

Nonaqueous Polymerization of Vinyl Chloride: An Environmentally Friendly Process

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ABSTRACT: Poly(vinyl chloride) (PVC) is produced via a nonaqueous polymerization process in which hexane is used as a diluent. This nonaqueous process can lead to significant energy savings, significant reductions in carbon dioxide emissions, and the elimination of wastewater. Various suspending agents have been used to evaluate their effects on the shape and morphology of PVC grains. The nonaqueous process leads to the formation of PVC

grains with higher porosity than that of typical suspension PVC. The bulk density is slightly lower than that of suspension PVC, but the thermal stability seems to be similar. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2472–2481, 2009

Key words: morphology; poly(vinyl chloride) (PVC); radical polymerization

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important commodity thermoplastics because of its versatility, which stems from its unique morphological characteristics. These allow PVC to be combined with a number of additives,¹ and this results in a wide range of end-use properties, from plasticized flexible materials to rigid plastics. The unique morphology of PVC grains is derived from the insolubility of the polymer in its own monomer and from the polymerization process. The most widely used polymerization route for the production of PVC is suspension polymerization,^{1–3} a process in which large quantities of water are used that have to be decontaminated and discarded at the end of the process (the quantities of wastewater and polymer produced are approximately equal). The polymerization is often quenched at conversions around 80–85% because a further increase in the conversion when the monomer is almost depleted results in the occurrence of side reactions and the formation of defect structures in the polymer chain, some of which act as initiation sites for the thermal degradation of the polymer.^{4,5}

As the remaining unreacted monomer is toxic, after polymerization, the PVC grains are stripped to remove it. The monomer tends to diffuse slowly from the center of the resin particle to the surface, so removal can be incomplete. To facilitate and improve stripping, high porosity is essential. After the stripping and washing of PVC grains with water to remove the excess of the suspending agents, a wet PVC cake is produced with a water content of approximately 20–30%. The polymer cake is then subjected to an energy-consuming drying process for the removal of water and the production of dry PVC powder.

The generation of contaminated water from the polymerization reactor and the large amount of energy consumption during product drying give rise to sustainability and environmental concerns. However, the environmental impact of PVC production could be reduced significantly by the replacement of water with a hydrocarbon diluent. Then, contaminated water is no longer produced, and the overall energy consumption is lowered because, in comparison with water, hydrocarbons have a low thermal capacity and a smaller enthalpy of evaporation. The use of standard tabulated thermodynamic data shows that overall energy consumption for a nonaqueous process is about 60% of that for conventional aqueous polymerization. Virtually all the hydrocarbons can be recycled, and the PVC that is produced can be stripped more easily as it is more porous than PVC from conventional aqueous suspension polymerization.^{6,7} The solubility of the monomer in

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hydrocarbons exceeds its solubility in water, so unreacted monomer is removed from the polymer more easily. In industrial processes, existing techniques for monomer recovery would ensure that the monomer would not escape to the environment.

Previous work on a nonaqueous polymerization process using *n*-butane as the reaction medium showed that the PVC grains produced had a different morphology and different features from typical suspension PVC grains, and hence a different mechanism of particle formation was proposed⁷ to explain those features. The morphology of the PVC grains influences the processability of the resin to a great extent as some of the properties of the polymer, such as flow properties, miscibility with various additives, and plasticizer adsorption, depend on it. One of the factors that determine the shape and morphology of the particles is the type of suspending agent used during the polymerization process. The aims of this work were to characterize the morphology of the polymer product and to assess the effect of using different suspending agents with different hydrophile-lipophile balance (HLB) values on the grain features. Various suspending agents were used with a range of HLB values, and their effects on the particle shape and morphology were evaluated. The criteria for the choice of suspending agents for this process were environmental friendliness, low hazard for human health, ease of removal from the particle surface, and low impairment of the polymer properties.

In this study, hexane was used as the reaction medium because it is less volatile than butane and allows more flexibility in reactor charging sequences at atmospheric pressure. Investigations of the particle size distribution (PSD), thermal properties, and molecular weight of the polymer were included. This project also investigated the effects of the initiator concentration and monomer volume fraction on the polymer grain morphology.

EXPERIMENTAL

Materials

Vinyl chloride monomer (VCM) was supplied by Ineos ChlorVinyls (Runcorn, UK). A common peroxide, bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, was used as an initiator, and the following surfactants were used as suspending agents: glycerol monostearate, sorbitan monostearate, alcohol ethoxylate, glucose distearate, and poly(vinyl alcohol) with a 55% degree of hydrolysis. These had HLB values of 3.8, 4.7, 8.1, 11.5, and 15.7, respectively. Those suspending agents are called SA 3.8, SA 4.7, SA 8.1, SA 11.5, and SA 15.7. Hexane was used as the diluent and was purchased from Fisher Scientific (Loughbor-

ough, UK). Two commercial PVC grades, SH6030 and SH6830, were obtained from Ineos ChlorVinyls.

Methods

Nonaqueous polymerization experiments were run with a 1-L-capacity stainless steel jacketed reactor with magnetic stirring. A flat four-blade stirrer was used. The reactor was equipped with a pressure transducer and a thermocouple, which were connected to a control panel to monitor the temperature and pressure variations during polymerization. A temperature controller was also used to maintain a constant reaction temperature. The stirring speed was 400 rpm. The reaction temperature was 45°C. Hexane (in a liquid form), the suspending agent, and the initiator were charged in the reactor, and the mixture was purged with nitrogen several times to remove oxygen from the reactor. After the diluent was treated with nitrogen, the monomer was charged in the reactor. The mixture was stirred at the ambient temperature for 30 min to dissolve the surfactant and initiator, and then the reactor was heated up to the reaction temperature. During the reaction, the reactor pressure decreased from an initial value of 4 bar to 2 bar. Various suspending agents were used to examine their effect on the PVC grain morphology and structure.

The morphology, particle size, thermal properties, molecular weight, and porosity of the polymer product were investigated. The PVC samples produced were examined with scanning electron microscopy (SEM), differential scanning calorimetry, gel permeation chromatography, thermogravimetric analysis, and torque rheometry. Surface area and porosity analysis was achieved with Brunauer-Emmett-Teller (BET) analysis, which was carried out at the temperature of liquid nitrogen (77.2 K) and within a pressure range of 0.05–0.3 P_0 for surface area analysis and within a pressure range of 0.3–0.99 P_0 for the pore size distribution at 77.2 K (P_0 is the saturation pressure). Particle sizes were determined with laser diffraction.

RESULTS AND DISCUSSION

The features of the particles produced with hexane are very similar to those of the particles produced in *n*-butane, and the mechanism of particle formation proposed by Bao and Brooks⁷ has also been verified for the VCM/hexane system. VCM and hexane are miscible in any ratio, and the reaction system is initially homogeneous. According to this mechanism, as polymerization starts, the formed PVC chains precipitate at a very low conversion because of the insolubility of PVC in a mixture of VCM and hexane. The solubility parameters of hexane, VCM, and

TABLE I
Effect of the Suspending Agent Type on the Morphology of the PVC Grains

Suspending agent	Shape of the PVC grain	Surface texture	Primary particles
SA 3.8	Regular	Even, semismooth	Unequal sizes
SA 4.7	Regular	Even, smooth	Uniform, equal sizes
SA 8.1	Very regular, almost spherical	Rough, uneven	Nonuniform, different shapes and sizes
SA 11.5	Irregular	Uneven, smooth	Uniform, equal sizes
SA 15.7	Regular	Rough, uneven	Nonuniform, different shapes and sizes

PVC are 7.0, 7.8, and 9.7 (cal/mL)^{1/2}, respectively.⁸ Hence, the solubility of PVC in a mixture of VCM and hexane is lower than the solubility of PVC in VCM alone. In other words, the solubility of PVC can be described as hexane < VCM/hexane < VCM. The precipitating chains aggregate to form small particles that will grow further as newly formed PVC chains aggregate with them and polymerization occurs inside them. These are designated primary aggregates of PVC chains. The primary aggregates of PVC chains are unstable and aggregate to form primary particles. Most primary particles will further aggregate to form grains. Therefore, the polymerization is carried out in a VCM/hexane mixed medium, the composition of which will change continuously as the polymerization proceeds and VCM is consumed. Together with the changing composition, the solubility of PVC in the mixture also decreases with conversion as PVC is less soluble in hexane than in VCM. As the composition changes with conversion, the PVC chains precipitate at an earlier stage, and primary aggregates and primary particles with different sizes are formed. The particle features of PVC resins prepared by the new polymerization process can be explained by the aforementioned particle formation mechanism. PVC grains are formed by the direct aggregation of primary particles in the agitated medium, so their shapes are more regular and their surfaces are smoother than those of the suspension PVC resin. Also, there is no evidence of the pericellular membranes (graft copolymers of the suspending agents with PVC) that exist on PVC grains from conventional suspension polymerization^{9,10}

Particle shape and morphology

The type of suspending agent was found to exert a strong influence on the shape and morphology of the polymer particles, as it also does in typical suspension polymerization processes.^{11–16} The shape of the particles varied from regular to irregular and the surface varied from even and smooth to rough and uneven, depending on the type and HLB value of the suspending agent, as shown in Table I.

The important aspects of grain morphology are (1) the shape and size of the primary particles, (2) the way in which the primary particles are packed together or agglomerate to form a surface, and (3) the shape and size of the grain.

Different types of suspending agents with different HLB values yielded PVC grains with different features.

HLB is not the only factor that determines the shape and morphology of PVC grains. In fact, the influence of the HLB value of the suspending agents on the shape and size of the primary particles is small. Two stearates, SA 4.7 and SA 11, 5 with very different HLB values (4.7 and 11.5) gave uniform, equally sized primary particles that did not agglomerate and were regularly arranged next to one another, creating a smooth and even grain surface. The high-magnification micrographs of the particle surface show that the PVC grains produced with SA 4.7 [Fig. 1(b)] and SA 11.5 [Fig. 2(b)] consisted of well-defined, discrete units (primary particles) with a similar diameter (ca. 0.1–0.2 μm) that were regularly arranged on the particle surface. The regularity in the arrangement of the primary particles in combination with the similarity in their sizes created the smooth appearance of the surface. This observation that the HLB properties are not the determining factor for the shape of the primary particles is confirmed by results obtained with a third stearate, SA 3.8. Although its HLB value is similar to that of SA 4.7, the primary particles formed were not uniform, they did not have equal sizes, and they agglomerated, creating a rough but even grain surface [Fig. 3(b)]. The regularity of the arrangement of the primary particles created an even surface, and the semismooth/rough surface texture was caused by the unequal sizes of the primary particles.

However, the effect of the HLB on the grain shape and size is greater. The suspending agents with low HLB values, SA 3.8 and SA 4.7, gave regularly shaped grains [Figs. 3(a) and 1(a), respectively], whereas SA 11.5 gave irregular, cauliflower-like grains that varied significantly in shape and size [Fig. 2(a)].

Thus, for stearates, the HLB value determines the shape and morphology of the grain, but it does not

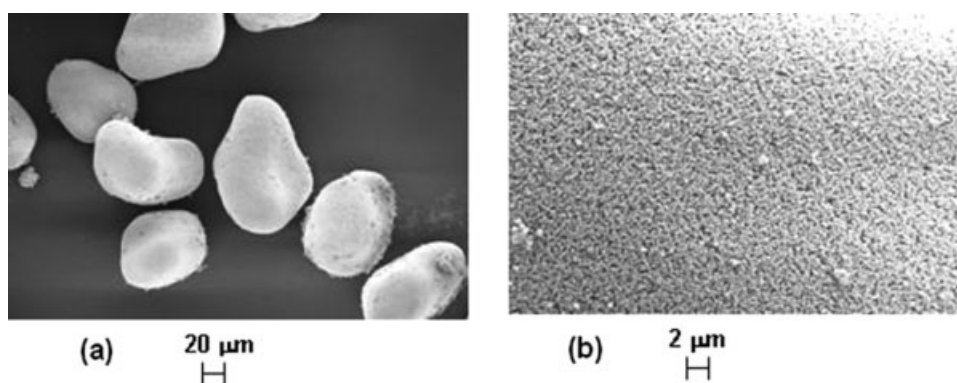


Figure 1 SEM micrographs of the PVC grains produced with SA 4.7: (a) PVC grains and (b) surface of a grain.

significantly affect the primary particle morphology. Stearates with low HLB values form regularly shaped grains, whereas those with high HLB values form irregularly shaped grains.

The alcohol ethoxylate SA 8.1 and the poly(vinyl alcohol) SA 15.7 both gave regularly shaped grains but with primary particles not well defined and partly agglomerated. In Figure 4, it can be seen that the particles produced with SA 8.1 were almost spherical in shape, with even surfaces and primary particles that were not very discrete because agglomeration seems to have taken place to some extent. The primary particles had different shapes and sizes. Finally, Figure 5 shows PVC grains produced with SA 15.7. Their shape was regular. Their surface, however, was uneven and had a rough appearance. The high-magnification micrograph [Fig. 5(b)] shows that the surface did not consist of well-defined units. The primary particles were not arranged in a regular manner and had different sizes. There seems to have been agglomeration and fusion of some primary units to some extent that, in combination with the way in which the units were packed together, created a rough, not uniform surface.

It could be suggested that, for alcohol compounds, the HLB does not affect the morphology of the grain. In both cases (SA 8.1 and SA 15.7), regular, almost

spherical grains were formed. There may have been a slightly stronger effect on the primary particle morphology because the agglomeration of primary particles seems to have taken place to a greater extent when SA 15.7 was used.

A wide range of suspending agents were used to produce PVC grains with different and varied morphologies, as shown in Table I. The morphology of PVC grains can be manipulated, depending on the suspending agent used, to a greater extent than that of the typical suspension grades. This provides the potential to further improve the properties of PVC to achieve the desirable levels for more potential applications.

Also, it has to be noted that one of the benefits of the nonaqueous polymerization process, compared to the usual suspension process, is that reactor fouling is either eliminated or significantly reduced.

Particle size and distribution

The particle sizes and PSDs of various PVC samples produced under a wide range of conditions were measured to identify some of the factors that may affect them. These were the following.

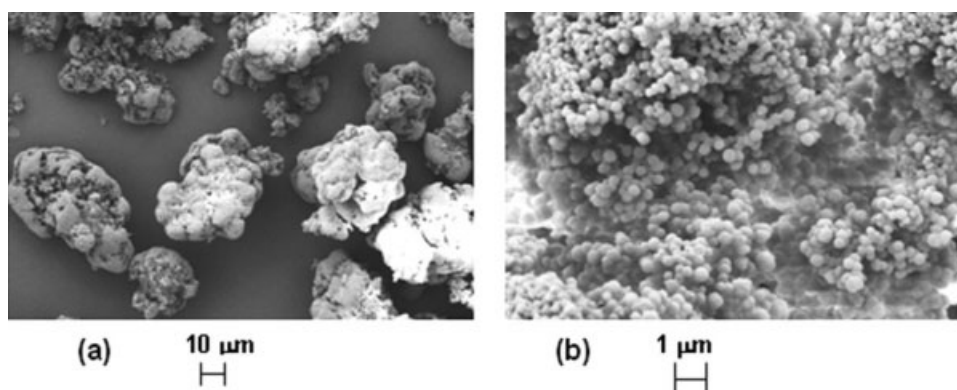


Figure 2 SEM micrographs of the PVC grains produced with SA 11.5: (a) PVC grains and (b) surface of a grain.

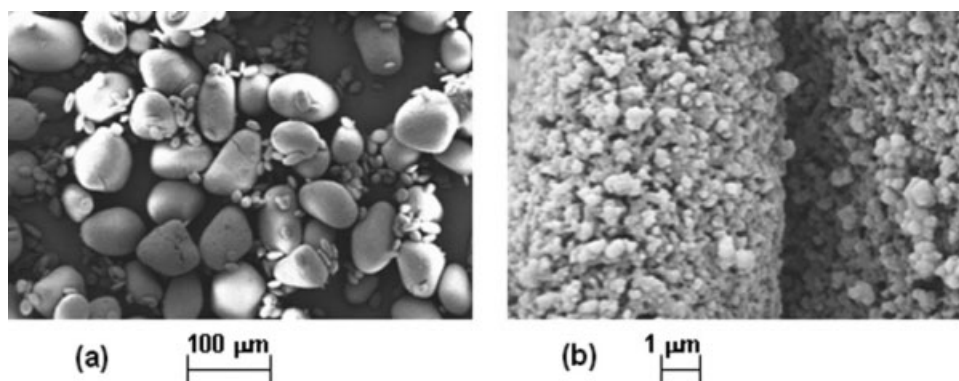


Figure 3 SEM micrographs of the PVC grains produced with SA 3.8: (a) PVC grains and (b) surface of a grain.

Suspending agent type

The type of suspending agent has a significant effect on the PSDs of the resin.

The PSDs obtained with different suspending agents were compared with those of a typical commercial resin, as shown in Figure 6. In all cases, the particles produced by the nonaqueous process were smaller than those of the commercial PVC. The PSD corresponding to the commercial PVC resin was narrow. The PSDs produced with SA 4.7 were very similar in shape to those of the commercial resins, but they were shifted toward smaller particle sizes. The other suspending agents produced PVC resins with wide PSDs that were also shifted toward smaller particle sizes.

Suspending agent concentration

The effect of the concentration of the suspending agent on the particle sizes is similar to the effect of the suspending agent concentration observed for typical suspension resins.^{17–21} Increasing the suspending agent concentration leads to a decrease in the particle size (Fig. 7). A comparison of nonaqueous resins with a commercial resin shows that for

low suspending agent concentrations (0.26% w/w VCM), the particle sizes are bigger than those of the commercial PVC, and the PSD is wider. As the concentration of the suspending agent increases, the particle sizes decrease and the PSD becomes narrower until a concentration is reached at which its shape is similar to the shape of the commercial resin, but it shifts to smaller sizes. If the suspending agent concentration is increased beyond that point, then the main PSD does not shift to smaller sizes, but a secondary distribution of fine particles appears.

The secondary peak corresponds to fine particles, the formation of which is triggered by specific conditions. These fine particles have an average size of 10–20 μm and a shape different from that of the big particles produced under the same conditions. They have a lentil-like shape, but their surface consists of the same well-defined, discrete primary particles found in the big grains.

Initiator concentration

The concentration of the initiator affects the particle sizes as well as the formation of the fine particles. When the initiator concentration decreases, big

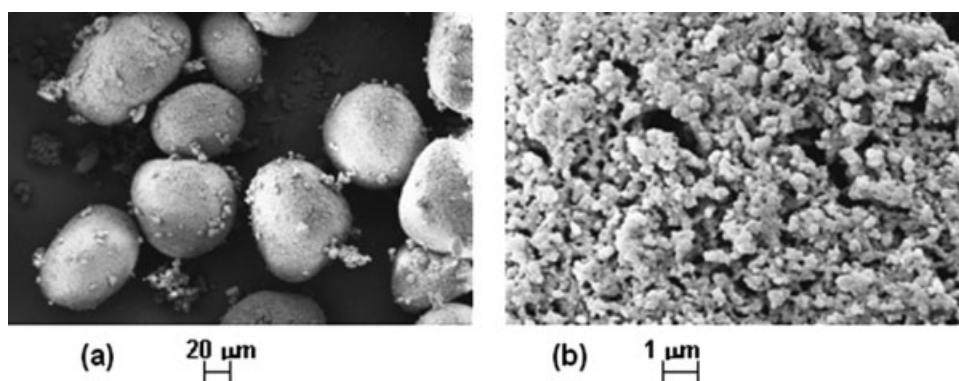


Figure 4 SEM micrographs of the PVC grains produced with SA 8.1: (a) PVC grains and (b) surface of a grain.

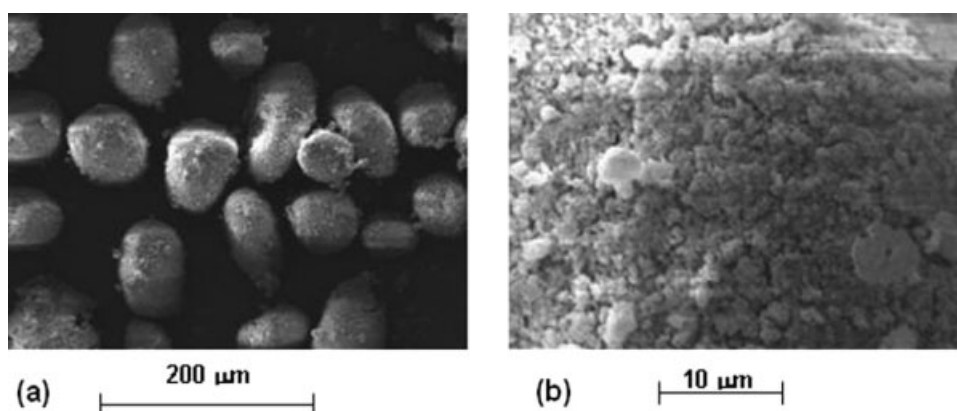


Figure 5 SEM micrographs of the PVC grains produced with SA 15.7: (a) PVC grains and (b) surface of a grain.

grains become bigger, whereas fine grains become smaller. This effect needs to be further investigated before a conclusion can be reached about the role of the initiator concentration in particle formation in the nonaqueous process.

Monomer volume fraction

In typical suspension polymerization processes, increasing the monomer volume fraction leads to the formation of larger particles. This has been mainly attributed to the increase in the collision rate between the particles.^{22–26} As the monomer volume fraction and hence the number of particles increase, so does the frequency of collisions between them. As a result, the frequency of successful collisions also increases, and this leads to an increase in the coalescence rate between the particles. Higher coalescence rates cause the formation of larger particles. In the nonaqueous process, when the monomer volume fraction was increased from 0.3 to 0.5, only a small

increase in the particle sizes occurred, as shown in Figure 8, where there is a slight shift of the main PSD toward bigger sizes. Simultaneously, it was observed that for a higher monomer volume fraction, fine particles started to form. Further experimental work is being performed to elucidate the mechanism of particle and fine particle formation.

Porosity, surface area, bulk density, and internal morphology

The porosity of PVC resins is of major importance not only because it improves the removal of unconverted VCM but also because it is essential for plasticizer uptake and additive uptake in various applications. An increase in the porosity of PVC resins has always been desirable for easier monomer removal, and so far, it has been achieved in suspension processes through the addition of secondary suspending agents such as poly(vinyl alcohol)s with low hydrolysis degrees^{16,27,28} to the polymerization reactor. The resins produced via the

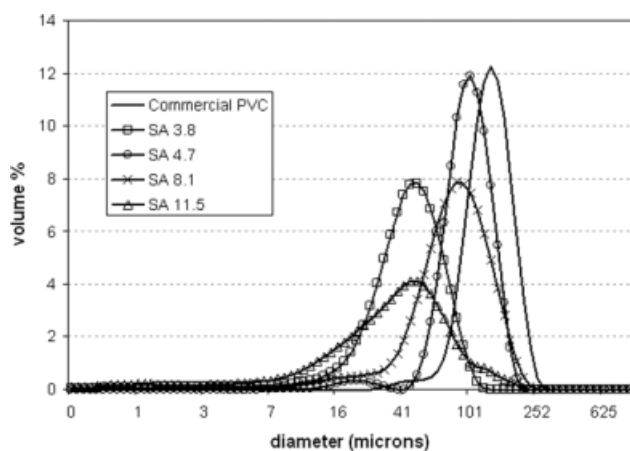


Figure 6 PSDs of commercial PVC and nonaqueous PVC samples produced with 0.3% various suspending agents.

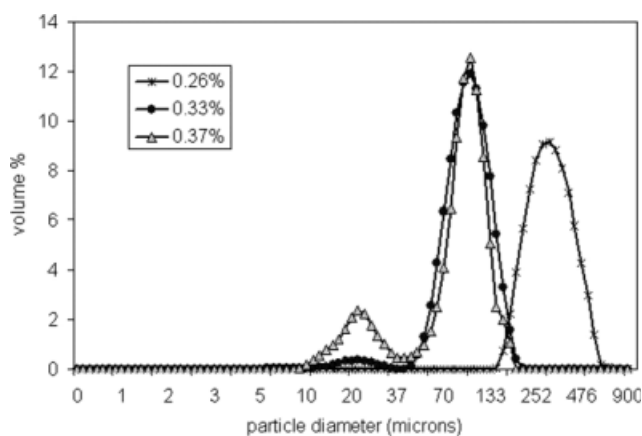


Figure 7 PSDs of nonaqueous PVC resins produced with various concentrations of SA 4.7.

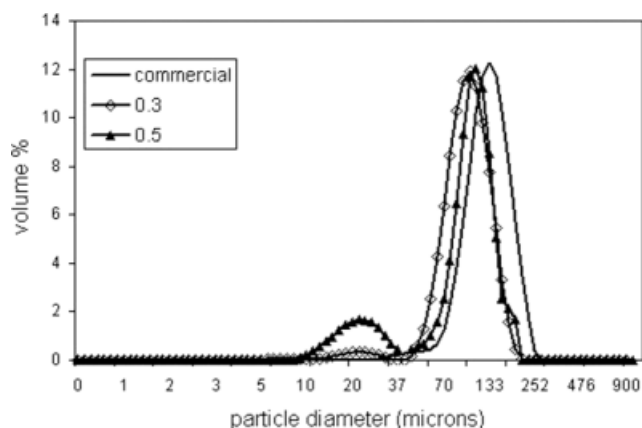


Figure 8 Effect of the monomer volume fraction on the PSD.

nonaqueous polymerization process, without the addition of any secondary suspending agents, have significantly higher porosity than typical suspension resins. Also, Table II shows typical porosity and bulk density values for commercial and nonaqueous PVC. The porosity of the nonaqueous PVC was 96% higher than that of the commercial sample, whereas the bulk density was only 16% lower.

The type of suspending agent exerts a strong influence on the porosity of PVC grains. Figure 9 shows the pore volume profile of nonaqueous PVC samples produced with various suspending agents and at a conversion of approximately 75–80% in comparison with two commercial suspension PVC grades. In all cases, the porosity of the nonaqueous samples was higher than that of the suspension resins. The pore volume profile of the PVC samples produced with SA 3.8 shows that the volume of pores was distributed almost equally over the entire pore size range. This profile is similar to that of the SH6830 grade but is shifted to higher pore volumes. SA 4.7 and SA 8.1 produced samples with pore volume profiles similar to that of the SH6030 grade, for which the pore volume was constant up to pore diameters of about 40 nm and then increased. SA 8.1 produced PVC samples with higher porosity than SA 4.7, and SA 3.8 produced the highest porosity of all.

The suspending agent concentration may exert an influence on the grain porosity as it affects the aggregation of the primary particles into grains. A comparison of the porosity of PVC particles pro-

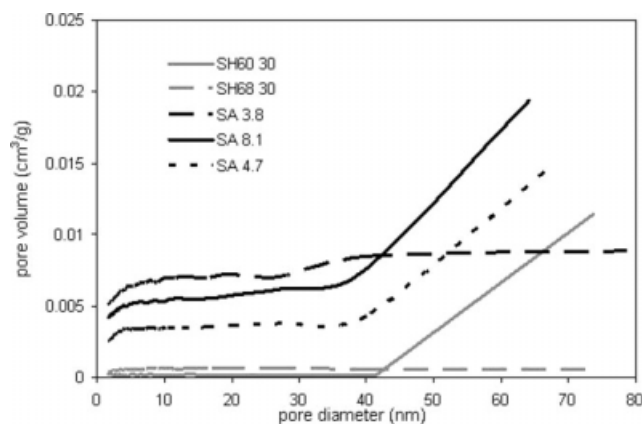


Figure 9 Effect of the suspending agent type on the porosity of nonaqueous PVC.

duced with low (0.24%) and high (0.36%) suspending agent (SA 4.7) concentrations and with a commercial resin (SH6830) is depicted in Figure 10. The porosity of the nonaqueous resins was significantly higher than that of the commercial PVC in both cases, and it increased for the higher suspending agent concentration. For pore diameters up to about 30 nm, no effect of the surfactant concentration on the porosity was observed. Only for pores with diameters larger than 30 nm was the effect of the surfactant concentration significant. This may be related to the way in which the primary particles are arranged to form a compact polymer grain. The difference in compactness could probably be explained by the difference in interfacial tension. Interfacial tension acts as a compaction force when primary particles agglomerate to form grains. An increase in the suspending agent concentration causes the interfacial tension to decrease, weakening the compaction force. The weaker the compaction force is, the looser the compaction of the primary particles is, so larger pores are formed.

The grain porosity also changes during polymerization as the conversion increases and particles

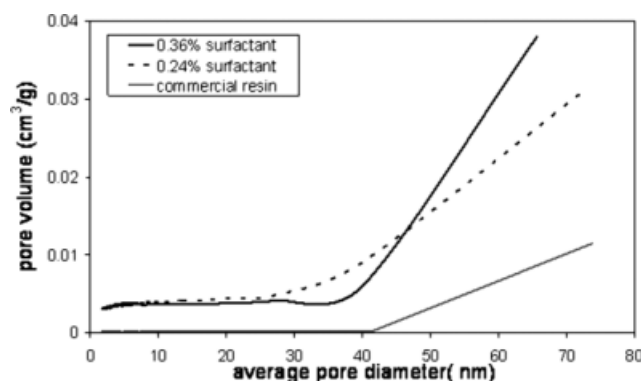


Figure 10 Porosity of nonaqueous PVC samples produced with various concentrations of SA 4.7.

TABLE II

Porosity and Bulk Density Values of the PVC Samples

	Bulk density (g/cm ³)	Porosity (cm ³ /g)
Commercial PVC	0.612	0.258
Nonaqueous PVC	0.514	0.498

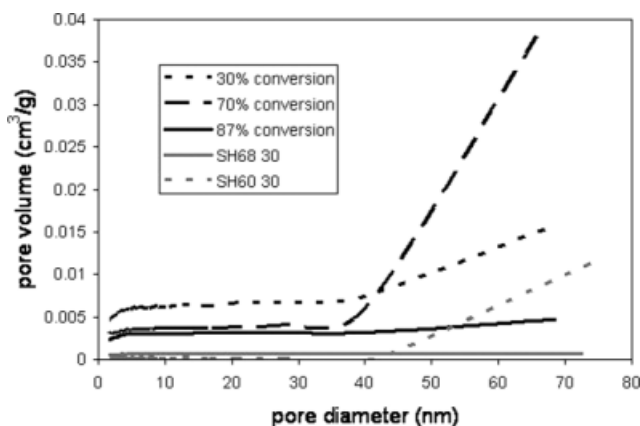


Figure 11 Effect of the conversion on the porosity.

form, grow, and agglomerate. At a low conversion of 30%, the porosity was higher than that of the commercial resin throughout the range of pore volumes (Fig. 11). As the conversion increased to 70%, the porosity decreased for pore diameters smaller than 40 nm but increased for pore diameters larger than 40 nm. A further increase in conversion to 87% resulted in a decrease in the particle pore volume for pore diameters larger than 40 nm, whereas the pore volume corresponding to pore diameters smaller than 40 nm remained constant. The evolution of the porosity of the PVC grains with conversion, in combination with the effects of various factors on the grains' porosity, can give us very useful information about the mechanism of particle formation. The initiator concentration was also found to exert a strong influence on the grain porosity, as shown in Figure 12. For a higher initiator concentration, the pore volume for pore diameters larger than 40 nm increased, whereas the pore volume for pore diameters smaller than 40 nm remained constant. The initiator concentration affects the reaction rate, which, in turn, may influence the aggregation rate of primary particles and as a result the rate of formation of primary agglomerates and the way in which they are arranged within the polymer grain. Further work is being carried out to elucidate the mechanism of particle formation.

The specific surface area of the nonaqueous resins was found to be significantly higher than that of the commercial PVC (Table III), but the average pore diameter was similar to that of the suspension resins.

The swelling capacity of a VCM/hexane mixture in PVC is very low, and the glass-transition temperature of PVC is greater than the polymerization temperature, so PVC particles do not adhere enough to fuse during the polymerization process. As a result, PVC grains with looser aggregates of primary particles and high porosity are formed. In Figure 13, in which the internal morphologies of nonaqueous and typical suspension PVC grains are shown, it can be

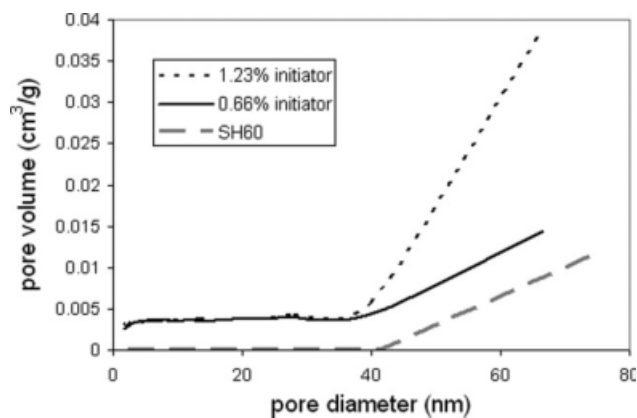


Figure 12 Effect of the initiator concentration on the porosity.

observed that the primary particles at the surface of the nonaqueous grain were smaller than those in the inner part of the grain. A similar observation was made with PVC that was formed from a VCM/*n*-butane mixture.⁷ Primary particles in the outer layer of PVC grains are always formed later and have a shorter residence time in the reactor, so they are smaller than the primary particles in the center part of the grain. Also, PVC grains with higher conversions have larger primary particles in their centers.

Thermal analysis

Radical polymerization of VCM results in the formation of various defect structures^{29–34} in the chain during polymerization, and this is unfavorable for thermal stability. The bond dissociation energies of the chlorine atom bonded to the tertiary carbon and of the chlorine at the allylic position are low.³⁵ If we take these bonds' dissociation energy into consideration, it is reasonable to suggest that the decomposition of PVC is easily initiated at these bonds. The dissociation of Cl from the polymer chain leads to PVC degradation with the emission of HCl. Thermogravimetric analysis of commercial PVC and nonaqueous resins has shown that their behaviors are similar. The left-hand peak in Figure 14 corresponds to the emission of HCl, and the right-hand peak corresponds to C–C scission. The release of HCl starts to occur in all cases at 200°C, but the peak for the

TABLE III
BET Surface Area of the PVC Grains Produced with Different Suspending Agents

	SH6830	SH6030	SA 3.8	SA 4.7	SA 8.1
BET surface area (m ² /g)	0.940	0.582	7.983	4.573	6.938
Pore size (nm)	9.070	45.746	9.197	14.294	13.618

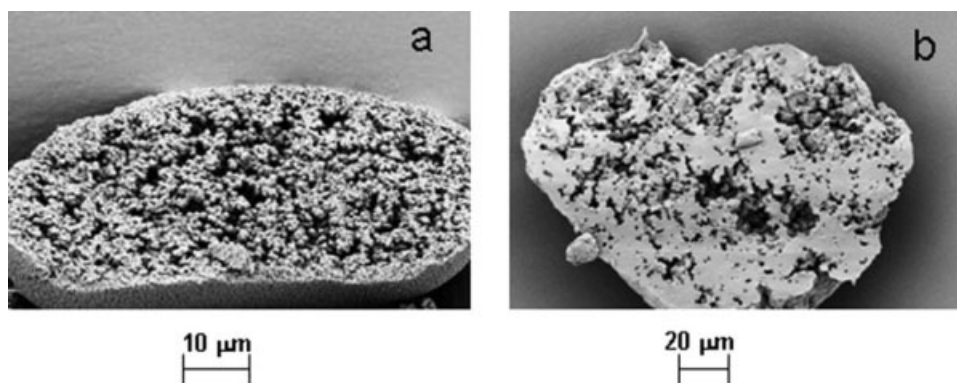


Figure 13 Sections of PVC grains: (a) nonaqueous and (b) suspension.

nonaqueous resins is slightly shifted to higher temperatures. The second peak is located at temperatures slightly lower than those of the commercial resins. The slight differences between the samples indicate that there may be some slight differences in the structure of the polymer chain or the type or frequency of defect structures. The thermal behaviors of both the commercial and nonaqueous resins are similar. The thermal stability of PVC can be tested with a Haake rheometer. Figure 15 shows that the degradation time for the nonaqueous resin at 180°C is slightly longer than the time for the commercial resin (SH6030). The torque is lower for the nonaqueous resin. This can be attributed to the higher porosity and lower bulk density of the nonaqueous PVC. Because of the lower bulk density, the mass of the resin that can be used to fill the volume of the rheometer is less for the nonaqueous PVC. When the resin melts, both the mass and volume of the nonaqueous melt are lower than those of the commercial resin. As a result, the torque that develops in the rheometer is lower than that of the commercial PVC. Differential scanning calorimetry analysis showed that the glass-transition temperatures of various nonaqueous and commercial PVC samples were similar,

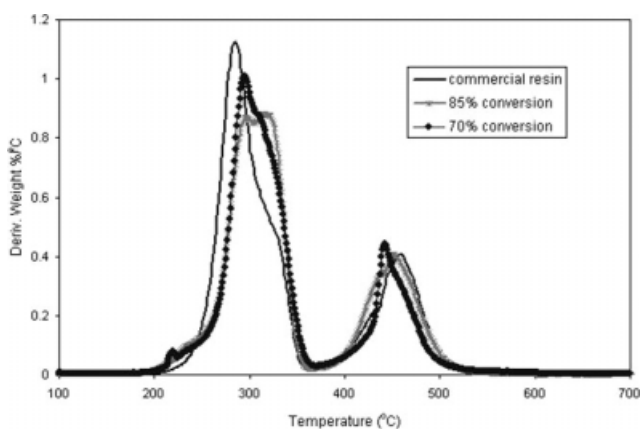


Figure 14 Thermogravimetric analysis of the commercial (SH 6030) and nonaqueous PVC resins.

around 80°C for the former and around 82°C for the latter.

Molecular weight

Gel permeation chromatography analysis of nonaqueous PVC samples and two typical suspension resins showed that nonaqueous resins with molecular weight averages similar to those of suspension grades, for example, SH6030 can be produced (Table IV). Only the number-average molecular weight is substantially smaller than that of aqueous PVC, and this could be explained by the fact that the solubility of PVC in hexane is lower than its solubility in VC. As a result, PVC chains precipitate at an earlier stage in nonaqueous polymerization, and hence a polymer with a lower number-average molecular weight is produced.

In radical polymerization, a decrease in the initiator concentration is expected to produce a polymer of a higher molecular weight unless chain transfer to the monomer is significant. With vinyl chloride polymerization, chain transfer to the monomer and chain

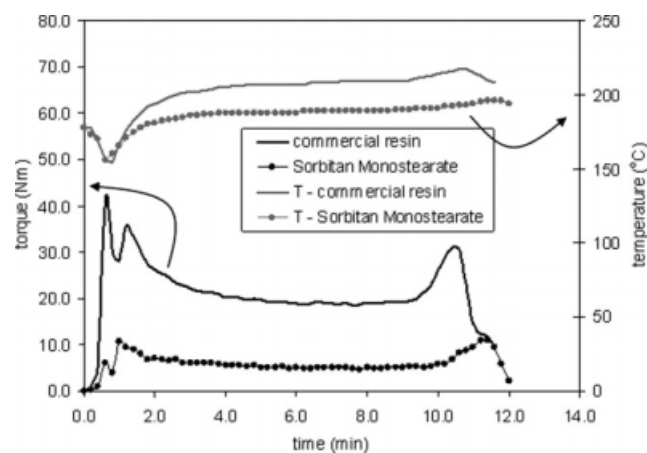


Figure 15 Thermal degradation of PVC in a Haake rheometer at 180°C.

TABLE IV
Molecular Weight Averages of the Commercial PVC Grades and Nonaqueous Samples Produced with SA 4.7

	SH6830	SH6030	1.2% initiator, 70% conversion	1.2% initiator, 80% conversion	0.66% initiator, 70% conversion
M_n	38,417	37,900	29,300	29,400	23,200
M_w	87,700	66,400	58,000	50,000	44,600
M_v	80,900	62,700	53,000	47,400	44,600

M_n = number-average molecular weight; M_w = weight-average molecular weight; M_v = viscosity-average molecular weight.

transfer to the polymer are both significant (so chain branching is expected). The incidence of chain transfer to the polymer in the continuous phase will depend on the concentration of completed polymer molecules (which will be low) and on the concentration of growing radicals. The radical concentration will be reduced if the initiator concentration is reduced. That may explain why a decrease in the initiator concentration produced a decrease in the molecular weight of the polymer, as shown in Table IV. The polymer molecular weight could be modified by the variation of some of the polymerization conditions, and this is something that has to be further explored.

CONCLUSIONS

The nonaqueous polymerization of vinyl chloride with hexane as a diluent leads to the production of PVC resins with a morphology different from that of suspension resins. The morphology can be manipulated to a great extent by the choice of the suspending agent. The shape of the particles varies from regular to irregular and the surface varies from smooth to rough, depending on the suspending agent used. The influence of the HLB values for the suspending agents can be small. The PSD is narrow and similar to the distribution of typical suspension resins, with smaller average particle sizes. The porosity of the nonaqueous grains is significantly higher than that of the suspension grains. That will have important benefits in terms of monomer removal and additive uptake without a significant change in the bulk density, which is only slightly lower than that of one of the suspension grades. The thermal stability seems to be similar to that of the suspension grades. Also, a polymer with a molecular weight similar to that of the suspension grades can be produced.

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