New aspects of the suspension polymerization of vinyl chloride in relation to the low thermal stability of poly(vinyl chloride)

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CHAPTER 3

Monomer conversion: Its influence on powder properties and thermal stability of PVC

Abstract

The suspension polymerization of VCM at 57.5 °C was studied for monomer conversions ranging from 13 to 96%.

After a monomer conversion of only 13% the resulting polymer grains are still very brittle, porous and elongated in shape. With increasing monomer conversion the polymer grains do not significantly grow in size anymore, whereas the primary particles inside the grains increasingly grow and thereby coagulate and fuse together. Therefore, the internal porosity of the grains decreases dramatically with increasing monomer conversion, as the pores will be increasingly filled up due to growth and coagulation of the primary particles. This process also provides a more robust particle, which does not shrink that much with removal of residual VCM and therefore the resulting polymer grains will retain the spherical shape.

The molecular weight of PVC increases during polymerization up to a monomer conversion of about 80%, due to an increasing contribution of the polymerization in the polymer-rich phase. Beyond this conversion a distinct decrease in molecular weight is observed as a result of the increasingly diffusion controlled propagation rate and the increasing importance of chain transfer to monomer.

Thermal degradation of PVC with different monomer conversions was studied by a standard dehydrochlorination test. The rate of dehydrochlorination increases enormously for monomer conversions beyond 80-85%, which means a dramatic decrease in thermal stability of the polymer. Simultaneously, a marked increase in the number of internal allylic structures and various types of branches linked with tertiary chlorines are observed, from which can be concluded that it is very likely that these defects are the origin of the low thermal stability of PVC.
3.1 Introduction

After having optimized the reaction procedure of the suspension polymerization of VCM in a 1-l autoclave, which is described elaborately in the previous chapter, the polymerization process will be studied in more detail over a range of monomer conversions between 13 and 96% in this chapter. Of interest are the development of various properties with increasing monomer conversion, such as molecular weight and grain morphology, but also the appearance of different types of defect structures and the thermal stability of the PVC, which is probably closely related to these defects.

The suspension polymerization of VCM can be subdivided in different stages, as already briefly described in the previous chapter. During the first stage, when monomer conversion is less than 0.1%, polymerization occurs homogeneously inside the monomer droplets. Subsequently, the first growing polymer chains start to precipitate. From this moment on a two-phase polymerization system is formed, consisting of the a so-called pure liquid polymer-lean phase, in which less than 0.1% of PVC is dissolved, and a so-called polymer-rich phase, which contains PVC, swollen in about 30 wt % of VCM, at polymerization temperatures between 50 and 60 °C. Polymerization takes place in both phases simultaneously up to the critical conversion $X_f$, after which the polymer-lean phase is completely consumed and polymerization continues inside the polymer-rich phase. $X_f$ is commonly considered to correspond to circa 70% of monomer conversion but depends on variables as polymerization temperature, VCM / water ratio and the filling grade of the reactor. In Figure 3.1 the pressure drop which occurs after $X_i$ is depicted together with the development of the polymer grains, which is already described extensively in Chapter 2.
Initially the total pressure inside the reactor consists of a combination of the vapor pressures of VCM, water and N₂, which comes along with VCM upon filling. As long as the separate polymer-lean phase exists, i.e. at monomer conversions below \( X_f \), the pressure inside the reactor is constant. However, in practice a small pressure drop is already observed before \( X_f \). This first stage of the pressure drop is caused by shrinkage of the polymerizing droplets due to large differences in density for VCM and PVC (\( \rho_{\text{VCM}} = 0.84 \text{ g·cm}^{-3} \), \( \rho_{\text{PVC}} = 1.40 \text{ g·cm}^{-3} \) at 57.5 °C) \(^4\), which induces enlargement of the volume of the gaseous phase. As the pure liquid polymer-lean phase is still present, VCM is expected to diffuse from this phase into the gaseous phase to re-establish its vapor pressure. According to Xie et al. \(^3\) the mass transport of VCM from the particles into the gaseous phase is hampered due to the dense internal structure of the polymerizing particles and the presence of a rigid skin surrounding these particles. As a consequence, the pressure inside the reactor is lowered when the
volume of the gaseous phase increases due to shrinkage of the polymerizing particles. At $X_f$ the pure liquid polymer-lean phase is completely depleted and polymerization continues inside the swollen polymer-rich phase only. From this moment on the pressure in the autoclave starts to drop dramatically with increasing monomer conversion because the equilibrium pressure of VCM in the concentrated polymer-rich phase is lower than the vapor pressure of pure monomer $^{2,5,6}$. In the Flory-Huggings equation $^4$, a relation between the volume fraction of polymer in the swollen polymer-rich phase $\phi_p$ and the ratio of the partial pressure $P_m$ and the vapor pressure of the monomer $P_{m,0}$ is given:

$$\ln\left[\frac{P_m}{P_{m,0}}\right] = \ln(1 - \phi_p) + \frac{1 - 1/n}{\phi_p} + \chi \phi_p^2$$

(3.1)

in which $n$ is the average number of monomeric units per polymer chain and $\chi$ the VCM-PVC interaction parameter, which is dependent on by temperature.

From equation 3.1 can be deduced that the growth of the volume fraction of PVC with increasing monomer conversion after $X_f$ results in a decrease in the partial pressure of monomer and consequently a lower pressure in the reactor. During polymerization after $X_f$, the volume fraction of monomer in the polymer-rich phase decreases and only VCM present in the gaseous phase and dissolved in the aqueous medium is now available to replace the reacted monomer (Figure 3.2) $^3$. The diffusion of VCM from these two phases into the polymerizing particles induces the pressure drop. Finally, when the polymer-rich phase becomes increasingly deficient of monomer the polymerization still continues although at a very low rate, as the diffusion of VCM into the solid, eventually hardly swollen and therefore very dense polymer grains becomes more and more limited.
In general, the polymerization of VCM in industry is terminated long before this final stage, as further polymerization would be extremely time-consuming. Another, probably more important reason is the dramatic decrease in thermal stability of the polymer formed during this final stage.

If the polymerization is continued, the reaction rate will eventually drop to zero before 100% monomer conversion is reached. The conversion at which this phenomenon occurs is denominated as the limiting degree of conversion $X_l$. At this particular moment the polymer-monomer mixture of the polymer-rich phase reaches a composition of which the glass transition temperature $T_g$ equals the polymerization temperature and therefore from this moment on the polymerization reaction is completely frozen. VCM acts as a plasticizer for PVC resulting in a lower glass transition temperature of PVC-VCM mixtures than of pure PVC. When the polymer-rich phase runs out of monomer the $T_g$ of this phase will gradually increase until it reaches the polymerization temperature. This implies that if the polymerization is...
performed at a higher temperature $X_i$ will also increase.

The optimization of the reaction conditions for the 1-l autoclaves at our laboratory, resulting in a polymerization process comparable to that in industry, has been described in Chapter 2. The current chapter describes the conversion study of the suspension polymerization of VCM. Similar research has been done by other research groups like for instance Xie et al. $^9$ and Ravey et al. $^5$. However, differences in the construction of the reactor, such as volume of the vessel, type of stirrer, presence and position of baffles, but also the polymerization recipe, heating rate and many other parameters can have an influence on the course of the polymerization process and possibly the product quality. Therefore, the suspension polymerization at 57.5 °C is studied over the whole range of monomer conversion using the polymerization conditions described in Chapter 2. This study will provide us with a well-defined base for our further research into the origin of the low thermal stability of PVC.

### 3.2 Experimental

#### 3.2.1 Polymerization

The optimal polymerization conditions were obtained by optimization of the polymerization process in the 1-l stainless steel autoclaves (Premex Reactor AG, Switzerland) located at our laboratory, as described in detail in the experimental section of Chapter 2. Only the polymerization time was altered for each experiment of the conversion series, while all the other parameters as defined in Chapter 2 were retained. Having reached the required polymerization time, ranging between 75 and 1340 minutes, the polymerization was terminated by the addition of the killing agent. After sufficient drying of the obtained polymer grains, the monomer conversion was determined by gravimetric analysis, being the ratio between the yield of PVC and the initial amount of VCM.
3.2.2 Characterization

Molecular weight determination

Molecular weights were determined by GPC using the universal calibration method as described in the experimental section of Chapter 2.

Porosity measurement by means of plasticizer absorption

The porosity of PVC grains was determined by the cold plasticizer absorption test (CPA) at the research laboratory of Shin Etsu PVC BV as described in Chapter 2.

Porosity measurement by means of mercury intrusion

The porosity measurements using the technique of mercury intrusion were performed at the PVC research laboratory of LVM in Tessenderlo (Belgium). An AutoPore II 9220 apparatus, equipped with a penetrometer with a capillary of 1.5 mm inside diameter and an intrusion volume of 0.38 ml, was used for the measurement of the volume distribution of the pores in PVC by mercury intrusion. The penetrometer consists of a sample holder attached to a stem, which contains a capillary system. At the beginning of the test, the space around the sample and in the capillary of the stem is filled with mercury under low pressure. Subsequently, the penetration of mercury into the pores of the sample is monitored by following the receding mercury column in the capillary as the pressure increases. The incremental intrusion volume (ml·g⁻¹) is plotted versus the pore diameter (µm), which is proportional to the applied pressure, providing clear information about the pore size distribution. Thereby the relative porosity between different samples can also be defined by comparison of the total area underneath this curve.
**Thermal stability test / Dehydrochlorination experiment**

The thermal stability of PVC is related to the rate of HCl elimination or dehydrochlorination and is tested by means of the standardized conductometric methods DIN 53 381 and ISO 182-3:1993. These thermal stability tests were carried out at the research laboratory of Shin Etsu PVC BV.

Inside a test tube 500 mg of a PVC sample was degraded in an oil bath at a temperature of 180 ± 0.1 °C under a constant N₂ flow of 116 ± 5 ml·min⁻¹. The formed HCl was purged through 60 ml of demineralized water. The conductivity of this water was continuously measured as a function of degradation time. The development of the conductivity as a function of time gives information about the initial moment (tᵢ) of HCl elimination and subsequently the degradation rate of the PVC sample. The time (tₚₕ) required to achieve a conductivity change of 50 µScm⁻¹, which corresponds to an elimination of 0.05 wt % HCl in relation to the weight of the PVC sample, is taken as a measure of the rate of degradation.

**Nuclear Magnetic Resonance (NMR) analysis**

¹H and ¹³C NMR spectra were recorded on a 500 MHz VARIAN - INOVA spectrometer. For ¹H NMR experiments 5% (w/v) solutions of PVC in THF-d₈ (Aldrich) were prepared. The spectra were recorded at 45 °C. The assignment of the signals in the ¹H NMR spectra known from literature was confirmed by ¹H homonuclear COSY experiments.

PVC was reduced to polyethylene (PE) with Bu₃SnH and Bu₃SnD to identify the presence of Cl at the branchpoint carbons in the original polymer chain. In ¹³C NMR spectra of PVC samples that are reduced using Bu₃SnD it is possible to see triplets of carbons attached to D, which has replaced Cl in the original polymer. The presence of D also influences the chemical shift values of the carbons, the so-called isotope shift. Taking into account both the presence of triplets and the occurrence of an isotope shift, it is possible to locate the position of Cl atoms in the original samples and to determine the exact microstructure of the branches.
These reduced PVC samples were dissolved (10% w/v) in a mixture of 1,2,4-trichlorobenzene and benzene-d6 (1:3). Proton decoupled spectra of these samples were run at 120 °C. Identification of peaks occurred by the use of spectra of model compounds and by means of computer simulations (ACD labs.). The calculation of the number of defects per 1000 monomeric units was based on the integration of corresponding peaks in both $^1$H and $^{13}$C NMR spectra. The standard deviation calculated from 3 independent $^1$H NMR measurements was taken as estimation for the experimental error.

A more elaborate description of the performed NMR techniques and the reduction of PVC into PE, both practically and theoretically, is given by Purmová et al. 12.

Scanning Electron Microscopy (SEM)

Images of the interior and exterior of the PVC particles, to study the development of particle size, shape and porosity with increasing monomer conversion, were made with Scanning Electron Microscopy (SEM, Jeol 6320 F), as described in Chapter 2.

3.3 Results and Discussion

3.3.1 Polymerization trends

Conversion experiments were performed in order to obtain a clear understanding of the suspension polymerization process of VCM. In total 17 polymerizations were carried out ranging from about 13% of monomer conversion, corresponding to 75 minutes of polymerization, to 96% (1340 min), which is the limiting degree of conversion.

In Figure 3.3 the growth of monomer conversion with increasing polymerization time is illustrated together with the course of the pressure inside the reactor during polymerization. From the moment the pressure inside the reactor starts to drop drastically, the polymer-lean phase is completely depleted. For this current system and recipe the critical conversion $X_f$ was determined by the use of a model proposed
by Xie et al. The calculation of $X_f$ and the distribution of monomer over the aqueous medium, the vapor phase and the polymerizing droplets during different stages of polymerization can be found in the Appendix.

For our polymerization setup $X_f$ is determined to be 60%, which corresponds to a polymer weight fraction in the polymer-rich phase $m_{p,X_f}$ of 0.66 for monomer conversions up to and including $X_f$. After $X_f$ this fraction will increase continuously as the monomer inside this phase will not be refilled completely anymore after polymerization.

After about 85 to 90% of monomer conversion the reaction rate starts to decrease dramatically. The reaction rate slows down as monomer supply within the particles itself runs short and can only be refilled by monomer present in the gaseous and aqueous phase, which is a time-consuming process as monomer has to diffuse from two low-density phases into the dense polymer grain, as already described earlier. Therefore, the polymerization reactions are normally terminated by the addition of a killing agent just before 90% of monomer conversion, after a pressure drop of approximately 3.5 bar.

Figure 3.3 Development of the pressure inside the reactor (solid line) and monomer conversion (■) with increasing polymerization time.
3.3.2 Molecular weight

The trends of number- and weight average molecular weights, $\bar{M}_n$ and $\bar{M}_w$ respectively, of the PVC samples with increasing monomer conversion have been determined (Figure 3.4). It should be kept in mind that all these values are cumulative, therefore changes in chain length of the polymer chains produced at higher conversions are not as distinct as they would have been in case of instantaneously obtained values.

Before 80% of monomer conversion both $\bar{M}_n$ and $\bar{M}_w$ show an increasing trend with increasing monomer conversion, which is caused by an increasing contribution of the polymerization in the polymer-rich phase at the cost of polymerization in the polymer-lean phase. The large effect of an increasing polymerization in the polymer-rich phase on the molecular weight is caused by the occurrence of a gel effect in this phase, which will be discussed elaborately in Chapter 4. Differentiating the curves shows that
the increase of $\bar{M}_n$ is slightly smaller than the increase of $\bar{M}_w$, which is a result of the predominant role of chain transfer to monomer over chain transfer to polymer $^{13}$. After reaching a monomer conversion of approximately 80%, $\bar{M}_w$ remains almost constant displaying hardly any decrease, while $\bar{M}_n$ decreases significantly. These results can be explained by means of a changing value for the constant of chain transfer to monomer $C_M$ with increasing monomer conversion beyond $X_f$.

$C_M$, which corresponds to the ratio of the rate constants for chain transfer to monomer and propagation, $k_{tr}$ and $k_p$ respectively, is constant for both phases during polymerization before $X_f$ $^{14}$. As $k_{tr}$ is inversely proportional to monomer concentration, as derived in the work of Xie et al. $^{14}$, the value of $C_M$ is not equal for both phases due to differences in monomer concentration.

After $X_f$, when only the polymer-rich phase remains, $C_M$ increases with increasing monomer conversion as the monomer concentration in this phase decreases continuously and the propagation reaction becomes more and more diffusion controlled, as is demonstrated by Hamielec et al. $^8$. They have shown that the value of $k_p$ in the polymer-rich phase decreases with increasing monomer conversion already after 45% of monomer conversion. Therefore, a significant effect of a diffusion controlled propagation reaction on the molecular weight is expected at higher monomer conversions. The value of $\bar{M}_n$ is very sensitive to chain transfer to monomer and thus decreases significantly with increasing $C_M$. Chain transfer to polymer ($C_p$) also becomes more important, which influences $\bar{M}_w$ significantly in contrast to the minimal effect of chain transfer to monomer on $\bar{M}_w$. However, as $C_p$ is only one hundredth or even less in value of $C_M$, $\bar{M}_w$ does not decrease as much as $\bar{M}_n$ $^{14}$. This difference immediately explains the significant increase in the molecular weight distribution or polydispersity ($D = \bar{M}_w/\bar{M}_n$) as $\bar{M}_w$ decreases dramatically compared to $\bar{M}_w$ $^{14,15}$. 
3.3.3 Particle morphology

The porosity of various PVC samples was examined by the determination of the cold plasticizer absorption. From the results of this test, which are presented in Table 3.1, a clear relation between the degree of plasticizer absorption and monomer conversion can be observed. The degree of plasticizer absorption is reported as the weight percentage of DOP, which is absorbed in the PVC sample.

<table>
<thead>
<tr>
<th>Monomer conversion (%)</th>
<th>DOP porosity (wt %)</th>
</tr>
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<tbody>
<tr>
<td>53</td>
<td>46</td>
</tr>
<tr>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>87</td>
<td>28</td>
</tr>
<tr>
<td>96</td>
<td>27</td>
</tr>
</tbody>
</table>

The porosity shows a distinct decrease with increasing in monomer conversion. When monomer conversion increases, the volume of free liquid VCM inside the droplet decreases and the primary particles inside the droplets increase in size and fuse together. The fusion of the primary particles together with the shrinkage of the PVC grains are the main causes for the decrease in PVC porosity with increasing monomer conversion 16.

The porosity has also been studied by means of mercury intrusion. It is known that mercury will not penetrate pores by capillary action but has to be forced into the pores. The pressure required to enter the pores is inversely related to the opening size of the pore 17. In Figure 3.5 the increment of intrusion is plotted against the pore diameter for PVC grains prepared with monomer conversions of 39, 87 and 96%.
These results confirm that the porosity decreases with increasing monomer conversion, as the total volume of mercury pressed into the grains is higher for the low conversion sample. This figure also shows that the pore size distribution is nearly similar for all samples, which seems illogical. It was expected that the same number of pores would be found for all conversions, but that these pores would become smaller as they will be gradually filled up with polymer with increasing monomer conversion. Such a system would lead to a shift of the pore size distribution towards lower values together with a decrease in intrusion volume.

The most probable reason for this unexpected result is the phenomenon called bottle-necked pore. Bottle-necked pores can be described as having a large volume, but being only accessible via a narrow channel. In the case of PVC this narrow entrance of a larger cavity is probably caused by the presence of the very dense crosslinked skin surrounding the PVC grains as described in Chapter 2.

Although the real cavities inside the grains of PVC with low monomer conversion are very large, this technique considers them as being small pores due to their very tight entry.

**Figure 3.5** Incremental mercury intrusion plot versus pore diameter for PVC with various levels of monomer conversion: 39% (●); 87% (■); 96% (▲)
This explains why a large intrusion volume is found for the PVC grains of the low conversion sample, although the pores are defined as being small due to the high pressure required to fill up these pores.

With increasing monomer conversion the cavities inside the grains will be filled up gradually, while the small channels, which connect them to the exterior of the grains, are becoming only slightly narrower, as can be concluded from the almost unaffected pore size distribution.

In the Figures 3.6 to 3.8 SEM pictures are shown of PVC grains prepared with different monomer conversions ranging from 13% to 96%.

**Figure 3.6** SEM pictures of PVC particles of different monomer conversions: (A) 13%; (B) 39%; (C) 53%; (D) 96%
At monomer conversions below 15% both the skin surrounding the polymerizing droplets, which is not yet tough enough, and the low density of the particles are not able to prevent the grain from collapsing dramatically when removing the residual monomer, as described in Chapter 2. This results in smaller, often elongated and more brittle polymer grains as is shown in Figure 3.6A. However, with increasing monomer conversion the polymerizing droplets soon become more resistant against collapsing or shrinking with removal or just polymerization of VCM. Therefore, no obvious difference in the average particle size is observed anymore for the PVC grains prepared with monomer conversions ranging between 39 and 96% (Figure 3.6B-D), which are on average also more spherical in shape.

Figure 3.7 SEM pictures of the interior of PVC particles of different monomer conversions: (A) 13%; (B) 39%; (C) 53%; (D) 96%
From the SEM pictures of the interior of PVC grains a decrease in porosity can be observed, which confirms the results obtained from the cold plasticizer absorption and the mercury intrusion tests (Figure 3.7). The PVC grains of 13% of monomer conversion are still very brittle and therefore easily break in two (Figure 3.7A), while the grains of higher monomer conversion really had to be cut in two.

![A](image1.png) ![B](image2.png) ![C](image3.png) ![D](image4.png)

**Figure 3.8** SEM pictures of the primary particles inside the PVC particles of different monomer conversions: (A) 13%; (B) 39%; (C) 53%; (D) 96%

Whereas the average size of the PVC particles does not change much with increasing monomer conversion, the size of the primary particles does, which is clearly visualized in Figure 3.8. The primary particles grow in size and thereby fuse together increasingly with increasing monomer conversion.
3.3.4 Thermal stability

The thermal stability of PVC was examined by the dehydrochlorination test. The HCl formed upon degradation of PVC was lead into a pure water medium, thereby increasing the conductivity of the water. The conductivity is therefore related to the extent of degradation. A typical conductivity curve of a PVC sample with a monomer conversion of 87% is shown in Figure 3.9.

![Conductivity curve obtained during dehydrochlorination test of PVC with a monomer conversion of 87%](image)

**Figure 3.9** Conductivity curve obtained during dehydrochlorination test of PVC with a monomer conversion of 87%

The starting point of HCl elimination or the so-called initiation time, $t_i$, is defined as the intersection of the two tangents as displayed in Figure 3.9. The time required to achieve a conductivity change of 50 $\mu$S cm$^{-1}$ ($t_{st}$ = stability time) is the measure of the degradation rate. The change in conductivity of 50 $\mu$S cm$^{-1}$ corresponds to a weight loss of 0.05% of the sample and thus the very beginning of the degradation of PVC is studied. However, the resulting color of the samples is already pale reddish brown after this stability test.

Both the initiation time of dehydrochlorination and the stability time for PVC samples with a monomer conversion ranging from 13 to 96% are depicted in Figure 3.10.
Figure 3.10 Results of dehydrochlorination test for PVC produced up to different monomer conversions: initiation time $t_i$ (●); stability time $t_{st}$ (■)

Three regimes can be identified. First a region up to about 40% of monomer conversion, in which both the initiation time and the stability time display a small increasing trend. This is probably caused by the change in powder morphology, as PVC with low monomer conversion is a material of high fluffiness and therefore the same weight of material occupies a larger volume of the test tube. The space in between the polymer grains is larger and as a consequence the route for HCl to leave the sample by the aid of nitrogen is easier. As a result the first molecules of HCl will be detected earlier. The difference between $t_{st}$ and $t_i$, however, is almost equal meaning that the dehydrochlorination rate is almost constant for these samples.

For the samples of the second region up to a monomer conversion of approximately 80-85%, the values for $t_i$ and $t_{st}$ were found to be practically constant and the time needed to release 0.05 wt % of HCl from the original sample is again constant for all these samples. For these samples the powder morphology is quite similar, as the particle size distribution of PVC grains is determined at low monomer conversion and therefore the PVC grains have now already obtained their final appearance, as is shown in Figure 3.6.
Finally, after about 80-85% of monomer conversion, both the initial time of HCl elimination and the stability time decrease significantly. The decrease in the initial time of HCl elimination indicates that degradation starts earlier for samples with very high monomer conversion. The stability time decreases even more strongly, which becomes more visible by plotting the rate of dehydrochlorination (dhc-rate) against monomer conversion (Figure 3.11).

![Graph](image)

**Figure 3.11** Rate of dehydrochlorination versus monomer conversion

From this curve can be concluded that the thermal stability of the polymers prepared up to a monomer conversion of about 80-85% is almost constant, while the thermal stability decreases dramatically at higher conversions.

Although the PVC samples of lowest monomer conversion display a somewhat lower $t_i$ and $t_{st}$ compared to those for monomer conversions between 40 and 80-85%, which is caused by difference in morphology of the grains as mentioned, their rate of dehydrochlorination is equal to those of all PVC samples up to a monomer conversion of 80-85%. Therefore, it can be concluded that no relation exists between the morphology of the PVC grains and the thermal stability of the polymer in this test.

As discussed by many authors $^{18-23}$, the presence of certain defect structures in the polymer chains, such as tertiary and allylic chlorines are believed to decrease the
thermal stability of PVC, which has been described elaborately in the introductory chapter of this thesis. In addition to the performed stability tests the structure of the polymers with different monomer conversions was also studied. This was done to get more insight in the moment at which and the conditions under which these defects are formed, and to examine the possible relation between these defects and the rate of dehydrochlorination.

3.3.5 Structural defects

The structure of the polymer chains was characterized in detail by the use of advanced NMR techniques\textsuperscript{12}. Figure 3.12 displays the development of the number of the most dreaded types of defects with increasing conversion, namely the internal allylic structures and different types of branches, which are suspected to be the most important initiation sites for dehydrochlorination.

![Figure 3.12 Number of defect structures per 1000 monomeric units: internal allylic structures IA (●); branches (▲)](image-url)
From these results it is clear that these structural defects are formed during the entire polymerization process, however, after a monomer conversion of approximately 80-85%, during the pressure drop, these defects are formed to a much larger extent. With that should be kept in mind that the values presented here are cumulative, meaning that the increase in the number of defects would be even more pronounced if the instantaneously formed polymer chains could be examined separate from the earlier formed polymer. When these results are compared with those of the dehydrochlorination test, a similar increasing trend is observed. Both the number of these defects and the rate of dehydrochlorination start to increase tremendously at monomer conversions of approximately 80-85%. This increase strongly indicates that the internal allylic structures and the branches, which are mainly formed during the final stages of polymerization at very high monomer conversion, are affecting the thermal stability of PVC.

However, according to literature only those branches containing chlorine at the branchpoint carbon, the so-called tertiary chlorine, are important concerning the thermal stability of PVC.\textsuperscript{11,24-27} To subdivide the branches in those connected to a branchpoint carbon carrying chlorine and those connected to a branchpoint carbon carrying hydrogen, the polymer had to be reduced into a deuterium-labeled polyethylene chain, after which the different types of branches can be distinguished by means of \textsuperscript{13}C NMR.\textsuperscript{12} The development of the different types of branches with increasing monomer conversion is shown in Figure 3.13.
Figure 3.13 Dependence of the number of different types of branches per 1000 VC units on monomer conversion: chloromethyl branch (♦); 2,4-dichloro-\(n\)-butyl branch (●); long chain branch (▲); 1,2-dichloroethyl branch (■)

Up to a monomer conversion of approximately 80-85%, the number of all types of branches is constant, while at higher monomer conversions they all increase except for the ethyl branches. This increase in number of branches with increasing monomer conversion during the pressure drop corresponds to results published by Hjertberg and Sörvik. After \(X_f\), the monomer concentration in the polymer-rich phase starts to decrease and, as a consequence, the active growing macroradicals will eventually have more difficulty encountering monomer molecules to react with. Therefore, more and more side-reactions are likely to occur, such as hydrogen abstraction from neighboring polymer chains and intramolecular backbiting reactions, causing different types of branches and internal unsaturation as described in Chapter 1. These side reactions are shown in Scheme 3.1, which gives an overview of the possible...
reactions in which a growing PVC chain can participate.

Scheme 3.1 Overview of all possible reactions occurring during the polymerization of VCM
The branches connected with tertiary chlorine are the 2,4-dichloro-n-butyl branches (BB) and various types of long chain branches (LCB). The number of both types of branches increases tremendously with increasing monomer conversion beyond 80-85%. As already shown in Fig. 3.13, the formation of LCB is more dependent on monomer conversion than the formation of BB, which can be explained by their different mechanisms. LCB are the result of intermolecular chain transfer to polymer, and at very high monomer conversions the overall polymer repeat unit concentration has become sufficiently high to become dominant over the intramolecular backbiting reaction, which would yield the BB, as was described by Ahmed et al. 29. However, it should be mentioned that the number of LCB contains all long chain branches irrespective of the presence of tertiary chlorine, as these two variations could not be distinguished quantitatively by NMR, in contrast to the other much shorter branches.

In case of the number of 1,2-dichloroethyl branches (EB) no clear trend with increasing monomer conversion can be established, probably because of the very small signal to noise ratio.

Finally, the number of chloromethyl branches (MB) shows a significant increasing trend with increasing monomer conversion. As EB are originating from the same reaction route, head-to-head addition followed by 1,2-Cl shift (Scheme 3.1), a similar growing trend with increasing monomer conversion is expected. Unfortunately this relation cannot be determined due to the very low signals for EB as just mentioned. The growth of MB with increasing monomer conversion cannot be explained as no reason can be found for a relative increase of head-to-head additions of monomer to the growing polymer.

A possible explanation for this increasing trend of the number of MB with increasing monomer conversion could be the occurrence of a second reaction route resulting in the same type of branch.

A plausible second mechanism for the formation of MB would be the rearrangement of a regular radical chain end by means of a 1,2-hydrogen shift followed by
propagation as shown in Scheme 3.2. This route has first been proposed by Overberger.\textsuperscript{30-33} The intermediate radical could also experience a subsequent 1,2-Cl-shift, which would again result in the formation of EB after regular addition of VCM.

Scheme 3.2 Possible second reaction route for the formation of the chloromethyl and 1,2-dichloroethyl branches

As at high monomer conversions, after $X_f$, the macroradicals have difficulty encountering monomer molecules to react with, these macroradicals will have a better opportunity to rearrange resulting in an increasing number of MB and possibly EB.

Despite the large growth in number for MB, BB and LCB with increasing monomer conversion beyond 85%, MB is not expected to affect the thermal stability. This type of branching is, in contrast to BB and LCB, not accompanied by tertiary chlorine, which is believed to be an initiation point of thermal dehydrochlorination.

According to these findings it is clear that the destructive defect structures which cause the thermal instability of PVC are increasingly formed at very high monomer conversion. Already from $X_f$, corresponding to a monomer conversion of about 60%, the polymer-rich phase becomes more and more viscous as the monomer concentration starts to decrease. The volume and weight fraction of PVC in the polymer particles after the critical conversion grow significantly as shown in Table A.1 in the Appendix. However, the decrease in monomer concentration does not
immediately result in an increasing occurrence of side-reactions. Only when polymer mobility becomes very low, as the $T_g$ of the composition of the polymer-rich phase gets closer and closer to the polymerization temperature, the side-reactions seem to gain the upper hand at the expense of the regular reaction routes.

### 3.4 Conclusions

Polymerizations with different conversions were carried out to obtain a more detailed view of the polymerization process and of the connection between the polymerization, particle morphology and thermal stability of PVC. Molecular weight measurements showed that both $M_n$ and $M_w$ increase with increasing monomer conversion up to about 80% due to the increasing contribution of polymerization in the polymer-rich phase. Hereafter, $M_n$ decreased dramatically as a consequence of an increasing importance of chain transfer to monomer over propagation as the propagation reaction becomes more and more diffusion controlled. The porosity of the polymer grains decreases with increasing monomer conversion as the interior of these grains becomes more compact due to growth and fusing of the primary particles and shrinking of the grains by the large difference in density of VCM and PVC.

The thermal stability of PVC decreases dramatically when monomer conversion exceeds approximately 80-85%, long after $X_f$ and the start of the pressure drop. From this moment on, the defect structures such as the internal allylic chlorines and different types of branches linked with tertiary chlorine also increase in number, which strongly indicates their influence on the thermal stability of the polymer.
3.5 References

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