

Experimental investigation of vinyl chloride polymerization at high conversion: effect of polymerization conditions on polymer properties

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A series of poly(vinyl chloride) (PVC) samples was synthesized under various polymerization conditions. It was found that the thermal stability of PVC as measured by dehydrochlorination rate is independent of monomer conversion when the conversion is less than X_f (the conversion at the pressure drop). However, the dehydrochlorination rate increases significantly with conversion for conversions greater than X_f . The thermal stability of PVC decreases with increase in polymerization temperature. These phenomena can be satisfactorily explained by accepted reaction mechanisms and diffusion-controlled kinetics. The reactions forming defect structures are favoured at low monomer concentrations. Therefore, the most effective way to minimize the formation of defect structures is to maintain monomer concentration as high as possible during polymerization after the pressure drop.

(Keywords: poly(vinyl chloride); microstructure; thermal stability; diffusion-controlled reactions)

INTRODUCTION

During the last 15 years there has been considerable progress in the understanding of the molecular structure and the thermal stability of poly(vinyl chloride) (PVC) due to the improvement in n.m.r. and other characterization techniques. The main recent achievements are summarized in recent comprehensive reviews and monographs¹⁻¹². The main microstructural features of PVC have been well identified and the mechanisms forming the defect structures have been deduced¹³⁻⁴¹. Nevertheless, there is still controversy in the literature⁴⁰ with regard to the relative importance, as labile moieties, of the various irregular structures that PVC contains. Based on PVC and model-compound thermal stability studies, the defect structures that are considered responsible for PVC thermal instability include mainly allylic and tertiary chlorine^{18,26,28,30,40,42-44}, carbonyl structure⁴⁵⁻⁵³ and other oxygenated structures^{40,54,55}. The allylic and tertiary structures are formed by secondary reactions during polymerization. Therefore, these structures are kinetically controlled. On the other hand, the oxygenated structures formed by unexpected oxygen impurity can only be eliminated by improving the quality of reactants. Although it is well recognized that the thermal stability of PVC is strongly related to the amount of structural defects, little work^{28,39,40,56} has been done on the effect of polymerization conditions on the concentration of defect structures and on the thermal stability of PVC.

In our previous publications⁵⁷⁻⁵⁹, the kinetic behaviour of vinyl chloride (VCM) polymerization in batch and

semi-batch reactors has been described quantitatively over the entire conversion range. The kinetic behaviour of VCM polymerization changes dramatically at high conversions owing to decrease in monomer concentration. In the present investigation, the effect of polymerization conditions on the molecular properties, especially thermal stability, of PVC is emphasized.

EXPERIMENTAL

To investigate the effect of polymerization conditions on polymer properties, a series of experiments using suspension polymerization of VCM with various reactor operational conditions were carried out. The equipment used for the experiments, reactor operational procedures and molecular-weight measurements have been given in previous publications^{57,58}. Temperature programming, increasing reactor temperature *versus* time to a desired temperature level when reactor pressure begins to fall, was used for some PVC syntheses. The conversion histories were measured by an on-line tracer method⁶⁰ and by gravimetry.

Dehydrochlorination rates of PVC were measured at 190°C by the conductimetric method. The PVC samples, in powder form (~150-180 mg), were put into quartz crucibles and inserted in a Pyrex degradation apparatus, which can be held at a constant temperature. Preheated high-purity nitrogen as a carrier gas (60 cm³ min⁻¹) was introduced into the reaction cell, so that the HCl evolved during degradation of PVC was removed by the carrier gas and dissolved in deionized water in the cell of a digital

conductivity meter (Amel model 134, Italy), which gave a continuous record of conductivity values as a function of time. The observed rates were transformed, through calibration of the electrode response, into evolved HCl in per cent of the theoretical amount per minute. All the measurements were carried out to 0.4% maximum conversion of HCl in the PVC samples. The standard deviation of the measurements, as determined by replicated experiments, was 1% of the mean rate values.

RESULTS AND DISCUSSION

Effects of conversion, monomer concentration, temperature, initiator type and other additives on the molecular structure and thermal stability of PVC are now discussed.

Conversion effect

Kinetic behaviour of VCM polymerization depends strongly on monomer concentration at high conversions. When conversion is greater than X_f at which the liquid monomer phase is consumed, the polymerization rate and instantaneous molecular-weight averages decrease dramatically with conversion owing to decrease in monomer concentration^{57,58}. We believe that the molecular structure of PVC produced instantaneously must change significantly with conversion at subsaturation pressure for a batch process. If the concentration of defect structures that are responsible for the decrease in thermal stability of PVC increases with conversion, dehydrochlorination rate increases with conversion should result. Figure 1 shows, as expected, that the dehydrochlorination rate increases significantly with conversion beyond X_f . When conversion is less than X_f , the dehydrochlorination rate appears independent of conversion. In the literature, PVC samples used for thermal stability studies often have unknown conversion histories. Hence, the effect of conversion history on thermal stability has not been emphasized. Hjertberg *et*

*al.*⁶¹ found that the dehydrochlorination rate of instantaneous PVC samples made by seed polymerization at subsaturation pressure increases significantly with conversion. They deduced that the dehydrochlorination rate of ordinary PVC would be a mild function of conversion. The present experimental results are consistent with Hjertberg *et al.*'s results⁶¹.

From data shown in Figure 1, one may conclude that the instantaneous defect structures that are responsible for thermal instability must increase dramatically with conversion. Unfortunately, it is impossible to separate the instantaneously produced molecules from the whole PVC sample. Recently, Llauro-Darricades *et al.*³⁹ determined the defect structures of PVC with different conversion histories made in both suspension and solution polymerizations. Their results show that the concentrations of most of the defect structures are higher when the polymerization is carried out in solution, and that internal double bonds, saturated and unsaturated end-groups and branches increase with conversion. These phenomena together with the present results can be explained by diffusion-controlled free-radical polymerization theory.

Based on VCM polymerization mechanisms discussed earlier^{57,58}, the effective transfer-to-monomer reaction rate constant is a function of monomer concentration and temperature. At high conversions ($X > X_f$), the monomer concentration decreases with increase in conversion. Reactions involving macromolecules become diffusion-controlled, so that the ratio of the transfer-to-monomer rate constant to the propagation rate constant increases significantly with conversion. As a result, the instantaneous number- and weight-average molecular weights decrease dramatically. Therefore, the number of groups on chain ends increases significantly with conversion. The main unsaturated end-group is 1-chloro-2-alkene ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$).

Long-chain branches are formed by tertiary hydrogen abstraction from polymer chain by polymer radicals (and perhaps by Cl^\cdot) and subsequent head-to-tail propagation as shown in the following equations:

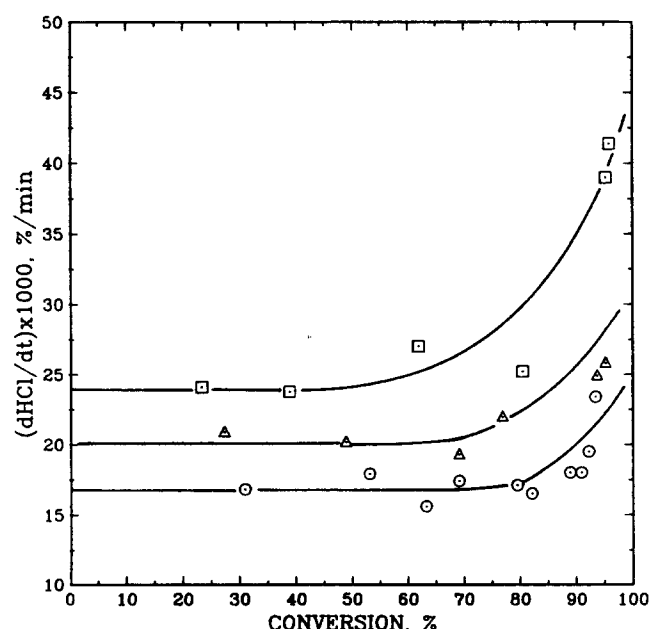
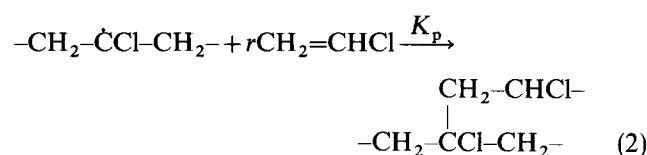
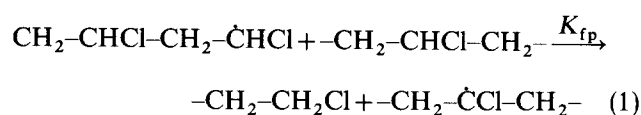
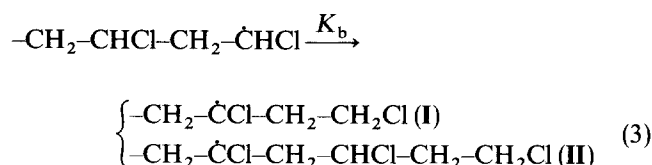
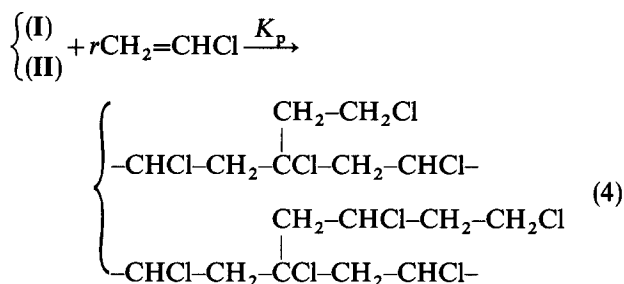


Figure 1 Effect of conversion on the dehydrochlorination rate of PVC at different polymerization temperatures: (○) 50°C; (△) 60°C; (□) 70°C



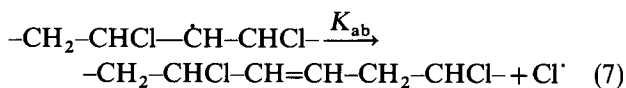
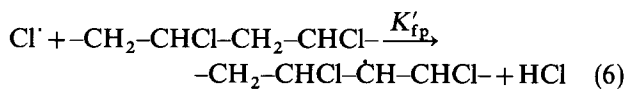
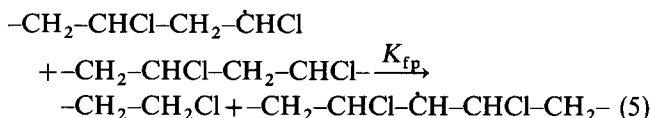
2-Chloroethyl and 2,4-dichloro-*n*-butyl branches are formed by mechanisms involving the intramolecular abstraction of hydrogen from a backbone CHCl moiety (back-biting reaction) and subsequent head-to-tail propagation^{11,18} as follows:





Reactions (1) and (3) are competing with propagation reactions during polymerization. At low conversions ($X < X_f$), monomer concentrations in both monomer and polymer phases are constant and all these reactions are chemically controlled. Therefore, the number of branches per PVC chain should be independent of conversion. This may also be the reason why the dehydrochlorination rate is independent of conversion for $X < X_f$. However, at high conversions ($X > X_f$), monomer concentration decreases with conversion, the number of chain entanglement points increases rapidly and the bimolecular-termination rate constant for polymer radicals falls dramatically. Consequently, the total radical concentration increases significantly with conversion⁵⁷. Although the ratio of K_{fp} to K_p should increase, assuming it is to be constant, the long-chain branches still increase with conversion owing to increase in radical and polymer concentrations. Reaction (3), which is unimolecular, will probably not be diffusion-controlled. At high conversions, reaction (3) is favoured owing to the significant increase in radical concentration. Therefore, short-chain branches should increase significantly with conversion.

Internal unsaturated structures can be formed by mechanisms involving abstraction of hydrogen from a backbone $-\text{CH}_2-$ moiety by polymer radicals^{3,62} or chlorine radicals^{8,25,26} and subsequent abstraction of chlorine radicals as follows:



Reaction (5) is equivalent to reaction (1) and should be diffusion-controlled at high conversions. Reactions (6) and (7) should be chemically controlled over the entire conversion range. All these reactions (5)–(7) are favoured at high conversions owing to the increase in radical and polymer concentrations. Therefore, the number of internal unsaturated structures should increase with conversion.

Based on the qualitative discussion above, it is likely that the internal and terminal unsaturated groups, allylic and tertiary chlorine, increase with decrease in monomer concentration. From Llauro-Darricades *et al.*'s results³⁹, one can deduce that the instantaneous number of these structures must increase dramatically with conversion. This also explains why the defect structures are concentrated in low-molecular-weight fractions⁶³. The phenomenon in which the number of defects is higher in solution polymerization can also be explained by the same

argument. The initial monomer concentration of 2 mol l^{-1} is equivalent to monomer concentrations at 85–90% conversion for suspension polymerization. Reactions (1), (3) and (5)–(7) are competing with the propagation reaction during polymerization. Although all the reactions in solution polymerization are chemically controlled, reactions (1), (3) and (5)–(7) are favoured at very low monomer concentration. In fact, the number of defects in solution polymerization can be understood as instantaneous number of defects. Therefore, it is not surprising that the number of defects is much higher when the polymerization is carried out in solution with low monomer concentration.

Comparing the end-groups before and after degradation at 180°C in helium, Van den Heuvel *et al.*³⁵ experimentally demonstrated that the end-groups formed from chain transfer-to-monomer reactions are not significantly involved in the degradation of PVC. Therefore, the dehydrochlorination rate increases with conversion shown in *Figure 1* cannot be attributed to increase in terminal unsaturated and other end-groups. This suggests that the internal defect structures, tertiary and allylic chlorine, should be responsible for the deterioration in thermal stability of PVC at high conversions. This is in agreement with Hjertberg *et al.*'s^{25,26} and Li *et al.*'s⁴⁴ experimental results. More recently, Starnes⁶⁴ found that, in model-compound experiments, a high HCl concentration makes internal allylic chlorine less stable than tertiary chlorine, but the stability order reverses when the HCl concentration is low. Hence, it depends on the environment of degradation whether tertiary or allylic chlorine is the most important type of labile moiety in a PVC chain.

It is now clear that the dehydrochlorination rate increase with conversion is due to an increase in the number of tertiary and allylic chlorines as a result of a decrease in monomer concentration. Therefore, these defects can be minimized if a constant monomer concentration were maintained at high conversions by semi-batch operation as described in a previous publication⁵⁹. As expected, the thermal stability of PVC made by the semi-batch process operated at the vapour pressure of VCM is improved significantly as shown in *Figure 2*. One can see, from *Figure 2*, that the dehydrochlorination rate is independent of conversion for a semi-batch process operated at the saturation

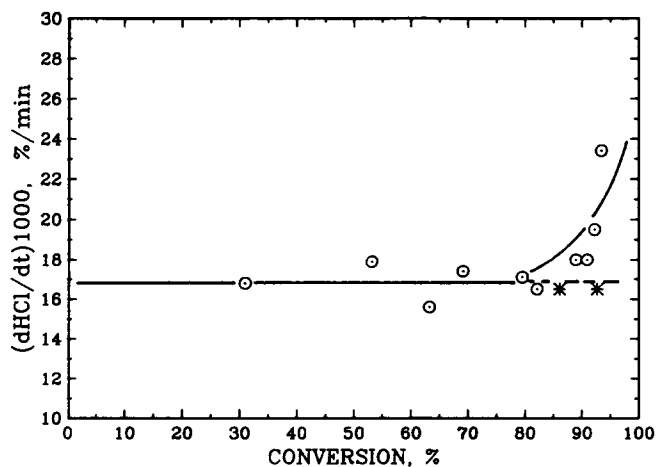


Figure 2 Effect of polymerization processes on the dehydrochlorination rate of PVC at high conversions: (○) batch polymerization at 50°C ; (*) semi-batch polymerization at 50°C

pressure. These results further confirm the mechanisms discussed above. The experimental results shown in Figures 1 and 2 cannot be explained by the defects having carbonyl structure emphasized by Minsker *et al.*⁴⁵⁻⁴⁸.

Cuthbertson *et al.*⁵⁶ recently studied the thermal stability of PVC prepared at very low conversions (0.1–2.0%) and found that the dehydrochlorination rate decreases significantly with increase in conversion. Compared with high-conversion PVC, the low-conversion PVC is more syndiotactic and less thermally stable. This phenomenon is different from the behaviour of PVC discussed in the present investigation. For the very low-conversion PVC, the effect of impurities, oxygen and residual initiator on thermal stability may be more significant.

Temperature effect

The effect of polymerization temperature on thermal stability has not been extensively studied. From Figure 1, one may notice that the dehydrochlorination rate is a function of both conversion and polymerization temperature. Therefore, conversion and polymerization temperature should be specified to compare the dehydrochlorination rate of PVC. Figure 3 shows the dehydrochlorination rate as a function of polymerization temperature at conversions (89–97% corresponding to 40–80°C) close to limiting conversion, which depends on synthesis temperature. The dehydrochlorination rate increases linearly with temperature. Hjertberg *et al.*³⁰ found that, in seed polymerization under subsaturation pressure, there is a minimum dehydrochlorination rate at 55°C. However, the present experimental results do not give such a minimum. Dehydrochlorination rate increases with temperature imply that the reactions forming defects are most sensitive to the polymerization temperature. In general, reaction rate constants, such as those in reactions (1), (3) and (5), are 3–5 orders of magnitude smaller than propagation rate constants. Hence, the activation energies for the reactions forming defects are much higher than that for the propagation reactions, so that these reactions are favoured with increasing temperature.

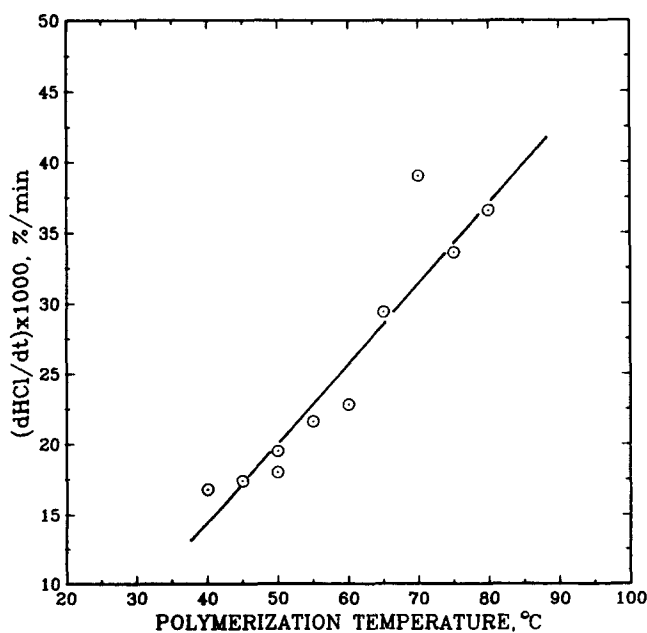


Figure 3 Effect of polymerization temperature on the dehydrochlorination rate of PVC at high conversions

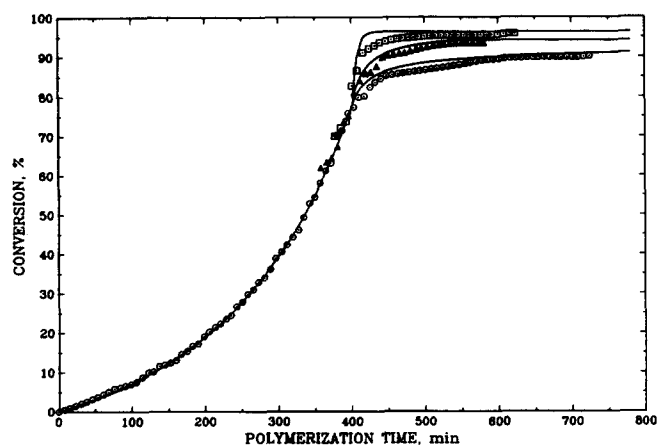


Figure 4 Effect of temperature programming on the conversion histories of VCM polymerization at high conversions: (O) at 40°C; (Δ) at 50°C; (□) at 60°C; (—) model

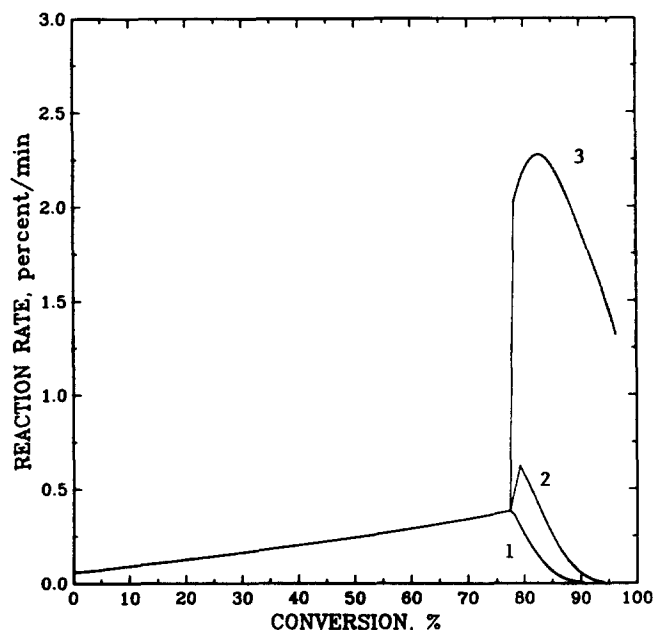


Figure 5 Effect of temperature programming on the polymerization rate: curve 1, at 40°C; 2, at 50°C; 3, at 60°C

A batch reactor can be operated under non-isothermal conditions, e.g. increasing polymerization temperature to a desired level at a certain conversion. Hamielec *et al.*⁶⁵ suggested that the procedure of raising the temperature at the end of the batch would maximize productivity and limit the effect of diffusion-controlled reactions on PVC thermal stability. The present investigation further pursues the effect of temperature programming on the reactor performance and polymer properties. Figure 4 shows conversion histories of VCM polymerization with rising temperature at the point when the reactor pressure begins to fall. It took less than 5 min to raise the temperature from 40°C to 50 and 60°C under the present experimental conditions. One can see, from Figure 4, that the conversion increases significantly within a short time. Figure 5 shows the model predictions of polymerization rates corresponding to the conversion histories shown in Figure 4. The polymerization rates increase dramatically with increase in temperature. The reactor pressure increases sharply at the point when the temperature is raised, then decreases gradually with conversion, as shown in Figure 6. However, the maximum pressure is

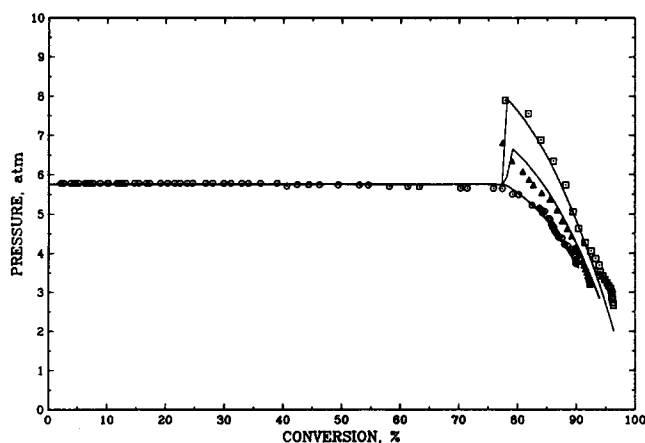


Figure 6 Effect of temperature programming on the reactor pressure: (○) 40°C; (△) 50°C; (□) 60°C; (—) model

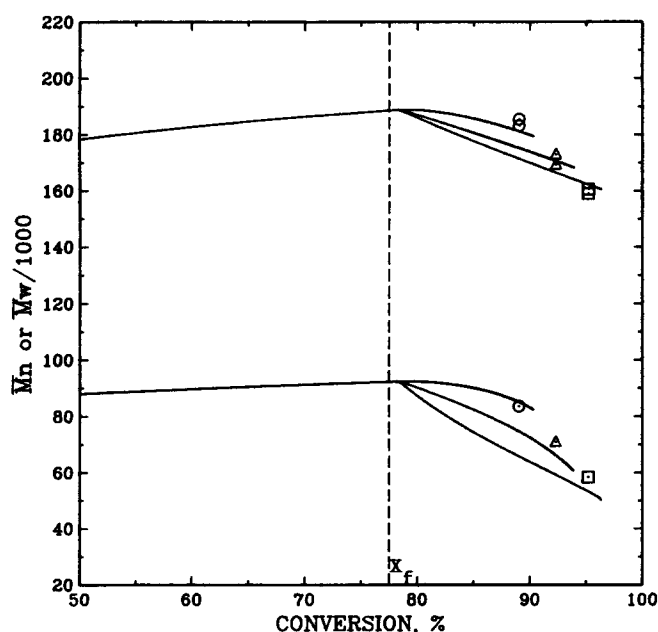


Figure 7 Effect of temperature programming on the accumulated number- and weight-average molecular weights at high conversions: (○) 40°C; (△) 50°C; (□) 60°C; (—) model

always less than the vapour pressure of VCM at the same temperature because the liquid monomer has been consumed at that conversion (X_f decreases with increase in temperature). It is obvious, therefore, that the higher productivity can be achieved using temperature programming at high conversions. This operational procedure is clearly safe owing to the low levels of monomer present. In the meantime, all the chemical reaction rates are affected by raising the temperature. The relative sensitivity to temperature depends on their activation energies and the level of diffusion control of individual reactions. Figure 7 shows the accumulated molecular-weight averages changing with conversion and temperature. It is not surprising that the accumulated molecular-weight averages decrease with increase in temperature owing to the increase in CM value (the ratio of K_{fm} to K_p), which dominates PVC molecular weight, increasing with temperature⁵⁸. However, the decrease in accumulated molecular-weight averages is not very significant because the amount of polymer produced at the higher temperatures is relatively small compared with the

accumulated polymer. Effect of temperature on the accumulated molecular-weight distribution (*MWD*) is shown in Figure 8. The *MWD* shifts towards lower molecular weight and the weight fraction of low-molecular-weight polymer increases with increase in temperature.

The effect of temperature programming on the dehydrochlorination rate is shown in Table 1. One can see that the dehydrochlorination rate increases with increasing programming temperature. This suggests that the reactions forming defect structures are more sensitive to temperature. However, the terminal conversions also increase with temperature. These terminal conversions are very close to the limiting conversions at the corresponding temperatures⁵⁷. Therefore, the results shown in Table 1 in fact include the effect of temperature, conversion and time. If the temperature increase is less than 10°C over the original temperature, the thermal stability decreases slightly. The last sample shown in Table 1 was made by increasing temperature at the limiting conversions. One can see that the dehydrochlorination rate increases significantly. Therefore, polymerization close to limiting conversions should be avoided if thermal stability is to be maintained. For commercial reactor operation, polymerization is not normally taken to limiting conversion. It should be possible to obtain higher productivity without losing the thermal stability significantly by using the temperature programming technique properly. To do this, one should vaporize the unreacted monomer to stop the polymerization at precisely the required terminal conversion.

The effect of conversion and temperature on the thermal stability of PVC involves very complicated phenomena. In the present investigation, we noticed that

Table 1 Effect of temperature programming on the dehydrochlorination rate of PVC

Temperature programming	Terminal conversion	$(d[\text{HCl}]/dt) \times 10^3$ (% min ⁻¹)
40°C	89%	18.6
40→50°C	92%	20.4
40→60°C	95%	21.3
40→70°C	97%	29.1
40→50→60→70°C	97%	31.5

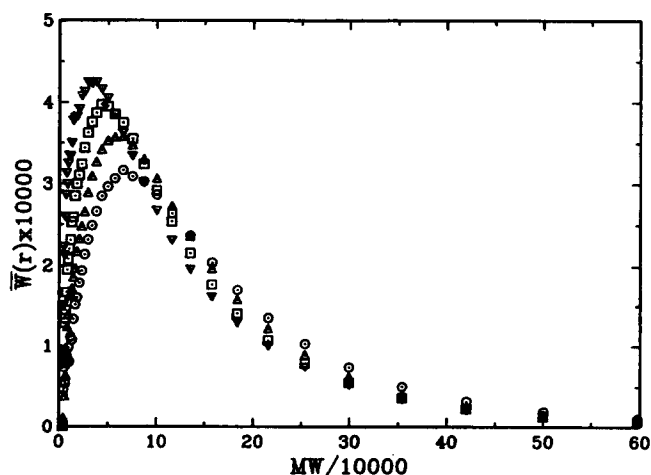


Figure 8 Effect of temperature programming on the accumulated molecular-weight distribution at high conversions: (○) 40°C, $X = 89\%$; (△) 50°C, $X = 92\%$; (□) 60°C, $X = 95\%$; (▽) 70°C, $X = 97\%$

Table 2 Effect of initiator type on the dehydrochlorination rate

Initiator	$[I]_0$ (wt%)	Temp. (°C)	Conversion (%)	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$(d[HCl]/dt) \times 10^3$ (% min ⁻¹)
AIBN	0.50	45	88	156	77	20.4
Perkadox 16-W40	0.175	45	90	161	77	17.4

Table 3 Effect of n-butane on the dehydrochlorination rate of PVC

Polymerization temperature (°C)	n-Butane (wt%)	Conversion (%)	$(d[HCl]/dt) \times 10^3$ (% min ⁻¹)
50	–	92	19.5
50	5.0	92	19.5
60	–	95	22.8
60	10.0	94	24.0
70	–	95	41.4
70	20.0	96	39.0

the PVC made at higher than 70°C is pink if conversion is higher than X_f . This implies that dehydrochlorination has occurred during polymerization at high temperatures.

Effect of initiator and other additives

Two initiators, azobis(isobutyronitrile) (AIBN) and bis(4-t-butylcyclohexyl)peroxydicarbonate (Perkadox 16-W40), have been used to synthesize the PVC samples in the present investigation. Typical results are shown in Table 2. At the same polymerization temperature, the molecular-weight averages are the same at similar conversion levels. However, the dehydrochlorination rates are quite different. These limited data suggest that the PVC synthesized with AIBN as initiator has lower thermal stability. Starnes *et al.*⁶⁶ found that the PVC structural segments derived from AIBN contain copolymer structure of VCM with methacrylonitrile. The effect of this structure on the thermal stability of PVC remains unknown.

As discussed above, PVC thermal stability decreases with conversion owing to the effects of diffusion-controlled reactions as a result of decrease in monomer concentration. Hence, the effect of diffusion-controlled reactions may be limited if the free volume of the polymer phase can be maintained by feeding in an inert chemical at high conversions. The PVC samples shown in Table 3 were synthesized by feeding in n-butane to the reactor at the pressure drop. No significant kinetic behaviour change can be determined. One can see, from Table 3, that there is no effect of n-butane on the thermal stability of PVC. These results imply that n-butane cannot sufficiently swell PVC to limit the effect of diffusion-controlled reactions. These results also suggest that the reactions competing with the propagation reactions are the most important ones in affecting the PVC thermal stability. Therefore, increasing the monomer concentration seems to be the most effective way to minimize defect structures during polymerization at high conversions.

CONCLUSIONS

Thermal stability of PVC depends strongly on polymerization conditions, in terms of conversion histories, reaction temperature and initiator types. When conversion is less than X_f , dehydrochlorination rate is independent of conversion. At high conversions ($X > X_f$), however, thermal stability of PVC decreases significantly with

increase in conversion. The reactions forming defect structures are favoured at high conversions owing to increase in radical and polymer concentrations as a result of decrease in monomer concentration.

Dehydrochlorination rates always increase with increase in polymerization temperature because the secondary reactions are more sensitive to temperature compared with the propagation reaction. However, the proper use of temperature programming techniques at high conversion can give benefits of higher productivity without a significant loss in thermal stability.

Based on kinetic studies and diffusion-controlled theory, tertiary and allylic chlorine should be responsible for the thermal instability of PVC. However, further microstructure measurements are required to confirm the conclusion.

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