

BATCH EMULSION POLYMERIZATION OF VINYL CHLORIDE: EFFECT OF OPERATING VARIABLES ON REACTOR PERFORMANCE

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Abstract

We analyze experimentally the effect of several operating conditions on conversion and molecular weight distributions of PVC obtained in batch emulsion polymerization. The operating variables studied were reaction temperature, water/monomer weight ratio, and the concentrations of initiator, emulsifier, pH regulating agent and inhibitor. We found that conversion increases with temperature and initiator concentration. It also increases with emulsifier concentration, but there is an asymptotic limit to that increase. There is an optimal water/monomer weight ratio at which the reaction rate is highest, and an optimal pH regulating agent concentration that optimizes latex quality. Average molecular weights tend to decrease slightly with conversion.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most broadly produced thermoplastic materials in use today, which may be employed to obtain, among other things, latex coatings, adhesives, pipes, and paints (Nass, 1976; Capek, 1995). It can be produced by three different processes: emulsion, suspension and bulk polymerization. Our interest is particularly focused on the emulsion process. The main technical advantages of emulsion polymerization are that the viscosity of the reactive mixture remains relatively low along the whole process, it presents excellent heat transfer and it is possible to obtain high reaction rates and high molecular weight products.

The reaction occurs in an aqueous medium where the monomer and water form an emulsion by means of stirring and the addition of an adequate emulsifier. The initiation step occurs at the aqueous phase by the initiator decomposition into free radicals. Dissolved monomer reacts with the radicals forming polymer particles which grow until they reach a critical size and precipitate (homogeneous nucleation) (Ugelstad and Hansen, 1976). Another path for particle generation is the introduction of these radicals into the emulsifier micelles (micellar nucleation) (Ugelstad and Hansen, 1976). The polymer is obtained as a latex made of spherical hollow particles surrounded by emulsifier. Depending on the monomer solubility, the kind and concentration of emulsifier, the particle generation stage can be homogeneous, micellar or both.

Emulsion polymerization is more complex than radical solution polymerization owing to the heterogeneous composition of the reaction system.

Different transfer processes between water and the organic phases and development of new phases are very important in the kinetics of the reaction. Thus, when investigating emulsion polymerizations, it is essential to contemplate every physical process and chemical reaction, which take place along the polymerization (Tauer *et al.*, 1991).

The polymer quality can be controlled by adopting a suitable operating strategy for the reactor, principally by choosing adequate initial conditions. In this work, we analyze the influence of temperature, water/monomer weight ratio, initiator and emulsifier concentration, the addition of a pH regulating agent and the presence of an inhibitor on the conversion, particle size distribution (PSD) and final properties of the polymer (molecular weight distribution (MWD)) in batch emulsion polymerization of vinyl chloride. For this purpose, several polymerizations were performed in order to obtain the conversion plots and product samples for all the cases analyzed. Prior to this analysis, we performed polymerizations at the operating conditions presented in a published work (Ugelstad *et al.*, 1969) in order to check our reaction system.

2. Experimental

A 600 ml stainless steel PARR reactor was used for batch emulsion polymerization of vinyl chloride (VCM). Figure 1 shows a scheme of the reaction system employed. The reacting mixture is stirred by a multipaddle agitator, which is connected to a constant velocity motor (200 rpm). The stirring system is cooled with water to avoid overheating. The emulsion

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temperature is measured by a thermocouple placed inside the reactor. A 2 mm-diameter stainless steel tube connects the reactor head ports with the bottom of the vessel and is sealed with a globe valve. This tube is used for sample collection. The temperature of reaction is controlled by an external water bath (Figure 1).

The reactions were carried out using a mass of water to mass of monomer ratio, R , ranging from 1.00 to 2.00. Sodium dodecyl sulfate (SDS) (Sigma Chem. Co., 99%) was used as emulsifier at concentrations between 1.0 and 6.1 g/L based in the amount of water used. In what follows concentrations are reported in the same basis. The initiator was potassium persulfate (KPS) (99%) and was employed between 0.8 and 3.2 g/L. In some reactions, sodium bicarbonate (99.7%) was added as pH regulator at a concentration 0.06 N. The water was distilled twice before use. Then the emulsifier and, eventually, the sodium bicarbonate were added. The initiator was added as an aqueous solution into the injection cylinder, where it remained until the reaction mixture achieved the desired polymerization temperature. The mixture of water, emulsifier and sodium bicarbonate is called "emulsion water". The mass of emulsion water used ranged from 300 to 390 g, depending on the reaction conditions.

After the emulsion water was introduced into the vessel, the reactor was closed and vacuum was applied in order to eliminate the dissolved oxygen, which affects the kinetics of the reaction (Garton and George, 1973; 1974). Then, the reactor was purged with chromatographic N_2 to ensure an inert atmosphere (see Figure 1).

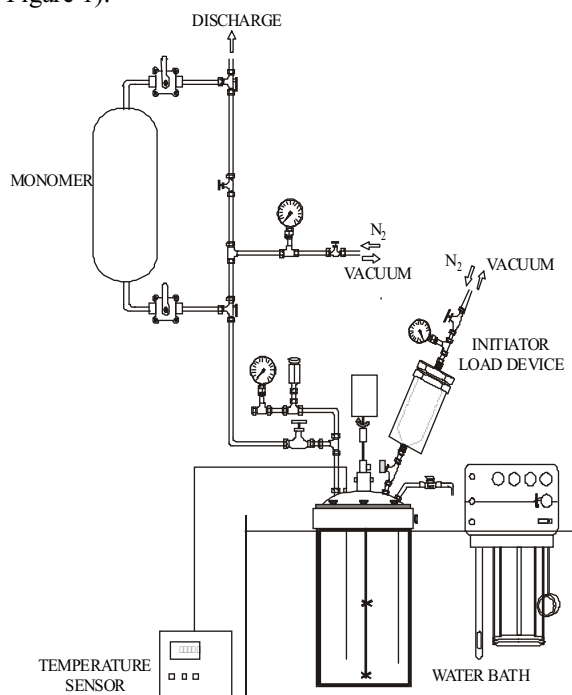


Figure 1. Scheme of the reaction system.

Vinyl chloride (SOLVAY Group, 99.5%) is added into the reactor by forcing it with N_2 from a 2 l

container. Immediately after this addition, the reactor is placed into a thermostatic water bath. Once the reaction mixture reaches the desired temperature of reaction (50, 55 or 60°C), the initiator solution is introduced into the reactor by means of a globe valve, using N_2 pressure. This moment is considered as zero reaction time.

For all the polymerizations, samples of about 2% of the total reaction mass were periodically extracted. To ensure the sample extractions did not affect the reaction medium conditions, several reactions with the same conditions were performed and only one or two samples at different times were extracted from each one of them.

The samples were weighted and dried at 40°C into a vacuum stove until the water in them was eliminated. Then they were weighted to calculate the conversion of the reaction, as follows:

1) We obtained P , the weight fraction of PVC in the wet sample (*i.e.* the reaction product without the unreacted monomer, which was previously eliminated):

$$P = \frac{\left(\frac{m_{DS}}{m_{WS}}\right) - C_S}{1 - C_S} \quad (1)$$

where m_{WS} is the mass of the wet sample (without unreacted monomer), m_{DS} is the mass of the dried sample and C_S is the weight fraction of solids (surfactant and bicarbonate) in the emulsion water.

2) The monomer conversion to PVC, X , was calculated as (Boieshan, 1990):

$$X = \frac{P R}{1 - P} \quad (2)$$

The conversion plots were constructed from points obtained in up to 4 different reactions performed at identical operating conditions, as explained above, using eq. (2).

Molecular weight distribution (MWD) and number (M_n) and weight (M_w) average molecular weights were determined by Size Exclusion Chromatography (SEC). Waters 150C chromatograph with a set of three PL-gel columns (500, 10^4 and 10^6 Å), coupled with a DAWN DSP Multiangle Laser Light Scattering (MALLS) device (Wyatt Technol. Co.) with 18 detectors, was used. The polymer samples were diluted in tetrahydrofuran (THF) and heated at 40°C during 1 hour before they were injected into the columns. The samples were then analyzed at room temperature.

SEC calibration was performed with polystyrene (PS) standard samples with molecular weights ranging from 9,000 to 900,000. Benoit universal calibration (Grubisic *et al.*, 1967) was used and the Mark-Houwink constants for PVC and PS in THF at room temperature were obtained from the literature (Brandrup and Immergut, 1975). The values used here for PS are K_{PS}

$= 1.6 \times 10^{-4}$ and $\alpha_{PS} = 0.706$ and for PVC, $K_{PVC} = 1.5 \times 10^{-4}$ and $\alpha_{PVC} = 0.77$.

For the MALLS measurements, the laser light wavelength was 6328 Å and THF was also used as solvent at room temperature. The variation of the refractive index with concentration (dn/dc) in THF was 0.1845 ml/g for PS and 0.101 ml/g for PVC. The concentration of the different solutions ranged from 0.12 to 0.5 g/100 ml.

The final latex PSD was measured by means of transmission electronic microscopy (TEM). For this purpose, the original latex was previously modified in order to be examined. The sample preparation method consists of diluting the latex with bidistilled water, to eliminate the emulsifier. Then, the solution is introduced in an ultrasonic bath to achieve the dispersion of the particles. Some latex droplets are supported on a 200 mesh metal grid. It is dried for an hour and finally, carbon shadowing at an angle of 45° is employed to add contrast to the surface material prior to examination (Sawyer, 1996). We employed a TEM, JEOL 100 CX, with a nominal resolution of 3Å. The acceleration voltage was 80 KV and the magnification ranged from 20,000 to 27,000 X, depending on the latex sample.

3. Results and Discussion

3.1 Comparison with a literature case

In order to check our reaction system, we performed a series of reactions under previously reported conditions. The check case was reported by Ugelstad *et al.* (1969) and the operation conditions were:

Temperature: 50°C,
[SDS] = 3.93 g/L,
[KPS] = 1.6 g/L,
Water/monomer weight ratio, $R = 1.40$.

Figure 2 shows the resulting conversion plots and the comparison with the studied literature example. It can be seen that our reaction system reproduces satisfactorily the experimental data for an isothermal batch reactor previously reported.

3.2 Influence of temperature

The effect of temperature on polymerization rate has been rarely investigated (Capek, 1995). Figure 2 compares our conversion results from the polymerizations at 50°C, 55°C and 60°C. In these reactions the following operating conditions were maintained:

[SDS] = 3.93 g/L,
[KPS] = 1.6 g/L,
 $R = 1.40$.

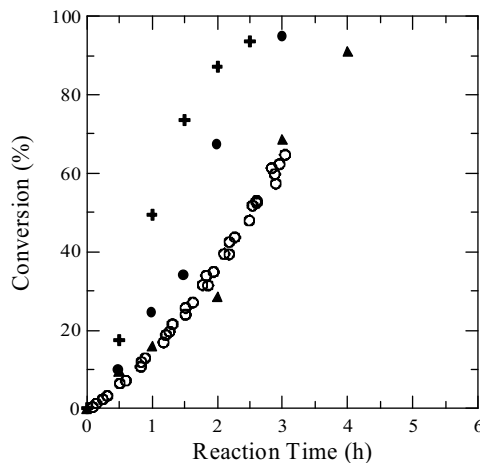


Figure 2. Conversion (%) as a function of the time of reaction for polymerizations at different temperatures. Ref.: (○) T=50°C, Ugelstad *et al.* (1969), (▲) T=50°C, this work, (●) T=55°C, (+) T=60°C.

As temperature increases the initiator decomposes faster. Moreover, monomer solubility increases. Regardless of the particle nucleation mechanism, the faster production of initiation radicals and the higher monomer concentration lead to higher conversions at any given time. In accordance with these considerations, Figure 2 shows that the reaction at 60°C is faster than the ones corresponding to 50°C and 55°C, although the shapes of the curves are similar. At 60°C the conversion is higher than 95% after 2 hours of reaction.

3.3 Influence of water/monomer weight ratio, R

Other authors report that increasing R leads to higher reaction rates (Boieshan, 1990) for this process. He worked in an R range from 1.13 and 2.50, with potassium persulfate as initiator and sodium alkylsulfonate as emulsifier. He found that reaction rate depends almost linearly with R for conversions up to 40%; afterwards an autoaccelerated effect was observed. The latter effect disappeared for R higher than 2.25.

Figure 3 presents our conversion plots for polymerizations with different water/monomer weight ratio, ranging from 1.00 to 2.00. The operating conditions of the reactions were:

Temperature: 55°C,
[SDS] = 3.93 g/L,
[KPS] = 1.6 g/L.

In our case, polymerization rate increases when using $R = 1, 1.4$ and 1.7 . From this point on we found that increasing the water/monomer weight ratio leads to a slower reaction and a departure from the typical S-shaped conversion curves reported by Boieshan (1990). This may be attributed to monomer depletion in the polymerization sites due to an earlier disappearance of the monomer droplets at higher R .

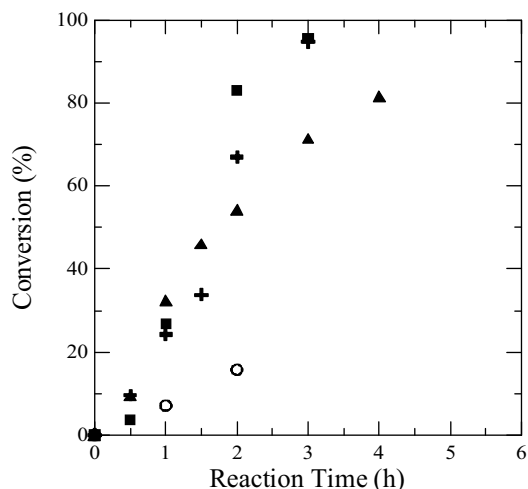


Figure 3. Conversion plots for polymerizations with different water/monomer weight ratio, R . Ref.: (○) $R=1.00$, (+) $R=1.40$, (■) $R=1.70$, (▲) $R=2.00$.

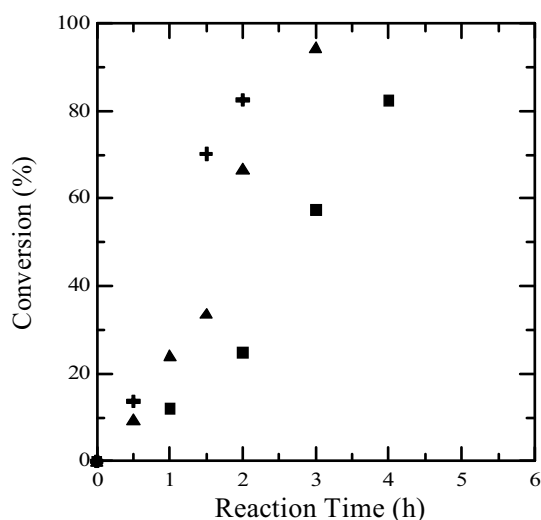


Figure 4. Conversion plots for polymerizations with different initiator concentration, [KPS]. Ref.: (■) [KPS]=0.8 g/L, (▲) [KPS]=1.6 g/L, (+) [KPS]=3.2 g/L.

3.4 Influence of initiator concentration

In order to analyze how the initiator concentration affects the rate of reaction, several polymerizations were carried out with different KPS concentrations. The conditions of those reactions were:

Temperature: 55°C,
[SDS] = 3.93 g/L,
 $R = 1.40$.

Figure 4 shows the resulting conversion *versus* time plots. The rate of reaction increases with increasing initiator concentration. An initiator concentration four times higher than the original value allows conversion to reach 82% in half the reaction time (four hours against two hours).

Ugelstad *et al.* (1969), who worked with SDS at the same concentration and used KPS as initiator in a range from 0.4 to 3.2 g/L, also found that polymerization rate increases with KPS concentration. We were able to reproduce results by Ugelstad when using a KPS concentration of 0.8 g/L water. We also used other KPS concentrations in the same range in order to complete Ugelstad's information. If they are analyzed together, both sets of data confirm the prediction of increasing polymerization with increasing initiator concentration.

From a more theoretical point of view, our results indicate that the polymerization rate is proportional to the 0.6th power of the initiator concentration. The micellar theory predicts a dependence to the 0.4th power of the initiator concentration (Smith and Ewart, 1948; Harkins, 1945), for the case of slightly soluble monomers. A literature review on the special case of vinyl chloride polymerization reveals that the mentioned exponent ranges from 0.5 to 0.8 (Gerrens *et al.*, 1967; Boeishan, 1990; Peggion *et al.*, 1964). Taking into account those values, one may expect that homogenous nucleation occurs in the case of vinyl chloride, a monomer with moderate water solubility. Deviation from the micellar theory can also be explained by monoradical and biradical termination reactions occurring simultaneously at different proportions.

3.5 Influence of emulsifier concentration

In the case of emulsifier concentration effect, Figure 5 shows our conversion plots for reactions with different SDS concentrations. The other conditions were:

Temperature: 55°C,
[KPS] = 1.2 g/L,
[Bicarbonate] = 0.06 N,
 $R = 2.00$.

Ugelstad *et al.* (1969) worked at a concentration of KPS of 1.63 g/L covering SDS concentrations from 0.123 to 7.87 g/L. We completed Ugelstad's results performing polymerizations with different SDS concentrations covering the same range, as shown in Figure 5. It is important to keep in mind that in all cases we worked with SDS concentrations higher than its critical micelle concentration (CMC).

When the concentration of emulsifier is increased from 1 to 3 g/L, the polymerization is evidently faster. Nevertheless, a further increase from 3 to 6 g/L results in no significant differences between conversion curves.

At low conversions, our results agree with the tendency reported by those authors. At high conversions, and high enough SDS concentration no difference between conversion curves were noted, in agreement with results reported by Peggion *et al.* (1964).

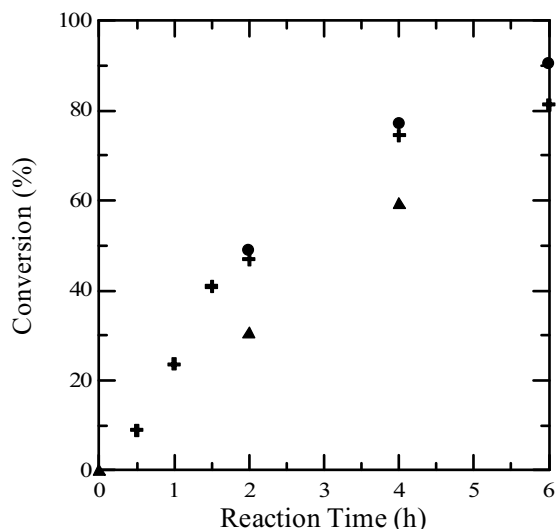


Figure 5. Conversion plots for polymerizations with different emulsifier concentrations, [SDS]. Ref.: (▲) [SDS]=1.05 g/L, (+) [SDS]=3.03 g/L, (●) [SDS]=6.14 g/L.

The initial polymerization rate depends directly on the number of micelles available to become polymerization sites. It is known that this quantity depends on the type of emulsifier, which determines the CMC and the amount of emulsifier in excess available to form micelles. This depends on the total emulsifier concentration. Nevertheless, the existence of a concentration beyond which the addition of extra emulsifier has no effect on micelle formation, indicates that there are micelles in excess of the maximum amount of particles that can be formed by the initiation radicals.

3.6 Influence of pH regulating agent

As mentioned above, the addition of a pH regulating agent (sodium bicarbonate, in this work) is necessary to stabilize the micelle formation and avoid precipitation. Nevertheless, pH regulator concentration affects the rate of reaction. We operated with different bicarbonate concentrations in order to find the optimal one at which particles did not agglomerate significantly and the resulting latex maintained a pH value of about 7. This value falls in the recommended working range of pH reported by Capek (1995). In this work we have found that the optimal concentration of pH regulating agent is 0.06 N.

3.7 Influence of inhibitor concentration

If inhibitors are present in the reaction mixture, they may form inactive species with the radicals. Once the inhibitor is consumed the newly formed radicals proceed with the polymerization reaction at normal rates (Oadian, 1993).

When vinyl chloride is stored for a long time, an inhibitor is usually added into the container to avoid the autopolymerization of the monomer. Therefore we analyze how a commonly used inhibitor, hydroquinone, affects the rate of reaction.

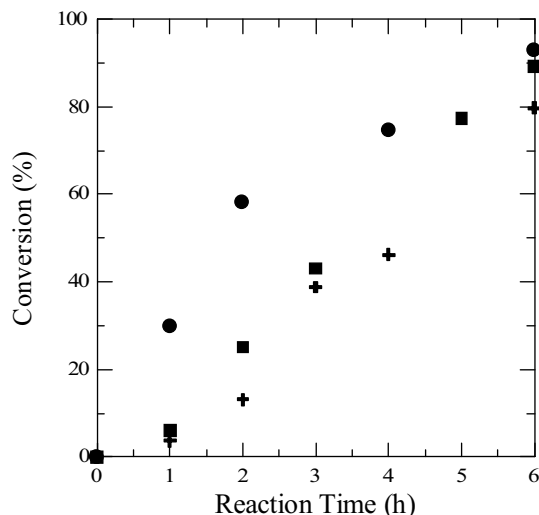


Figure 6. Conversion plots for polymerizations with different inhibitor (hydroquinone) concentration, [HQ]. Ref.: (+) [HQ]=30 ppm, (■) [HQ]=15 ppm, (●) without hydroquinone.

Reactions with 15 and 30 ppm of hydroquinone are compared with a reaction without inhibitor in Figure 6. The reaction conditions are:

Temperature: 50°C,
 [SDS] = 6.14 g/L,
 [KPS] = 1.2 g/L,
 [Bicarbonate] = 0.06 N,
 $R = 2.00$.

It can be seen in Figure 6 that increasing the concentration of hydroquinone reduces polymerization rate until a critical value is reached, beyond which a further increase has no effect. Evidently that critical value corresponds to the concentration of hydroquinone necessary to inhibit all radicals formed by the persulfate initiator. Our results confirm the inhibiting effect of hydroquinone and stress the importance of purifying the monomer prior to the start of the polymerization.

3.8 Determination of molecular weight

Few results are available in the literature on molecular weight for vinyl chloride emulsion polymerization.

Figure 7 shows the number (M_n) and weight (M_w) average molecular weights and polydispersity (M_w/M_n) of several samples extracted from different reactions performed at 55°C. It can be seen that both M_w and M_n decrease with conversion, while polydispersity increases, until a value of 2 is reached at conversions higher than 85%. At these conversions, M_w was found to be 80,000 and M_n 40,000.

Our polydispersity values indicate that the monoradical termination is dominant. This is in agreement with transfer to monomer reaction being the more important termination step (Jorgensen, 1971; Nass, 1976).

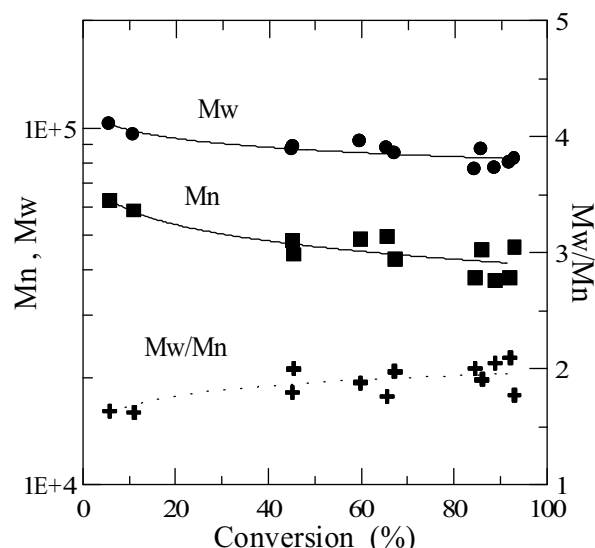


Figure 7. Number (M_n) and weight (M_w) average molecular weights and polydispersity (M_w/M_n) of different PVC samples obtained at 55°C. Ref.: (●) M_w , (■) M_n , (+) M_w/M_n .

3.9 Latex Particle Size Distribution (PSD).

Some of the latexes were observed employing TEM as described in the experimental section. Figure 8 shows a typical latex TEM micrograph which corresponds to polymerization conditions reported in section 3.1. In all cases, we find similar particle size distributions with an average particle size of around 0.04 μm . This value is in accordance with the ones reported for commercial PVC obtained by emulsion processes (Nass, 1976).

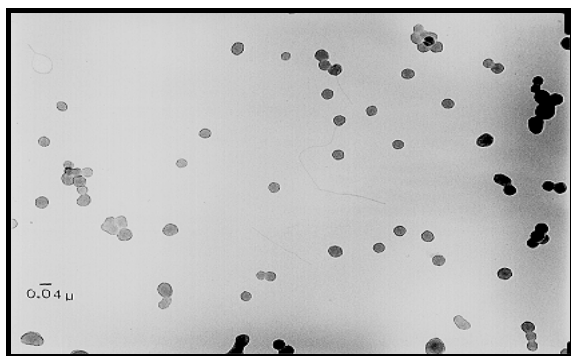


Figure 8. TEM Micrograph. Magnification 27000X.

4. Conclusions

We performed a series of reactions in order to analyze how different operation conditions affect the conversion plots in batch emulsion polymerization of vinyl chloride. The main conclusions are:

- 1) Increasing temperature or initiator concentration considerably accelerates the rate of polymerization, due to a larger number of initiator radicals produced per unit time.
- 2) The influence of the water/monomer weight ratio

(R) on the polymerization rate is different depending on the R range. Our experimental results indicate the existence of an optimal value of R , somewhere in the range of 1.4-1.7. A depletion of monomer must be occurring at high values of R .

3) Increasing emulsifier concentration enhances the rate of reaction until a given value, above which it does not affect the conversion curve. In this case an insufficient amount of radicals is produced for the increasing number of micelles.

4) When the acidity of the reaction medium is high enough to provoke instability on micelles, it is necessary to add a pH regulating agent, to keep the solution neutral or basic. We found an optimal concentration of sodium bicarbonate (0.06 N) to assure micelle stability and minimize agglomerate formation.

5) It is important to work with highly purified monomer in order to avoid a severe diminution on the rate of reaction due to the presence of traces of hydroquinone.

6) Average molecular weights slightly decrease and polydispersity increases with conversion. But it is important to note that, in the polymerizations analyzed in this work, operating conditions do not affect these molecular properties. This is a consequence of transfer to monomer reaction being the main termination step. In this case the only operating condition expected to control molecular weight is the reaction temperature.

7) We were able to obtain an average latex particle size of around 0.04 μm , which is in the order of the ones of commercial PVC.

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