict monomer feed rate, total monomer consumption, conversion history, polymerization rate and molecular weight development of VCM polymerization in a semi-batch process at different pressure levels. The model predictions are in excellent agreement with the experimental data.

The advantages of the semi-batch process operated at vapour pressure include increase in productivity and improvement of molecular properties, such as narrowing *MWD* and enhancing thermal stability of PVC. However, PVC molecular properties will deteriorate if the semi-batch process is operated at subsaturation pressure; the lower the pressure, the poorer the thermal stability of PVC at a given temperature.

The present model should be useful for commercial semi-batch reactor design and operation.

ACKNOWLEDGEMENT

Financial support from the National Science and Engineering Research Council of Canada and the McMaster Institute for Polymer Production Technology is appreciated.

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NOMENCLATURE

A	Ratio of monomer to polymer at X_f
C	Constant defined in equation (15)
CM	Ratio of chain transfer to monomer rate constant to propagation rate constant
D	Constant defined in equation (17)
D_g	Density in gas phase (g l^{-1})
D_m	Density of liquid monomer (g l^{-1})
D_p	Density of polymer (g l^{-1})
f	Initiator efficiency
F_{in}	Monomer feed rate (mol min^{-1})
F_I	Initiator feed rate (mol min^{-1})
I_o	Initial mole of initiator (mol)
$[I]_p$	Initiator concentration (mol l^{-1})
I_{xf}	Mole of initiator at X_f (mol)
K	Solubility constant of VCM in water
K_d	Initiator decomposition rate constant (s^{-1})
K_{p2}	Propagation rate constant (l mol^{-1} s^{-1})
K_{t2}	Termination rate constant (l mol^{-1} s^{-1})
M_m	Molecular weight of monomer
M_g	Monomer amount in the gas phase (g)
M_o	Initial monomer (g)
$[M]_p$	Monomer concentration (mol l^{-1})
M_w	Monomer amount in the water phase (g)
N_F	Accumulated moles of monomer feeding into reactor
N_{mv}	Mole of monomer in the vapour phase (mol)
N_{mp}	Mole of monomer in the polymer phase (mol)
P_m	Partial pressure of monomer (atm)
P_{mo}	Vapour pressure of monomer (atm)
r	Polymer chain length
R	Gas constant (l atm mol^{-1} K^{-1})
R_p	Polymerization rate (mol l^{-1} min^{-1})
t	Polymerization time (min)
t_{xf}	Polymerization time at X_f (min)
t_{xp}	Polymerization time at pressure P_m (min)
T	Temperature (K)
V_p	Volume of polymer phase (l)
V_r	Reactor volume (l)
W_i	Reactor charge (fraction)
$W(r)$	Weight fraction of PVC with chain length r
X	Conversion
X_f	Critical conversion at which liquid monomer is consumed
X_p	Conversion at time t_{xp}