Experimental investigation of vinyl chloride polymerization at high conversion: polymer microstructure and thermal stability and their relationship to polymerization conditions

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Suspension poly(vinyl chloride) (PVC) samples with various monomer conversions were synthesized using batch and semi-batch polymerization processes at different temperatures. The concentration of tertiary chlorines in the PVC was determined using ^{13}C nuclear magnetic resonance, and the concentration of internal double bonds was analysed by ozonolysis. The dehydrochlorination rate of the PVC was measured at 190°C by the conductimetric method under nitrogen environment. It was found that the concentration of tertiary chlorines increases significantly with increase in monomer conversion after the critical conversion at which the reactor pressure starts to fall. At the same conversion level, it increases with polymerization temperature. The concentration of allylic chlorines is much lower than that of tertiary chlorines. A conversion dependence of allylic chlorines was not found for the present PVC samples. However, the concentration of allylic chlorines increases with polymerization temperature. Excellent correlation between the dehydrochlorination rate and the concentration of tertiary chlorines was found based on the present experimental data, but no significant relationship was found between dehydrochlorination rate and concentration of allylic chlorines. Therefore, tertiary chlorines in PVC chains are probably the defect structure that is most responsible for the reduced thermal stability of PVC. The mechanisms of formation of internal defect structures and the effects of polymerization conditions on the concentration of the defect structures are discussed in some detail based on diffusion-controlled free-radical polymerization theory, and the monomer concentration effects are further confirmed by the results using a semi-batch polymerization process. The concentration of tertiary chlorines can be minimized by semi-batch operation at or near the saturation pressure, providing PVC of higher thermal stability.

(Keywords: poly(vinyl chloride); suspension polymerization; monomer conversion)

INTRODUCTION

The relationship between molecular structure and thermal stability of PVC has been studied extensively in the literature. The major achievements are summarized in recent reviews[1-5]. The relevant microstructural features of PVC include short- and long-chain branching, internal unsaturation, head-to-head structures, endgroups and oxygen-containing groups. Based on the thermal stability and molecular structural studies of PVC and its model compounds, the defect structures that are considered responsible for lowered thermal stability of PVC are mainly allylic and tertiary chlorines[1,6-16], carbonyl structures[4,17-24] and other oxygenated structures[25,26]. Although it is well recognized that the thermal stability of PVC is strongly dependent on defect structures, little work[10,11,13,27-31] has been done on the effect of polymerization conditions on the formation of the defect structures and on the thermal stability of PVC.

The allylic and tertiary chlorine structures are formed by mechanisms involving inter- and intramolecular chain transfer during vinyl chloride (VCM) polymerization. Therefore, these structures are kinetically controlled. On the other hand, the oxygenated structures, except the initiator residuals, are formed by the reactions involving oxygen with VCM and PVC during polymerization. In commercial reactor operating practice, the initial oxygen level in the reactor has been used to control PVC particle size and morphology[32]. Hence, commercial PVC most probably contains certain levels of oxygenated structures. The concentrations of oxygenated structures are, however, controlled by the polymerization conditions used. Therefore, to study the relationship between microstructure and thermal stability, it is very important to know the synthesis history of PVC samples. In the

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present investigation, the emphasis is placed on the effect of polymerization conditions on the kinetically controlled defect structures and their relationship with thermal stability of PVC. Oxygenated structures are probably absent in the PVC samples used in the present investigation.

In the recent publication of Xie *et al.*[31] the thermal stability of PVC synthesized under various polymerization conditions was studied. It was found that the dehydrochlorination rate of PVC is independent of monomer conversion when the conversion is less than the critical conversion X_f at which the reactor pressure starts to drop. However, the dehydrochlorination rate increases significantly with increase in monomer conversion for conversions greater than X_f. If the concentration of monomer is kept constant using a semi-batch process at high conversions, the thermal stability does not reduce at monomer conversions beyond X_f. The dehydrochlorination rate increases with increase in polymerization temperature in the range 40–80°C. These results indicate that the concentration of defect structures that are responsible for the thermal instability of PVC must change significantly with polymerization conditions. It is of interest to know how the defect structures change with polymerization conditions and what the relationship is between the defect structures and thermal instability. Therefore, in the present work, the microstructure and thermal stability of the PVC samples synthesized under different polymerization conditions were further investigated, and the relationship between defect structures and thermal instability of PVC is further illustrated.

EXPERIMENTAL

To investigate the effects of polymerization conditions on the formation of defect structures of PVC, a series of experiments using suspension polymerization of VCM with various reactor operating conditions was carried out in a 5 litre stainless steel reactor. VCM was provided by the B. F. Goodrich Company (Niagara Falls, Ontario, Canada). Poly(vinyl alcohol) with a degree of hydrolysis of 71–75 mol% (Goshenol KP-08) was used as a suspending agent. Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (Perkadox 16-W40) provided by AKZO Chemicals was used as an initiator for the polymerizations at 50°C. Recrystallized azobis(isobutyronitrile) (AIBN) was used as an initiator for the polymerizations at 65 and 70°C. The reactor operating procedures, polymerization recipe, monomer conversion determinations and polymer molecular weight measurements have been given in Xie *et al.*[33–35].

The concentration of tertiary chlorines was calculated as the sum of ethyl, butyl and long-chain branches. The content of these branches was determined by ^{13}C nuclear magnetic resonance (n.m.r.) after reductive dechlorination. The reduction was performed in a mixture of tetrahydrofuran and xylene with Bu_3SnH as reducing agent[36]. Proton-decoupled ^{13}C n.m.r. spectra were obtained with a Varian VXR-300 spectrometer. The sample was observed at 110°C as 10–15% (wt/vol) solution in 1,2,4-trichlorobenzene with 20% benzene-d_6 to provide a deuterium lock. The acquisition time was 2 s, the tip angle 60°, and the pulse interval 8 s. The number of scans accumulated was 8000.

The concentration of internal double bonds (or sequences) was determined by following the changes in number-average molecular weight ($\bar{M}_n$) caused by ozone oxidative cleavage of all double bonds[37]. The PVC sample (500 mg) was dissolved in cyclohexanone (100 ml) and a small amount of methanol was added to facilitate the cleavage of the ozonide formed. The ozonolysis was performed at −20°C for 2 h, and the polymer was recovered by precipitation in methanol and dried in vacuum for 24 h. The experimental details have been given earlier[8]. The number of internal cleavages per 1000 monomer units (VCM) was calculated from the number-average molecular weights before ($\bar{M}_{n,0}$) and after ($\bar{M}_n$) the oxidative treatment:

$$(\mathrm{C{=}C})_n/1000\ VCM = 62\,500(1/\bar{M}_n - 1/\bar{M}_{n,0}) \qquad (1)$$

The dehydrochlorination rate was measured in a specially designed apparatus described earlier[38]. Bulk sample (100 mg) was heated at 190°C in nitrogen atmosphere (< 5 ppm O_2). The dehydrochlorination was followed conductometrically and the rate was calculated as evolved HCl as a percentage of the theoretical amount per minute.

RESULTS AND DISCUSSION

The PVC samples in the present studies were prepared essentially in the absence of oxygen. After the reactor was evacuated, the residual air was further removed by five cycles of evacuation and purging using small amounts of VCM vapour. The oxygen level in the reactor could not be detected using gas chromatography. Thus, the oxygenated structures in the PVC samples were eliminated, except for the peroxide initiator fragments which are on the end of some PVC chains. Therefore, in the following discussion, the emphasis is placed on the internal microstructures of PVC which are kinetically controlled.

Microstructure of PVC

The effects of monomer conversion and polymerization temperature on dehydrochlorination rate of PVC are shown together with previous experimental data in *Figure 1*[31]. The present dehydrochlorination rates are about 25% lower than those measured previously at another laboratory[31], but the relationship between dehydrochlorination rate and monomer conversion is the same. The data shown in *Figure 1* indicate that the defect structures in the PVC chains that are responsible for the lowering of thermal stability must increase significantly with monomer conversion for conversions beyond X_f for an isothermal batch polymerization process. For the same conversion level, the concentration of defect structures increases with increase in polymerization temperature. *Figure 2* shows that, as expected, the number of tertiary chlorines in PVC chains increases dramatically with conversion beyond X_f. At the same conversion level, the concentration of tertiary chlorines increases with increase in polymerization temperature. It is interesting to note that the response of tertiary chlorines to the polymerization conditions is similar to that of the dehydrochlorination rate to the polymerization conditions, as shown in *Figure 1*. *Figure 3* shows the concentration of internal double bonds in the PVC samples, synthesized at 50°C, against monomer conversion. Comparing the data in *Figure 3* with those in *Figure 2*, one can see that the concentration of internal

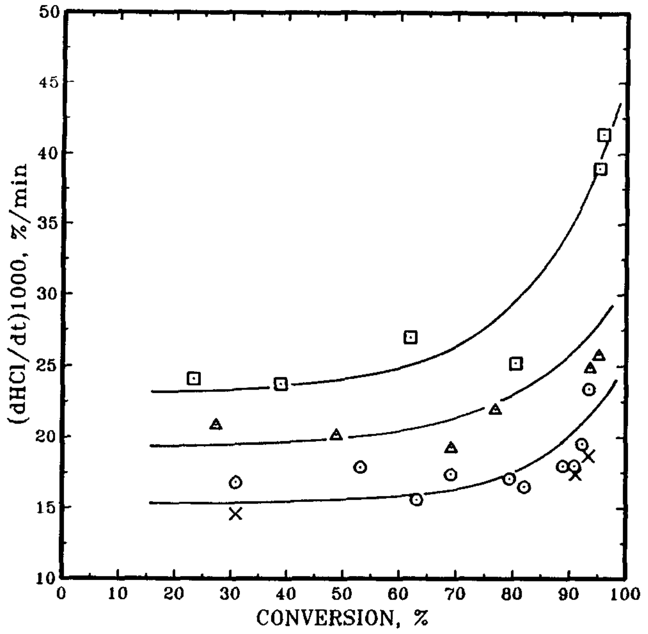


Figure 1 Effects of monomer conversion and polymerization temperature on the dehydrochlorination rate of PVC. ○, 50°C; △, 60°C; □, 70°C (ref. 31); ×, 50°C (this study)

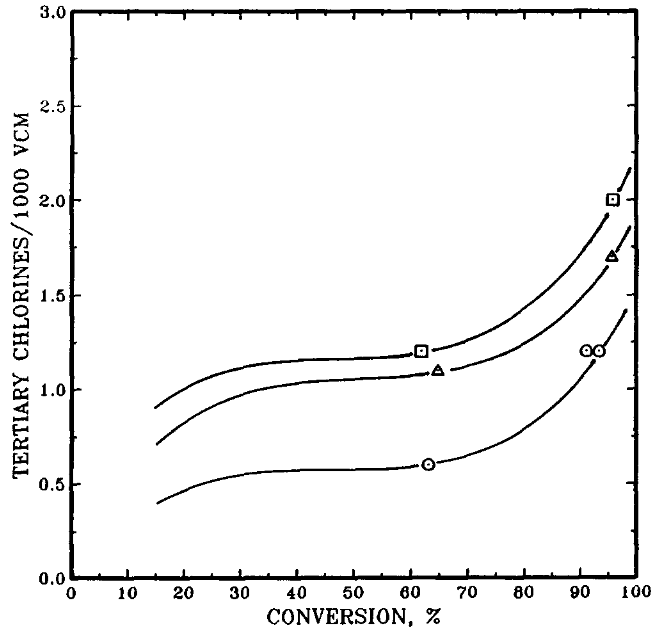


Figure 2 Conversion and temperature dependence of the concentration of tertiary chlorines in PVC chains. ○, 50°C; △, 65°C; □, 70°C

double bonds in PVC chains is about ten times smaller than that of tertiary chlorines. Based on the limited data shown in *Figure 3*, one cannot find a relationship between internal double bond concentration and monomer conversion. However, *Figure 3* does suggest that the concentration of internal double bonds does not change significantly with monomer conversion over the entire conversion range, or that the dependence of the concentration of internal double bonds on monomer conversion is so small that the concentration change with conversion cannot be detected by the present measurement technique. Using average values of the concentration of internal double bonds for PVC synthesized at the same polymerization temperature, one finds that the concentration of internal double bonds increases linearly with polymerization temperature, as shown in *Figure 4*. From the results in *Figures 3* and *4*, one may conclude that the maximum concentration of allylic chlorines in PVC chains is much smaller than that of tertiary chlorines and does not change with monomer conversion significantly, but it increases with increase in polymerization temperature.

Figure 5 shows the concentration of tertiary chlorines in PVC at different conversions measured by Bensemra *et al.*[13] and Liauro-Darricades *et al.*[29]. The concentration of tertiary chlorines in PVC increases significantly with conversion beyond X_f. The concentration of internal double bonds measured by Liauro-Darricades *et al.*[29] using ^{1}H n.m.r. does not show any correlation with monomer conversion either. In recent work Rogestedt and Hjertberg[39] found that ^{1}H n.m.r. and ozonolysis are in surprisingly good agreement for whole polymer samples. For fractions of rather low molecular weight the ^{1}H n.m.r. method gave much higher values. Qualitatively, the present experimental results are in agreement with the data in the literature[13,29].

The concentrations of tertiary chlorines shown in *Figure 2* were obtained using samples of accumulated

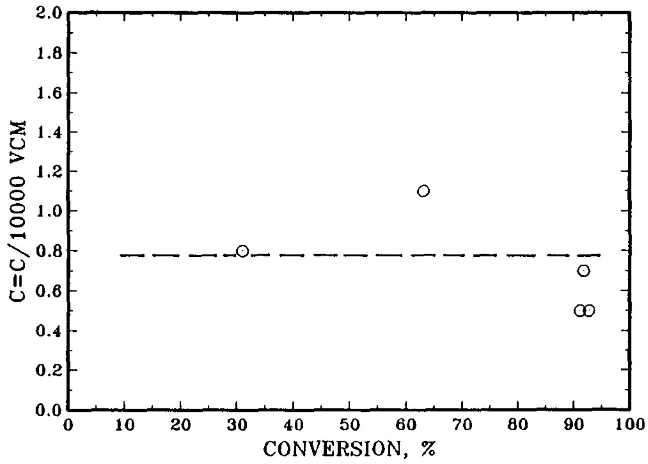


Figure 3 Conversion dependence of internal double bonds of PVC synthesized at 50°C

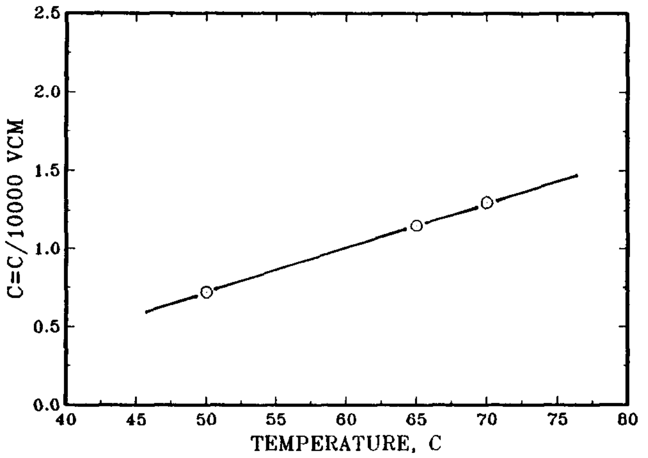


Figure 4 Polymerization temperature dependence of internal double bonds of PVC

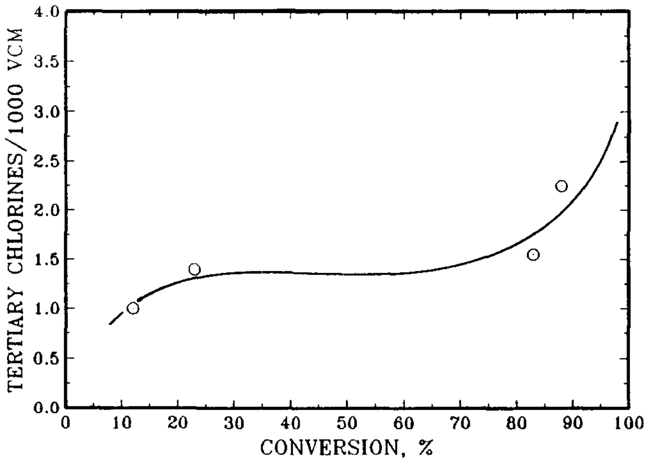


Figure 5 Conversion dependence of the concentration of tertiary chlorines in PVC chains (data from ref. 13)

PVC. For the PVC samples with conversion 90–95%, the PVC chains generated beyond X_f are about 20–25% of the total weight. However, the concentration of tertiary chlorines in PVC at 90–95% conversion is at least 60% higher than that at conversions less than X_f, as shown in *Figure 2*. This suggests that the concentration of tertiary chlorines in PVC chains generated beyond X_f is much higher than that in PVC produced before X_f. Therefore, the instantaneous concentration of tertiary chlorines must increase dramatically with increase in conversion after X_f. Unfortunately, instantaneous PVC samples cannot be obtained by the experimental method used here. In the previous work of Hjertberg *et al.*[10,27,28], it was found that the concentration of tertiary chlorines in the PVC made using unsaturated seeded polymerization is much higher than that in the PVC made by the conventional processes. The concentrations of short- and long-chain branches in the PVC increase dramatically with decrease in monomer concentration in the polymer phase, and increase with increase in polymerization temperature[7,10]. Therefore, the present results obtained using normal suspension polymerizations are in agreement with the previous work of Hjertberg *et al.*[7,10].

From the preceding discussion, one can conclude that the concentration of tertiary chlorines increases with conversion for conversions beyond X_f. Conversion dependence of internal double bond concentration is not obvious for normal PVC samples. Concentrations of both tertiary and allylic chlorines in PVC chains increase with increase in polymerization temperature. To explain these phenomena, the mechanisms and kinetics of formation of the defect structures need to be further illustrated. In previous publications[34,35], the kinetics of VCM suspension polymerization were studied quantitatively over the entire conversion range considering most of the relevant elementary reactions. Elementary reactions associated with the formation of defect structures were only qualitatively discussed[31]. It is of interest to know how these reactions are affected by the polymerization conditions. The formation of tertiary chlorines in PVC chains is associated with ethyl, butyl and a major part of the long-chain branches. These reactions might occur simultaneously over the entire conversion range during VCM polymerization as follows.

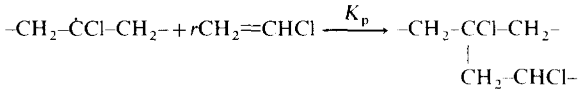
Propagation:

$$-(\mathrm{CH_2{-}CHCl})_r{-}\mathrm{CH_2{-}\dot{C}HCl} + \mathrm{CH_2{=}CHCl} \xrightarrow{K_p} -\mathrm{CH_2{-}CHCl}{-}(\mathrm{CH_2{-}CHCl})_{r-1}{-}\mathrm{CH_2{-}\dot{C}HCl} \qquad (2)$$

Chain transfer to polymer and formation of long-chain branches:

$$-\mathrm{CH_2{-}CHCl{-}CH_2{-}\dot{C}HCl} + -\mathrm{CH_2{-}CHCl{-}CH_2}- \xrightarrow{K_{fp}} -\mathrm{CH_2{-}CH_2Cl} + -\mathrm{CH_2{-}\dot{C}Cl{-}CH_2}- \qquad (3)$$

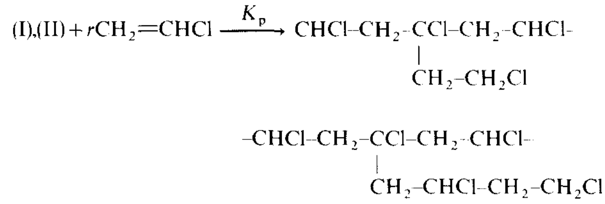
$$\mathrm{Cl^{\bullet}} + -\mathrm{CH_2{-}CHCl{-}CH_2}- \xrightarrow{K_{fp}} -\mathrm{CH_2{-}\dot{C}Cl{-}CH_2}- + \mathrm{HCl} \qquad (4)$$



$$-\mathrm{CH_2{-}\dot{C}Cl{-}CH_2}- + r\mathrm{CH_2{=}CHCl} \xrightarrow{K_p} \begin{array}{l} -\mathrm{CH_2{-}CCl{-}CH_2}- \\ \qquad\quad | \\ \qquad\ \mathrm{CH_2{-}CHCl}- \end{array} \qquad (5)$$

Backbiting reactions and formation of short-chain branches[3,12,40]:

$$-\mathrm{CH_2{-}CHCl{-}CH_2{-}\dot{C}HCl} \xrightarrow{K_b} -\mathrm{CH_2{-}\dot{C}Cl{-}CH_2{-}CH_2Cl\ (I)\ or} \; -\mathrm{CH_2{-}\dot{C}Cl{-}CH_2{-}CHCl{-}CH_2{-}CH_2Cl\ (II)} \qquad (6)$$



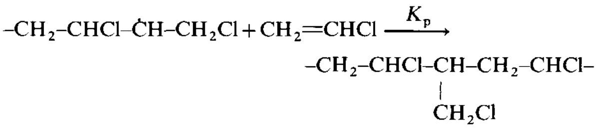
$$\mathrm{(I),(II)} + r\mathrm{CH_2{=}CHCl} \xrightarrow{K_p} \begin{array}{l} \mathrm{CHCl{-}CH_2{-}CCl{-}CH_2{-}CHCl}- \\ \qquad\qquad\quad | \\ \qquad\qquad \mathrm{CH_2{-}CH_2Cl} \end{array}$$

$$\begin{array}{l} -\mathrm{CHCl{-}CH_2{-}CCl{-}CH_2{-}CHCl}- \\ \qquad\qquad\quad | \\ \qquad\qquad \mathrm{CH_2{-}CHCl{-}CH_2{-}CH_2Cl} \end{array} \qquad (7)$$

Formation of tertiary chlorines in PVC chains depends on the reaction rates of reactions (2), (4) and (6). However, reactions (3) and (6) are in competition with propagation reaction (2), and reaction (4) is in competition with chain initiation (chlorine atom radicals reacting with monomer) during VCM polymerization over the entire conversion range. Before the critical monomer conversion, polymerization occurs in the monomer and the polymer phase simultaneously. The reaction environment in the two phases is quite different. The polymer concentration in the monomer phase is very low owing to low solubility of PVC in its monomer. Hence, reactions (3) and (4) are negligible in the monomer phase. Although reaction (6) is possible in the monomer phase, the radical concentration in the monomer phase is low ($\sim 10^{-8}\,\mathrm{mol\,l^{-1}}$), and the monomer concentration is high ($\sim 13\,\mathrm{mol\,l^{-1}}$) at normal polymerization temperature. Furthermore, the propagation rate constant K_p is much higher than backbiting reaction rate constant K_b. Thus, reaction (2) is favoured over reaction (6) in the monomer phase. Therefore, the formation of tertiary chlorines in PVC generated in the monomer phase is very limited. On the other hand, the polymer phase is formed at very early conversion[34,41]. In the polymer phase, PVC is swollen with about 30 wt% monomer[34,42]. Polymer concentration in terms of monomeric units per volume is much higher than monomer concentration in the polymer phase. The radical concentration in the polymer phase is about 30 times higher than that in the monomer phase according to kinetics modelling[34]. Thus, reactions (3), (4) and (6) are favoured in the environment of the polymer phase compared with that in the monomer phase. PVC chains generated in the monomer phase will lose their identity as soon as they precipitate from the monomer phase because they will participate in reactions (3) and (4). Therefore, the concentration of tertiary chlorines in PVC chains is determined by the polymer phase even before X_f although the polymerization occurs in both phases simultaneously. The relative percentage of PVC produced in the polymer phase increases significantly with increase in monomer conversion, and the opposite is true for the monomer phase[34]. Hence, the concentration of tertiary chlorines in the PVC at early conversion should be relatively low due to domination of polymerization in the monomer phase. However, it is expected that the concentration of tertiary chlorines in PVC chains increases significantly at low conversions ($<10\%$ conversion) due to increase in importance of the polymer phase[34]. Unfortunately, information regarding the concentration of tertiary chlorines at such low conversions has never been published. After a conversion around 10%, the concentration of tertiary chlorines should only increase very slightly with increase in conversion until X_f because the polymer phase dominates the polymerization and the relevant conditions in the polymer phase are constant up to X_f. The data shown in *Figure 5* are consistent with this mechanism.

When monomer conversion is greater than X_f, the monomer phase no longer exists, the concentration of monomer in the polymer phase decreases with increase in conversion, and the reactor pressure falls dramatically for isothermal batch polymerization[43]. The decrease in monomer concentration and the increase in polymer concentration lead to an increase in the number of polymer chain entanglement points. The free volume of the polymer phase decreases appreciably with increase in monomer conversion, so that the diffusion-controlled bimolecular termination rate constant for polymer radicals falls dramatically as does the propagation rate constant somewhat later. Consequently, the radical concentration should increase significantly with increase in monomer conversion beyond X_f, as predicted by kinetics modelling[34]. The polymerization rate decreases due to both lack of monomer and decrease in propagation rate constant even though the radical concentration is high, and reactions (3), (4) and (6) are favoured beyond X_f due to increase in both radical and polymer concentrations. Furthermore, chain transfer to polymer and backbiting reaction rate constants are much smaller than propagation and termination rate constants at normal polymerization conditions. It is expected that K_{fp} and K_b do not become diffusion-controlled. In particular, reaction (6), which is unimolecular, may not be affected by the significant fall in free volume. Thus, the ratios of K_{fp} to K_p and K_b to K_p should increase with increase in monomer conversion. In addition, the concentration of chlorine radicals should increase at high conversions due to the competition of the following reactions:

$$-CH_2-CHCl-\dot{C}H-CH_2Cl \xrightarrow{K_{ab}} -CH_2-CH{=}CH-CH_2Cl + Cl^{\bullet} \qquad (8)$$



$$-CH_2-CHCl-\dot{C}H-CH_2Cl + CH_2{=}CHCl \xrightarrow{K_p} -CH_2-CHCl-\underset{\substack{|\\ CH_2Cl}}{CH}-CH_2-CHCl- \qquad (9)$$

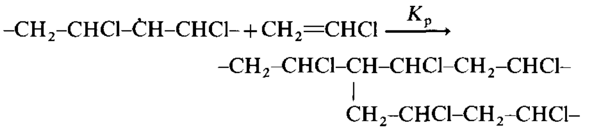
As a result, the concentration of tertiary chlorines in PVC chains increases significantly with conversion, as shown in *Figure 2*. Beyond X_f, accumulated and instantaneous molecular weight averages of PVC decrease significantly with increase in conversion[35]. Thus, PVC chains generated beyond X_f will have higher concentration of tertiary chlorines. Guyot *et al.*[44] reported that the defect structures are concentrated in the low-molecular-weight fractions of accumulated PVC. This may be due to the significance of backbiting reactions at high conversions where polymeric radicals have lower molecular weights. The mechanisms discussed here are consistent with the experimental observations of Guyot *et al.*[44]. The concentration/conversion profile for tertiary chlorines, therefore, should at least qualitatively follow that given in solid curves in *Figures 2* and *5*.

Internal unsaturated structures can be formed by the mechanisms involving abstraction of hydrogen from a backbone $-CH_2-$ moiety by polymer radicals[45,46] or by chlorine radicals[1,8] and subsequent abstraction of chlorine radical as follows:

$$-CH_2-CHCl-CH_2-\dot{C}HCl + -CH_2-CHCl-CH_2-CHCl- \xrightarrow{K'_{fp}} -CH_2-CHCl-CH_2-CH_2Cl + -CH_2-CHCl-\dot{C}H-CHCl-\ (III) \qquad (10)$$

$$Cl^{\bullet} + -CH_2-CHCl-CH_2-CHCl- \xrightarrow{K''_{fp}} -CH_2-CHCl-\dot{C}H-CHCl-\ (III) + HCl \qquad (11)$$

$$-CH_2-CHCl-\dot{C}H-CHCl- \xrightarrow{K_{ab}} -CHCl-CH{=}CH-CH_2-CHCl- + Cl^{\bullet} \qquad (12)$$



$$-CH_2-CHCl-\dot{C}H-CHCl- + CH_2{=}CHCl \xrightarrow{K_p} -CH_2-CHCl-\underset{\substack{|\\ CH_2-CHCl-CH_2-CHCl-}}{CH}-CHCl-CH_2-CHCl- \qquad (13)$$

The concentration of long-chain branches with tertiary hydrogen shown in reaction (13) is much less than that with tertiary chlorines formed in reaction (5) according to ^{13}C n.m.r. measurements[8,12]. The concentration of internal double bonds is much smaller than that of tertiary chlorines, as shown in *Figures 2* and *3*. Reaction (12) should be relatively rapid and be chemically controlled over the entire conversion range. The reaction rate constant K_{ab} should be at least as large as K_p. Therefore, low concentrations of tertiary hydrogen and internal double bonds are due to low concentrations of radicals of type (III) in the system. This suggests that the abstraction of hydrogen from a $-CH_2-$ moiety is much more difficult than abstraction of hydrogen from a $-CHCl-$ moiety in PVC chains. This is in agreement with the conclusion of Starnes *et al.*[12] in comparing (K_{fp}/K_p) values estimated in model PVC compound studies. Therefore, K'_{fp} and K''_{fp} in reactions (10) and (11) may be much smaller than K_{fp} in reactions (3) and (4). Thus, reactions (10) and (11) might be chemically controlled and independent of monomer conversion. Hence, the concentration of internal double bonds is not sensitive to monomer conversion. This is why the concentration of internal double bonds has no significant correlation with monomer conversion, as shown in *Figure 3*. However, chemically controlled reactions (10) and (11) are most probably sensitive to polymerization temperature. Therefore, the concentration of internal double bonds increases with increase in temperature, as shown in *Figure 4*.

The polymerization conditions change beyond X_f due to a fall in monomer concentration in the polymer phase. If a constant monomer concentration in the polymer phase can be maintained at high conversions by semi-batch operation[47], the concentration of tertiary chlorines can be reduced for the PVC made using a batch process at the same conversion level. For instance, if semi-batch polymerization is operated at the saturation vapour pressure, the monomer concentration after X_f is the same as that at X_f for batch process. *Figure 6* shows the comparison of the concentration of tertiary chlorines in PVC chains made by batch and by semi-batch processes at saturated vapour pressure. One can see that the concentration of tertiary chlorines is lower for the PVC sample synthesized using the semi-batch process. However, the concentration of tertiary chlorines still increases with increase in monomer conversion. This is because the proportion of PVC generated in the polymer phase increases. If semi-batch polymerization is operated at subsaturated pressure, the concentration of tertiary chlorines is higher than that at saturated pressure, as shown in *Table 1*. The effect of semi-batch operation on the formation of internal double bonds is, however, not significant, as shown in *Table 1*. These results further confirm the kinetic mechanisms discussed above. In a previous publication[31], it was found that the dehydrochlorination rate of PVC is constant for semi-batch operated at saturation pressure. However, the limited data in *Figure 6* show that the concentration of tertiary chlorine is not constant for PVC made using semi-batch operation at saturated pressure. Therefore, defect structures other than tertiary chlorine may have an effect on the dehydrochlorination rate of PVC and these other defects are also minimized by semi-batch operations.

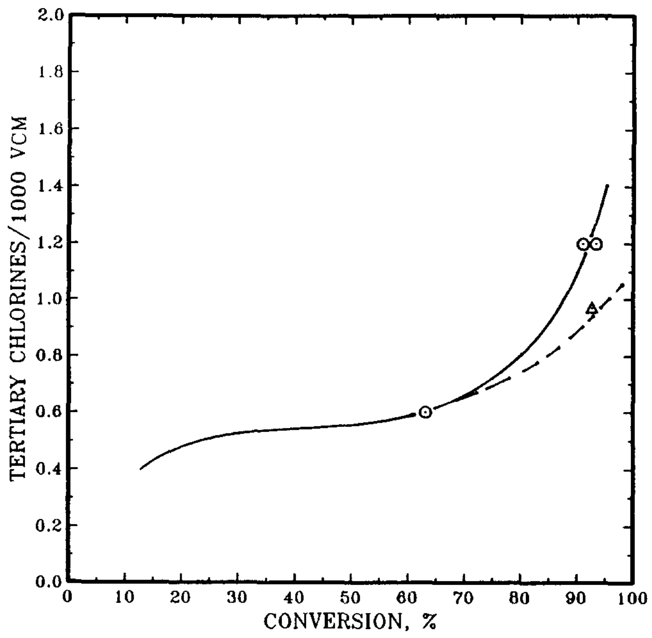
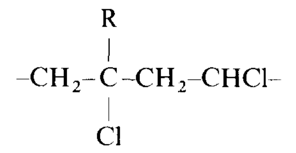


Figure 6 Effect of semi-batch operation on the concentration of tertiary chlorines in PVC chains. ○, Batch polymerization at 50°C; △, semi-batch polymerization at 50°C

Thermal stability

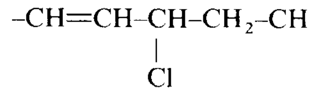
Many attempts to obtain quantitative relationships between the defect structures and the thermal stability of PVC have been made in the literature[7,8,10,13,44,48–53]. Hjertberg *et al.*[7,8,10] found that the thermal stability of PVC strongly depends on the concentration of internal defect structures, especially tertiary chlorines. The results obtained by the IUPAC cooperative working party[49] are in agreement with Hjertberg *et al.*[7,8,10]. However, there are conflicting opinions in the literature regarding the effect of defect structures on thermal stability of PVC[52,54]. Van den Heuvel and Weber[53] found that the number of defect endgroups of PVC chains does not change after degradation at 180°C in helium. Therefore, it seems that the endgroups on PVC are not significantly involved in the degradation process of PVC. Thus, thermal stability of PVC is most likely affected by the internal defect structures. The internal defect structures of PVC can be summarized as follows.

Tertiary chlorines:



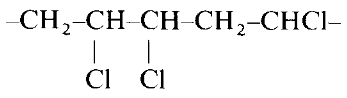
$$-CH_2-\overset{\displaystyle R}{\underset{\displaystyle Cl}{C}}-CH_2-CHCl- \qquad (IV)$$

Allylic chlorines:



$$-CH{=}CH-\underset{\displaystyle Cl}{CH}-CH_2-CHCl- \qquad (V)$$

Head-to-head chlorines:



$$-CH_2-\underset{\displaystyle Cl}{CH}-\underset{\displaystyle Cl}{CH}-CH_2-CHCl- \qquad (VI)$$

Table 1 Effect of polymerization conditions on the formation of defect structures

Polymerization process[a]	Terminal conversion[b] (%)	Pressure level (% P_{mo})[c]	Tertiary chlorines /10^3 *VCM*	Allylic chlorines /10^3 *VCM*	Number-average chain length	(dHCl/d*t*) × 10^3 (% min^{-1})
Batch	91.1	45	1.20	0.05	1038	17.4
Semi-batch	92.7	100	0.97	0.05	1034	14.6
Semi-batch	91.8	90	1.00	0.07	1068	15.5
Semi-batch	101	78	1.10	0.07	978	18.8

[a] The samples were synthesized at 50°C
[b] Conversion was calculated based on the initial monomer charged
[c] P_{mo} is the saturation vapour pressure of VCM

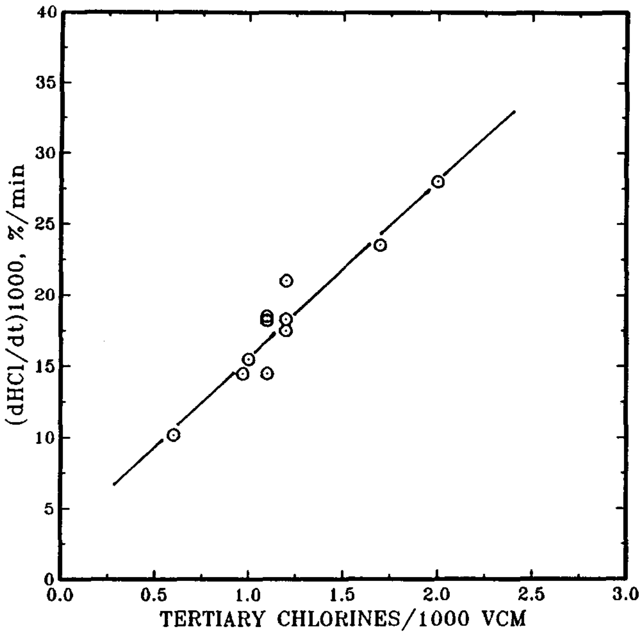


Figure 7 Correlation between the dehydrochlorination rate and the concentration of tertiary chlorines in PVC

where R is a 2-chloroethyl, a 2,4-dichloro-n-butyl, or a long-chain branch. Structure (IV) is formed by reactions (5) or (7). Structure (V) is formed by reaction (12). Structure (VI) is formed by bimolecular combination termination[34,35] or by head-to-head addition[55] followed by propagations.

Kitamura *et al.*[56] synthesized a copolymer with high concentration of dichloroethylene structure in copolymer chains and found that the thermal stability of copolymer is much better than that of homopolymer PVC synthesized at similar reaction conditions. This suggests that the structure (VI) is relatively stable in PVC chains. Furthermore, the concentration of structure (VI) in normal PVC chains is very low[9]. The relationship between concentration of structure (VI) and monomer conversion is not available in the literature. Structure (VI) might not play an important role in lowering thermal stability of PVC, although it cannot be ruled out in the consideration of its effect on thermal stability of PVC until significant experimental evidence is accumulated.

Hjertberg *et al.*[7] found a good correlation between the dehydrochlorination rate and the concentration of tertiary chlorines. Ivan *et al.*[50] found that there is a linear relationship between the initial rate of HCl loss and the concentration of tertiary chlorines for the copolymer of vinyl chloride and 2-chloro-propene. However, these PVC samples have much higher concentration of tertiary chlorines than normal PVC. Valid correlations between the dehydrochlorination rate and concentration of tertiary chlorines have not been published to date for PVC synthesized using the conventional commercial processes. *Figure 7* shows a correlation found in this study between the dehydrochlorination rate and the concentration of tertiary chlorines for PVC synthesized by suspension polymerization in the absence of oxygen. These PVC samples were made at different conversions, at different polymerization temperatures and at different final pressures. The dehydrochlorination rate is a function of monomer conversion and polymerization temperature, as shown in *Figure 1*. Hence, it is difficult to correlate the dehydrochlorination rate with polymerization conditions. *Figure 7*, however, indicates that the dehydrochlorination rate can be correlated as a function of the concentration of tertiary chlorines regardless of the polymerization conditions. As different polymerization temperatures were used, i.e. the polymers have different tacticities[57], the influence of the stereostructure on thermal stability of PVC should be small according to the present results. Using linear regression, one can obtain the following correlation from the data in *Figure 7*:

$$\frac{\mathrm{dHCl}}{\mathrm{d}t} = 3.3 + 12.4[\mathrm{Cl}]_{\mathrm{T}} \qquad (10^{-3}\%\ \mathrm{min}^{-1}) \qquad (14)$$

where $[\mathrm{Cl}]_{\mathrm{T}}$ is the concentration of tertiary chlorines (number/1000 *VCM*). The correlation coefficient of equation (14) is 0.96. One can also see that the dehydrochlorination rate against the concentration of tertiary chlorines does not go through the origin. The intercept of the line is 3.3×10^{-3}, which gives the rate of dehydrochlorination without tertiary chlorines in the PVC chains. This rate could be the random dehydrochlorination rate of PVC or the contribution of other defect structures of PVC. However, the contribution of other defect structures is very minor according to the results shown in *Figure 7*. It should be mentioned that the total concentration of tertiary chlorines is assumed to be the summation of ethyl, butyl and long-chain branches in the present work. Starnes *et al.*[58] recently showed that most of ethyl branches have tertiary hydrogen atoms. If the results of Starnes *et al.*[58] are correct, the concentration of tertiary chlorines is overestimated in the present work. However, this will not affect the mechanisms and conclusions discussed herein.

Allylic chlorines in structure (V) have been considered the most important labile structures in PVC[59,60]. However, conclusive results regarding the effect of allylic chlorines on thermal stability have not been achieved. One of the reasons is the low concentration of the internal unsaturation in normal PVC. In order to increase the concentration of allylic chlorines in PVC, Ivan *et al.*[61] used the controlled chemical dehydrochlorination method. The same authors[51] found that the initial dehydrochlorination rate increases with increase in the concentration of allylic chlorine. Similar results were found by Hjertberg *et al.*[8]. However, the data are rather scattered. *Figure 8* shows the dehydrochlorination rate for the present PVC samples *versus* concentration of allylic chlorines. One can see from *Figure 8* that the data are very scattered and a reasonable correlation cannot be obtained from the present data. Although *Figure 8* cannot prove the independence of the dehydrochlorination rate on the concentration of allylic chlorines, the data in *Figure 8* suggest that the allylic chlorines are not dominant in affecting the thermal stability of PVC. Moreover, assuming allylic chlorines to be labile structures, how significantly can the allylic chlorines with the concentration in PVC as shown in *Figure 8* affect the thermal stability of PVC? In other words, what is the minimum concentration of labile structure required to affect thermal stability significantly? In fact, this is the question that has never been answered in the literature. Based on the present experimental results, only one of 10–15 PVC chains has one internal allylic chlorine, as shown in *Table 1*. The dependence of allylic chlorines on conversion cannot be found either. Therefore, the

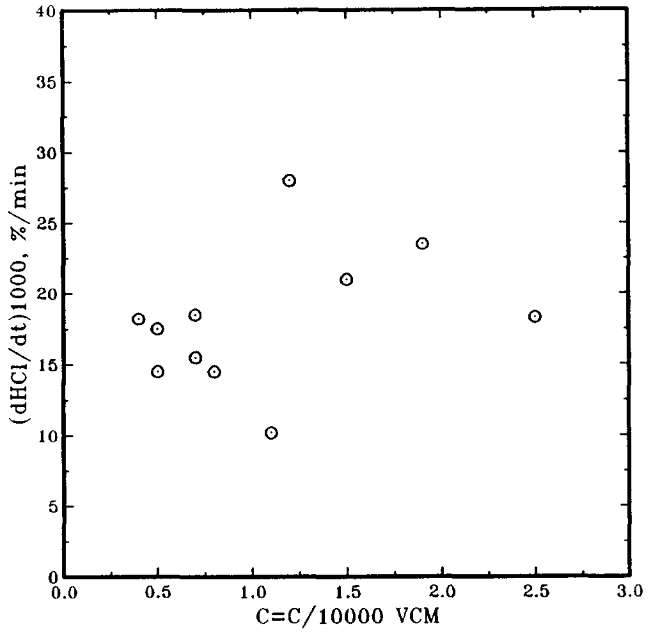


Figure 8 Dehydrochlorination rate *versus* the concentration of internal double bonds of PVC

phenomenon of decrease in thermal stability with increase in monomer conversion after X_f cannot be explained by the contribution of allylic chlorines.

One way to improve thermal stability of PVC is to minimize the concentration of defect structures. The concentration of tertiary chlorines can be controlled by the semi-batch operation at saturation pressure after X_f. One can see in *Table 1* that the dehydrochlorination rate of PVC synthesized at saturation pressure is smaller than that of PVC made using batch operation even though the conversion level (based on the initial monomer charged) is somewhat higher for the semi-batch process. These results further confirm the mechanisms discussed above.

CONCLUSIONS

For PVC synthesized using suspension polymerization in the absence of oxygen at normal polymerization temperatures, the concentration of tertiary chlorines in the PVC chains increases with increase in monomer conversion beyond X_f. At the same conversion level, the concentration of tertiary chlorine atoms increases with increase in polymerization temperature. The increase in tertiary chlorines at high conversions is probably due to increases in both polymer and radical concentrations. The reactions forming tertiary chlorines have higher activation energies than propagation reactions so that these reactions are favoured at higher polymerization temperatures. The concentration of allylic chlorines is about ten times smaller than that of tertiary chlorines, and is not sensitive to monomer conversion. However, the concentration of allylic chlorines increases with increase in polymerization temperature.

It was found that the dehydrochlorination rate depends linearly on the concentration of tertiary chlorines in PVC synthesized over a range of conditions. However, there is no correlation between the dehydrochlorination rate and the concentration of allylic chlorines based on the present experimental data. Moreover, the number of allylic chlorines in PVC chains is small compared to that of tertiary chlorines. Therefore, tertiary chlorine may be the most important defect structure that is responsible for the thermal instability of PVC.

Tertiary chlorines in PVC chains cannot be eliminated because of the nature of VCM polymerization. However, the concentration of tertiary chlorines in PVC chains can be minimized by semi-batch operation at saturation pressure beyond X_f. As a result, the thermal stability of PVC with high conversion can be improved without loss (or perhaps with gain) in productivity.

More experimental data on the variation of concentration of tertiary and allylic chlorines over the entire conversion range are required to confirm the kinetic mechanisms of the defect structure formation and to model quantitatively the microstructure development of PVC chains during synthesis.

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