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

Pauwels, Kim Francesca Daniëla

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CHAPTER 5

The suspension polymerization of VCM in the presence of a precipitant for PVC

Abstract

An attempt was made to manipulate the course of the polymerization of VCM by changing the composition of the polymer-rich phase. The addition of n-octane, which is a nonsolvent for PVC, will induce the polymer-rich phase to become denser due to the decreasing solvent quality of the VCM / n-octane mixture.

By increasing the amount of n-octane present in the polymerization mixture the appearance of the hot spot diminishes and finally disappears completely when more than 15 wt % of n-octane is added to the reaction mixture. This disappearance is due to a decreasing polymerization rate as the monomer concentration in the polymer-rich phase decreases with an increasing amount of n-octane.

During the overall polymerization process, the pressure inside the reactor decreases continuously with increasing monomer conversion due to a continuous increase of the concentration of n-octane in VCM, which causes a lowering of the vapor pressure of the latter.

The morphology of the PVC grains changes in case of the presence of n-octane during polymerization, which results in a higher porosity and smaller average pore diameters. Thermal stability of PVC seems to decrease when large amounts of n-octane are added to the polymerization system, as the rate of dehydrochlorination increases significantly. However, besides an obvious increase in the number of chloromethyl branches no significant difference in the number of other defect structures was found.
5.1 Introduction

In Chapter 3 a clear relation was established between the increasing number of internal allylic structures and certain types of branching, and the decreasing thermal stability of PVC. The number of these detrimental defect structures in PVC increases dramatically with increasing monomer conversion exceeding 85%; way beyond the critical conversion $X_f$ and just after the hot spot has ended (Chapter 4). From this moment on the polymerization decelerates as the monomer concentration in the polymer-rich phase becomes very low and therefore the viscosity of this phase increases tremendously. This increased viscosity results in hindered dynamics of the polymer chains and therefore propagation, as well as bimolecular termination and chain transfer to monomer transfer, become more and more diffusion controlled, while side-reactions obviously start to take place to a much larger extent. For this reason, the polymerization process in the polymer-rich phase is a very important location to study in more detail.

It is of interest to modify the composition of the polymer-rich phase by changing the amount of VCM present in this phase. The addition of a solvent for PVC is expected to increase the mobility of the polymer chains in the polymer-rich phase, while adding a nonsolvent or precipitant for PVC will probably result in the opposite, as PVC chains will be collapsed much stronger and will therefore become less accessible for VCM. The effect of the addition of o-dichlorobenzene, being a solvent for PVC and VCM, on the course of the polymerization process is described in detail in Chapter 6. In this current chapter the result of the presence of n-octane, which is a nonsolvent for PVC while miscible with VCM, during the suspension polymerization will be discussed. The polymerization of VCM in nonsolvents, such as cyclohexanone, tert-amyl alcohol, neo-pentane, and methanol, was studied in comparison to the bulk polymerization of VCM $^{1-3}$. Although the results from these publications could also be valid for a suspension polymerization of VCM, in the presence of a nonsolvent for PVC, there are too many differences in the polymerization conditions with the current polymerization process to provide us with enough relevant information. Besides this,
the influence of the presence of a nonsolvent for PVC during the polymerization of VCM on the formation of defect structures in the polymer chain and the resulting thermal stability has not been described before.

When n-octane is added to the reaction mixture it will mix with VCM, which is suspended in the aqueous phase. Soon after the polymerization reaction has started, a two-phase system is obtained inside the polymerizing droplets, as already mentioned in Chapter 3. However, the presence of n-octane transforms the binary system as discussed in Chapter 3 into a ternary system. A theoretical ternary phase diagram of this reaction system, consisting of PVC, VCM, which is a poor solvent for PVC, and n-octane, which is a nonsolvent for PVC while completely miscible with VCM, is shown in Figure 5.1. This schematic ternary phase diagram is constructed after the examples presented by Tompa 4.

**Figure 5.1** Schematic ternary phase diagram for the PVC / VCM / n-octane system: binodials (solid line); proposed tie lines (dotted line); constant weight fraction of n-octane in overall polymerization system (dashed line)
The weight fraction of n-octane in relation to the overall composition is constant during the entire polymerization, as this component does not participate in the polymerization process. Therefore, the polymerization occurs along the dashed line, which is drawn in the ternary phase diagram, corresponding to a certain amount of n-octane that has been added to the reaction mixture. This line could also be regarded as a kind of conversion scale. Moving along this line, the polymerization starts from the n-octane / VCM side corresponding to 0% of monomer conversion and finally ends at the n-octane / PVC side when the theoretical monomer conversion of 100% is reached. As can be observed from the ternary phase diagram, polymerization occurs in a homogeneous or one-phase system for a very short period of time, after which the polymerization mixture phase separates resulting in a two-phase system consisting of a polymer-lean and a polymer-rich phase. In the two-phase region the dashed line, corresponding to a certain amount of n-octane, is crossed by tie lines at every possible monomer conversion. The intersection of these lines corresponds to the overall composition of the polymerization mixture. The tie lines, of which a few of them have been proposed in Figure 5.1, connect the corresponding compositions of the two phases in which the polymerization mixture has been split up at that point. This ternary phase diagram shows that, although both phases contain all three components, the ratio between VCM and n-octane is not equal for both phases. Such inequality in the ratio of solvent to nonsolvent for both phases was already mentioned by Scott and Tompa 4,5 and is in our case probably caused by the fact that the presence of VCM in the polymer-rich phase will be more preferable than the presence of n-octane. With an increasing amount of n-octane added to the polymerization mixture the corresponding dashed line in Figure 5.1 will shift from the VCM / PVC side towards the n-octane vertex. When only a small amount of n-octane is added, the polymerization system will finally, at high monomer conversions, end up in a one-phase system again, consisting of PVC swollen in a mixture of VCM and n-octane. In this case the pure liquid polymer-lean phase will be depleted and a critical conversion $X_f$ can still be defined. However, when this dashed line does not cross the binodial at any monomer conversion anymore, no $X_f$ will ever be reached and therefore the polymerization mixture will remain a two-phase system throughout the entire
polymerization reaction. With the consumption of VCM during the polymerization, the ratio between VCM and n-octane will change in both phases, as only VCM is consumed while the amount of n-octane in the polymerization mixture is constant during the entire reaction. This changing ratio with increasing monomer conversion already occurs from the start of the polymerization reaction and results in a continuous declining solvent quality of the VCM / n-octane mixture for PVC. As a consequence, PVC coils collapse more and more, and the composition of the polymer-rich phase will therefore change continuously. The weight fraction of VCM in this phase decreases uninterruptedly already from the beginning, whereas in case of a regular polymerization the composition of the polymer-rich phase is constant until the critical conversion $X_f$ has been reached. From this continuous changing monomer concentration in the polymer-rich phase can be concluded that in case of the addition of n-octane no single $X_f$ can be assigned, as it will shift simultaneously with increasing monomer conversion to higher values.

The influence of various amounts of n-octane on the course of the suspension polymerization of VCM, the resulting particle morphology, the presence of defect structures in the polymer chain and the allied thermal stability were investigated.

### 5.2 Experimental

The polymerization process as well as the different characterization methods have been described in detail in the experimental sections of the previous chapters. The only variation in the polymerization process is the addition of n-octane purchased from Acros (99+%) and used as received, which was added to the aqueous medium consisting of PVA and the buffer salt both dissolved in RO-water before evacuation of the reactor to remove oxygen. Various amounts of n-octane were added viz. 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0 wt % in proportion to the initial amount of VCM. All these experiments were terminated by the addition of the killing agent after a
pressure drop of 3.5 bar, which corresponds to a monomer conversion of approximately 87%.

5.3 Results and Discussion

5.3.1 Polymerization trends

The effect of the presence of n-octane during the polymerization of VCM on the course of the pressure drop and the temperature of the heater during polymerization is shown in Figure 5.2 and 5.3, respectively.

![Figure 5.2](image)

Figure 5.2 The course of the pressure during polymerization of VCM for various amounts of n-octane: 0 wt % (dashed line); 5.0 wt % (dotted line); 10.0 wt % (dash / dotted line); 20.0 wt % (solid line)

The vapor pressure of n-octane is very low in comparison to that of VCM, namely < 0.1 versus 8.6 atm at 57.5 °C, respectively. Due to the presence of n-octane, which is
miscible with VCM, the vapor pressure of VCM will be lowered in accordance to Raoult's law, causing a decrease in the total pressure of the gaseous phase. As the concentration of n-octane increases continuously with increasing monomer conversion, the pressure in the reactor also drops continuously already from the beginning of the polymerization. Likewise, the initial pressure in the reactor is significantly lowered when a larger amount of n-octane is loaded, which can be clearly observed in Figure 5.2.

With an increasing amount of n-octane initially added to the reaction mixture, the hot spot first shifts towards a later moment and eventually diminishes completely as can be observed in Figure 5.3.

![Figure 5.3](image-url)

**Figure 5.3** The course of the temperature of the heating system during polymerization for various amounts of n-octane: 0 wt % (dashed line); 5.0 wt % (dotted line); 10.0 wt % (dash / dotted line); 20.0 wt % (solid line)

Due to the presence of n-octane, first of all the monomer concentration in both the polymer-lean and the polymer-rich phase will decrease. Secondly, the growing
polymer chains will collapse more strongly in the presence of n-octane in comparison to the standard polymerization reaction, which can be concluded from an increased polymer weight fraction in the polymer-rich phase at a certain monomer conversion, as can be diagnosed from the ternary phase diagram of PVC / VCM / n-octane. In Figure 5.4 the schematic ternary system is presented in which, as an example, a construction line is drawn corresponding to a monomer conversion of 50%.

![Figure 5.4 Schematic ternary system PVC / VCM / n-octane: effect of various amounts of n-octane present during the suspension polymerization of VCM on the composition of the polymer-poor and polymer-rich phase at a arbitrary monomer conversion](image)

This line will intersect the dashed lines corresponding to 10 and 20 wt % of n-octane at different positions. The corresponding tie lines crossing these intersections will eventually lead us to the different compositions of the polymer-lean and the polymer-rich phases in the presence of the different amounts of n-octane after reaching the monomer conversion of 50%. When more n-octane is added, the polymer-rich phase will contain a higher weight fraction of PVC at this particular monomer conversion. This increasing polymer concentration means that the polymer-rich phase becomes more viscous and therefore bimolecular termination also becomes more retarded.
This will induce an increasing radical concentration as the formation of new growing polymer chains, which mainly occurs in the pure liquid polymer-lean phase, will continue without hindrance. The growing macroradicals will phase-separate already shortly after their formation and attach to the polymer-rich phase, which becomes even more pronounced with the increasing concentration of n-octane. This growth in radical concentration will counteract the decreasing reaction rate as a consequence of the decreasing monomer concentration with the increasing participation of n-octane in the polymerization system.

The first observed shift in the occurrence of the hot spot to a later period in time, with the addition of 5 wt % of n-octane, is probably a consequence of a shift in the critical conversion $X_f$. Due to the diluting effect of n-octane the overall monomer concentration will be lower, which induces a lower polymerization rate. Therefore, it will take longer before the pure liquid polymer-lean phase is completely consumed and polymerization will continue in the polymer-rich phase only. When a larger amount on n-octane is added to the polymerization system, such as 10 wt % or higher, the magnitude of the heat effect simultaneously diminishes, which probably results from a larger limitation of the diffusion of VCM into the very dense collapsed polymer-rich phase.

With the addition of about 15 wt % of n-octane no clear hot spot can be observed anymore and for 20 wt % of n-octane the hot spot seems to have disappeared completely. In the presence of a large amount of n-octane the growing polymer chains will already collapse very strongly early during the polymerization process and the polymer-rich phase will become very viscous. As already mentioned, the radical concentration will increase dramatically as bimolecular termination will be retarded largely and, therefore, polymerization will be able to continue with a considerable reaction rate despite the decreased monomer concentration. In the presence of the large amount of n-octane the pure liquid polymer-lean phase will not become completely depleted, but becomes continuously richer in n-octane during polymerization. Diffusion of VCM from this phase into the polymer-rich phase is expected to be the rate-determining step. For these reasons the gel effect during the
suspension polymerization of VCM in the presence of large amounts of n-octane, exceeding 15 wt %, will be present almost from the beginning of the reaction, but with a smaller magnitude due to hampered diffusion of VCM into the very dense polymer-rich phase. Eventually the reaction is probably completely terminated way before the limiting conversion in the conventional suspension polymerization of VCM would have been reached, as the polymer-rich phase will be collapsed to such extent that the T_g will be reached.

5.3.2 Molecular weight

In Figure 5.5 the number and weight average molecular weights, and the corresponding molecular weight distribution of the PVC products prepared in the presence of different amounts of n-octane are depicted.

![Molecular weight development graph](image)

**Figure 5.5** Molecular weight development with increasing amount of n-octane in the reaction mixture: $\bar{M}_n$ (▲); $\bar{M}_w$ (●); $D = \bar{M}_w/\bar{M}_n$ (■)
Due to the decrease in monomer concentration as a result of dilution by n-octane the polymerization rate will decrease, which in turn causes the decrease in the average degree of polymerization (equations 4.1 and 4.1 Chapter 4). Besides the diluting effect, the diminished gel effect can also induce some lowering of the molecular weight of PVC.

### 5.3.3 Particle morphology

The effect of the presence of various amounts of n-octane during the polymerization of VCM, on the porosity of the resulting PVC grains, was determined by means of the Hg-intrusion test (Figure 5.6).

![Figure 5.6 Mercury intrusion test of PVC powders for various amounts of n-octane: 0 wt % (♦); 5.0 wt % (●); 10.0 wt % (▲); 15.0 wt % (■); 20.0 wt % (x)](image-url)

The porosity of PVC increases significantly when more than 10 wt % of n-octane was added. The increasing porosity with the addition of different types of alkanes to the polymerization process of VCM was already claimed in several patents, although no clear explanation was given. Simultaneously, the average pore diameter also
shifts to a lower value. The most probable explanation is the stronger and consequently earlier precipitation of growing polymer chains. This earlier precipitation is expected to provoke an increase in the initial number of primary particles, which formation has been described in detail in Chapter 2. As a consequence, the final primary particles will end up being smaller than in case of a regular polymerization. The decrease in size of the primary particles with an increasing amount of n-octane can be verified from SEM-pictures of the inner part of PVC grains resulting from polymerizations in presence of different amounts of n-octane (Figure 5.7).

![Figure 5.7](image)

**Figure 5.7** SEM pictures of PVC particles prepared with different amounts of n-octane: (A) 0 wt %; (B) 10 wt %; (C) 20 wt %

When comparing the interior of a regular PVC grain with the interior of those grains obtained in the presence of n-octane, a clear difference in size and appearance of the primary particles can be observed. It becomes obvious that with an increasing
amount of n-octane the size of the primary particles decreases while simultaneously they also appear to become more separated from each other. As these primary particles have become less fused, the pores between them have become more accessible, resulting in an increased porosity of the PVC grains.

5.3.4 Thermal stability

When examining the influence of the presence of n-octane on the thermal stability of the final polymer by means of the dehydrochlorination test (Chapter 3), one observes that the stability time \( t_{st} \) shows a significant decreasing trend after approximately 10 wt % of n-octane (Figure 5.8).

![Figure 5.8 Dehydrochlorination test: \( t_i \), induction time (●) and \( t_{st} \), stability time (▲) versus amount of n-octane](image_url)

On the other hand the induction time \( t_i \) only shows a slightly, if any, decreasing trend. These results indicate that the polymer formed in the presence of n-octane does not start to degrade earlier when exposed to 180 °C, while it degrades much faster when the first molecules of HCl eventually have been eliminated. In Figure 5.9 the rate of
dehydrochlorination in relation to the amount of n-octane is presented, which clearly shows the dramatic increase in degradation rate.

![Graph showing the relation between the presence of n-octane during polymerization and the dehydrochlorination (dhc) rate of the resulting PVC product.]

**Figure 5.9** Relation between the presence of n-octane during polymerization and the dehydrochlorination (dhc) rate of the resulting PVC product

### 5.3.5 Defect structures

The effect of the presence of n-octane on the formation of defect structures within the polymer chain, during the polymerization of vinyl chloride up to a monomer conversion of approximately 87%, was also examined. No significant change in the number of internal allylic structures with the addition of n-octane was observed. The total number of branches, however, increased significantly with an increasing amount of n-octane. To determine which types of branching bring about this growth the numbers of the different types of branches have also been determined separately by means of $^{13}$C NMR after reduction of the PVC samples into PE as described in Chapter 3 (Figure 5.10).
The suspension polymerization of VCM in the presence of a precipitant for PVC

Figure 5.10 The number of different types of branches per 1000 monomeric units in relation to the amount of n-octane after a monomer conversion of approximately 87%: 1,2-dichloroethyl branches (●); long chain branches (▲); 2,4-dichloro-\textit{n}-butyl branches (■) and chloromethyl branches (♦)

From these results no significant changes in the numbers of the 1,2-dichloroethyl, 2,4-dichloro-\textit{n}-butyl and long chain branches can be determined as the minor changes in number are all within the experimental error. However, in case of the chloromethyl branches an evident increase in number is observed with the increasing amount of n-octane added to the polymerization mixture. As discussed in Chapter 3, this type of branching results from an occasional head-to-head addition of VCM to the growing macroradical followed by a 1,2-Cl-shift and subsequent regular addition of VCM, or from a 1,2-H-shift of the regular radical chain end followed by the regular chain growth. It seems to be likely that the frequency of intramolecular side-reactions,
such as Cl or H-shifts and backbiting reactions, will increase especially for the polymer-rich phase with the decreasing monomer concentration as both the mobility of the chains and the availability of VCM decreases. However, as no significant increase in the number of 2,4-dichloro-n-butyl and long chain branches can be observed, the effect of n-octane on the occurrence of intra- and intermolecular side-reactions can not be proven.

When the dramatic decreasing thermal stability of PVC with an increasing amount of n-octane is taken into account, it is tempting to speculate about the possible influence of the presence of chloromethyl branches on the thermal degradation, although these branches are not connected to a branch point carbon containing tertiary chlorine. So far all polymerizations in the presence of n-octane have only been carried out with a monomer conversion of approximately 87%. When the polymerizations are carried out up to the limiting conversion, perhaps a more clear effect of the presence of n-octane on the formation of defect structures and the resulting thermal stability could be found.

5.4 Conclusions

In the presence of n-octane, which is a nonsolvent for PVC but a solvent for VCM, the polymer-rich phase will become denser as PVC will precipitate more, resulting in a smaller amount of monomer present between the polymer chains. Thereby, the monomer concentration in the polymer-lean phase also changes continuously during the course of polymerization, as this phase becomes richer in n-octane. Due to a continuous change in the ratio between VCM and n-octane within the polymer-lean and the polymer-rich phases, no unequivocal critical conversion $X_f$ can be defined. With increasing monomer conversion, $X_f$ will simultaneously shift towards higher monomer conversions.

It was found that changing the composition of the polymer-lean and the polymer-rich phase clearly affects the course of the pressure inside the reactor and the occurrence of the heat effect during the reaction. The pressure in the reactor drops continuously already from the start of the polymerization as n-octane, which dissolves in VCM,
lowers the total vapor pressure. The composition of the polymer-lean phase changes continuously with increasing monomer conversion and so does the pressure inside the reactor.

The heat effect first shifts towards a later period in time when more n-octane is added to the polymerization mixture. This shift is probably the result of a decreasing reaction rate due to the decrease in monomer concentration in the polymer-rich phase. Additionally, the heat effect diminishes in magnitude as also the gel effect decreases. When over 15 wt % of n-octane is added the hot spot has disappeared completely. As a consequence, the polymerization time needed to reach a monomer conversion of 87% increases significantly.

The presence of n-octane during the polymerization of VCM provokes an increase in the porosity of the resulting polymer grains, which is probably caused by the stronger and earlier precipitation of the growing polymer chains. The resulting primary particles will therefore remain smaller while, as a consequence, their total number will increase. The increase in porosity is most probably due to the decreasing extent of fusion of the primary particles. As the primary particles are less fused, more space between these particles will be accessible and therefore the porosity is increased.

The presence of n-octane during the polymerization of VCM affects the thermal stability of the final polymer negatively as the rate of dehydrochlorination increases dramatically with an increasing amount of n-octane. Simultaneously, the number of the chloromethyl branches shows a significant increase, which suggests that, although they do not contain tertiary chlorine at the branch point carbon, the chloromethyl branches might have a significant influence on the thermal stability of PVC after all.
5.5 References


