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ORIGINAL PAPER

Competitive particle growth at different conditions of oligo-micelle formation in hydro-alcoholic solution of anionic double-chain emulsifier via batch emulsion polymerization of vinyl chloride

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ABSTRACT

The condition of oligo-micelle formation of sodium di-isodecyl sulfosuccinate (SDIDS) emulsifier in hydro-alcoholic solutions is used to study particle formation of vinyl chloride emulsion polymerization in a batch reactor. The change on micellization behavior was investigated by critical micelle concentration (CMC) and zeta potential parameters. To detect the occurrence of secondary nucleation or particle aggregation, or both the particle size and number of particles were investigated as a criterion for the particle nucleation and growth process. The results showed that the alcohol (co-solvent) content had a strong effect on the oligo-micelles formation and emulsion polymerization performance. Namely, decreasing the alcohol content and increasing the anion content in the SDIDS samples increased the overall reaction rate and latex stability. This also decreased the chain growth rate, the particle size, and the coarse particle formation. Also, the results showed that different condition of oligo-micelle formation would lead to different particle growth history. **Polyolefins J (2020) 7: 33-44**

Keywords: Emulsion polymerization; poly (vinyl chloride); double-chain emulsifier; oligo-micelle; particle growth.

INTRODUCTION

The choice of a proper emulsifier to prepare stable polyvinyl chloride (PVC) latex by emulsion polymerization (E-PVC) is a complex problem because emulsifier greatly affects the reaction kinetics and the physico-chemical and colloidal properties of the final latex [1]. Several works have been reported in the literature on emulsifier type used in E-PVC polymerization [2 -8]. Type of emulsifier used is one of the important operating variables controlling E-PVC polymerization [1].

Both mono- and di-alkyl sulfosuccinates are one of the main anionic emulsifiers used in E-PVC [9-12]. They have excellent wetting, emulsifying, dispersing, and foaming properties [11-12]. Typically, di-alkyl sulfosuccinate emulsifier groups are used as viscosity depressant in emulsion PVC [10]. Also, from literature it is understood that emulsifiers from sulfosuccinate group give medium size particles [9]. Sodium di-isodecyl sulfosuccinate (SDIDS) is an anionic double-chain sulfonate emulsifier with long side-chain length

(around 10 carbons) in hydro-alcoholic solutions that is widely used in the E-PVC [10-12].

The double-chain emulsifier with long side-chains by a critical side-chain length (around six carbons) like SDIDS has the potential to form highly ionized small aggregates, regarded as oligo-micelles [13]. For this double-chain micelle, it has been reported that conductivity increases when micelles start to form which is in contrast to the single chain emulsifiers [14, 15] and double-chain emulsifiers with short-chain length [13].

On the other hand, the presence of short-chain alcohols as co-solvent in the emulsion system has shown an impact on the solubility, liquid structure and hydrophobic interactions between emulsifier and water molecules that are involved in the micellization process [16-22]. The effects involved in the changes of micellization parameters such as critical micelle concentration (CMC), the micelle size and etc. are depended on the partition of alcohols between micelles and intermicellar solution [16, 17, 19, 20]. For example, while methanol has shown an increase in the CMC, propanol has shown a minimum dependency on overall alcohol content [16, 17].

Isopropyl alcohol is a commonly used solvent in the synthesis of SDIDS [11, 12]. Suppliers usually change the concentration of this alcohol occasionally in their products for different reasons. In the case of SDIDS emulsifiers, different compositions of alcohol and aqueous phases have been observed, and lattices with different quality are introduced.

The relevant literature [13, 16, 17, 19, 20] reveals that the presence of isopropyl alcohol as a short-chain alcohol could have a key role on micellization process of SDIDS as a double-chain emulsifier with a long-side chain.

In spite of various articles published on E-PVC, i.e. the significant amount of research works which have been devoted for well-characterized single chain emulsifiers such as SDS and SDBS [2, 3,5,7, 23-28] and also limited reports on double chain emulsifiers [3, 9], to the best of our knowledge, no report is available in the open literature attributed to the presence effect of short-chain alcohols on micellization process of anionic double-chain sulfonate emulsifiers in hydro-alcoholic solutions in terms of vinyl chloride monomer (VCM) emulsion polymerization.

The principle objective of the work presented in this paper is to illustrate the source of quality variation of an industrial E-PVC process which is associated to SDIDS emulsifiers in hydro-alcoholic solution with more than one supplier and dissimilar compositions, while industrial materials and recipe on a pilot-scale reactor were employed. This work addresses the issue of alcohol content in a hydro-alcoholic solution of SDIDS samples which influence the latex properties of E-PVC. The changes observed in the CMC and zeta potential parameters have been used to interpret the interactions between alcohol and SDIDS.

EXPERIMENTAL

Materials
VCM was supplied by Arvand Petrochemical Company, with a purity of above 99.98% measured by gas chromatography. Three SDIDS samples ($C_{24}H_{45}NaO_7S$) in hydro-alcoholic solution with dissimilar compositions (Table 1) and sodium pentadecan-sulfonate (SPS) (Lanxess) were employed as emulsifier in the current study. Also, potassium persulfate (KPS) (Proxy Chem) and disodium phosphate (DSP) (Zohal Shimi) were used as the initiator and buffer, respectively. All the chemicals were used as supplied without further purification. Demineralized (DM) water (with conductivity below 2 μS/cm) was used throughout the work for the batch polymerizations. Cyclohexanone (Merck) was utilized as the solvent for K-value measurements.

Polymerization procedure
Polymerizations reactions were performed in a 15 L jacketed stainless steel reactor, equipped with a flat turbine (four-blade) impeller, two baffles, and a magnetic seal derives (MSD) to prevent gas leakage. The reaction temperature was constant and kept down at 50.0 (±0.3)°C. The stirring speed was constant and set at 150 rpm. In all reactions, the weight ratio of KPS and DSP to the VCM was 0.003 and 0.0012, respectively. Also, SPS and SDIDS concentrations were 1.81 and 14.74 g L^{-1}, respectively, based on the total volume of the water phase.

Zero-time of the reaction was considered when the reactor temperature was 49.0°C. For all reaction runs, the ratio of water/monomer was 1.25 (by weight). With a sample connection which was provided at the bottom of the reactor, latex samples were taken for monitoring the polymerization reaction at various times. The pH of the latex was monitored during the reaction by litmus paper. To have the same conversion

Table 1. Composition of the three SDIDS samples: (a) SDIDS1, (b) SDIDS2, (c) SDIDS3.

Sample	SDIDS1	SDIDS2	SDIDS3	Remark
Anion content (%wt)	65.8	68.5	72.4	Emulsifier
Water (%wt)	19.5	24.1	20.2	Aqueous phase
Isopropyl alcohol (%wt)	12.5	4.5	3.9	Alcohol phase
Isodecyl alcohol (%wt)	2.2	2.9	3.5	Co-emulsifier
				(SDIDS basis alcohol)

yield, the pressure drop to 5 barg was kept constant in all runs as the criterion for the ending of the reaction, unless the reaction temperature control was not possible. At the end of the reaction, coarse matter content (particles bigger than 300 μm in size) as a qualitative character of the final latex was used as the main parameter which indicates the reaction stability and is described by % wt coarse matter in the final latex.

Latex Characterization

Solid content (SC) of the latexes was measured gravimetrically during the reaction for conversion calculation [29, 30]. K-values were determined according to ISO 1628 with cyclohexanone as solvent

[26, 31]. Particle size and its distribution (PSD) were measured by scanning electron microscopy (SEM) (TEScan, VEGA 3) technique and proceeded with image analysis software (Image 1.51j8). At least 430 particles were measured on the micrographs for statistical validation of the results [32]. Also, the PSD curves were plotted based on frequency versus particle size. The necessary parameters were derived from refereed literature, and the calculations were based on the formulas listed in Table 2.

X_c (critical conversion) was considered as 0.7 for all runs, ρ_m (density of monomer) 850 g L^{-1}, ρ_p (density of polymer) 1380 g L^{-1}, and M_M (molecular weight of monomer) 62.5 g mol^{-1} [3, 33, 34]. C_{MP} was calculated approximately equal to 5.6 mol L^{-1} (in the current

Table 2. Necessary formulas derived from refereed literature for kinetic studies.

No.	Description	Formula	Reference
1	Overall mass conversion	$X_{ov}(t) = \dfrac{SC(t) - SC(initial)}{SC(final) - SC(initial)}$	[29, 30]
2	Overall polymerization rate	$R_P(t) = C_{M,0}\dfrac{d\theta(t)}{dt} \cong C_{M,0}\dfrac{dX_{ov}(t)}{dt}$	[29, 30]
3	Volume average diameters	$\overline{d_v} = \left(\dfrac{\sum_i n_i d_i^3}{\sum_i n_i}\right)^{1/3}$	[23, 36]
4	Total number of particles per unit volume of the aqueous phase	$N_P = \dfrac{6}{\pi} \times \dfrac{\rho_w}{\rho_P} \times \dfrac{P}{W} \times \dfrac{1}{\overline{d_v}^3}$	[23, 30, 36]
5	Weight ratio of polymer to water	$\dfrac{P}{W} = \dfrac{M}{W} \times X_{ov}$	[23, 30, 36]
6	Total number of polymer particles per unit mass of the latex	$N_{pm} = \dfrac{6}{\pi \rho_p} \dfrac{\sum_i n_i}{\sum_i n_i d_i^3}$	[5]
7	Average number of growing chain per particle	$\overline{n} = \dfrac{R_P N_{av}}{K_p N_p C_{MP}}$	[28, 34]
8	Overall monomer concentration in the polymer particles at interval II	$C_{MP} = \dfrac{(1 - X_c)\rho_M}{\left(1 - X_c + X_c\dfrac{\rho_M}{\rho_P}\right)}$	[28, 34]
9	Overall monomer concentration in the polymer particles at interval III	$C_{MP} = \left(1 - \dfrac{X - X_c}{100 - X_c}\right) \times C_{MP}$	[29]
10	Particles diameter swelled with the monomer	$\overline{d_{pswol}}^3 = \overline{d_v}^3\left(1 - \dfrac{M_M C_{MP}}{\rho_M}\right)^{-1}$	[29]

study). Also, propagation rate constant (K_p) is reported about 11000 mol^{-1}s^{-1} at 50°C for VCM polymerization [28, 34]. N_p was calculated by substitution of the calculated instead of .

RESULTS AND DISCUSSION

### Characterization of the Emulsifier

The compositions of the three selected SDIDS samples (hereinafter named SDIDS1, SDIDS2 and SDIDS3) extracted from thermogravimetric analysis (TGA, METTLER, 20°C.min^{-1} under nitrogen atmosphere) are listed in Table 1. Due to the different contents of ingredients in the SDIDS samples such as alcohol, water, and anion content, they have potential to change micellar properties [16-21] which play a very important role in emulsion polymerization [25, 35].

The results in Table 1 show increasing trends for iso-

decyl alcohol (%wt) and anion content (%wt), while they show a decreasing trend for isopropyl alcohol (%wt) by going from SDIDS1 to SDIDS3. Isopropyl alcohol is a short chain alcohol and can act as a co-solvent. It is preferentially solubilized in the palisade layer and decreases the dielectric constant of water upon solubilization [16, 17, 19- 21]. While isodecyl alcohol which is a longer chain alcohol can act as a co-emulsifier in micellization process [8, 21, 37-39] through solubilization in both the palisade layer and the micelle hydrophobic core [16, 17, 21], and consequently changing the emulsion parameters.

Determination of CMC using Conductometry

A 5-ring conductivity measuring cell (c=0.7 cm^{-1}) was used to monitor the conductivity during titrations using a Metrohm conductivity meter (Switzerland). The conductivity was measured stepwise by introducing an aliquot volume of the mother solution into ultra-pure
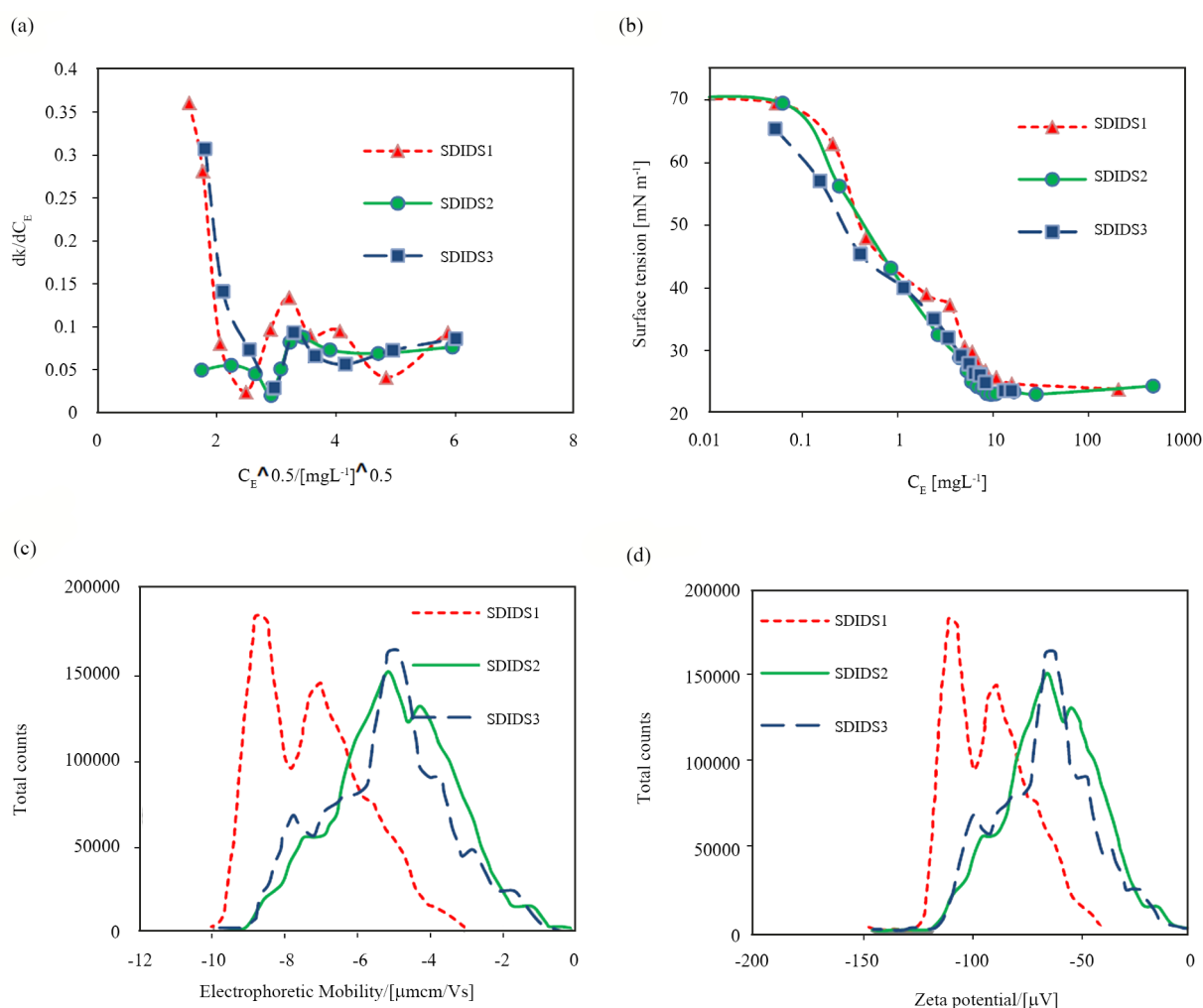
Figure 1. Characterization results of the three SDIDS samples: (a) concentration dependence of dκ /dC$_E$, (b) surface tension measurements, (c) electrophoretic mobility distribution, (d) zeta potential distribution.

water. Ultra-pure water with the conductivity of less than 0.5 μ S/cm was used for preparing all solutions. The temperature was controlled at 25°C ± 0.5°C.

For CMC determination of double-chain emulsifiers with long side-chains (more than around six carbons), differential conductivity which is defined as $d\kappa/dC_E = (\kappa_2 - \kappa_1) / (CE_2 - CE_1)$ vs. C_E 0.5 plot [13] is used in place of the traditional conductivities i.e., the κ vs. C plot [14, 15]. The transitional region between the first minimum and maximum of the plot is named CMC region and the first minimum and maximum are defined by CMC_L and CMC_H, respectively [13]. This behavior was observed for SDIDS samples (Figure 1a) and the obtained results are summarized in Table 3.

Determination of CMC using Tensiometry
Tensiometry measurement was made at 25°C using a Krüss K12 tensiometer under atmospheric pressure by the ring method. The platinum ring was thoroughly cleaned and then flame-dried before each measurement. When a series of at least 3 measurements were completed, the processor calculated the average value of the surface tension in mN m^{-1} (Figure 1b). The obtained CMC results are presented in Table 3.

The CMC reported from tensiometry is between the CMC_L and CMC_H, hence it could be concluded that the CMC reported by the two methods are reliable. CMC_L data in Table 3 (among the same data between SDIDS1-SDIDS3) represents the same trend as isodecyl alcohol (%wt) and anion content in Table 1.

In addition, electrophoretic mobility and zeta potential of the samples were determined by Zetasizer Ver. 6.01, Malvern Instruments Ltd, at room temperature (Figure 1 c and d and Table 3). The concentration of emulsifiers in water was about 14.74 g L^{-1}, the same as polymerization recipe. The distinguished bimodal distribution in both electrophoretic mobility and zeta potential parameter for SDIDS1 (Figure 1c and d) obviously indicates that two sizes of emulsifier aggregates exist in the media. It is assumed that the first peak is related to the smaller size structure like oligo-micelle

which has been further formed for SDIDS1, while the second peak indicates a structure near to micelle structure, similar to structure of SDIDS2 and SDIDS3.

Figure 1a shows CMC_L for SDIDS1 which is noticeably lower than that for SDIDS2 and SDIDS3. It also shows that CMC range (CMC_L and CMC_H) for SDIDS1 is wider than its amounts for SDIDS2 and SDIDS3. It is guessed that higher isopropyl alcohol content, especially for SDIDS1, lowers the dielectric constant of the medium and it causes the tendency for the formation of smaller aggregates [17,19,20]. On the other hand, the charged head groups are further apart due to smaller aggregates, hence the observation of lower zeta potential obtained for SDIDS1, is assumed to be the reason for a more closely packed structure for this sample. Furthermore, by decreasing the size of the micelles at higher alcohol contents, the self-diffusion coefficient can increase [20] and it is the main source of the change in the mobility for SDIDS1. For SDIDS2 and SDIDS3 with lower alcohol content, lower self-diffusion is expected. However, SDIDS3 with higher anion content and lower water content has upper mobility at the same mass concentration in comparison with SDIDS2.

Influence on the polymerization
A unique recipe was applied to study the behavior of the three SDIDS samples on the batch emulsion polymerization of VCM.

Conversion and Kinetic
Figure 2a shows the time evolution versus conversion. The overall slope of the linear portion of the conversion-time at the interval II was used as dx/dt for calculation of R_p (Table 4). Almost a constant rate of reaction was observed from 10 – 70 % of monomer conversion for SDIDS2 and SDIDS3 (Figure 2a), however, SDIDS1 has shown a different behavior in conversion-time from the first to the end of the reaction, almost a stop and jumping (step-like) behavior. It seems that SDIDS1 with higher alcohol content has

Table 3. CMC, electrophoretic mobility and zeta potential parameters of the three SDIDS samples.

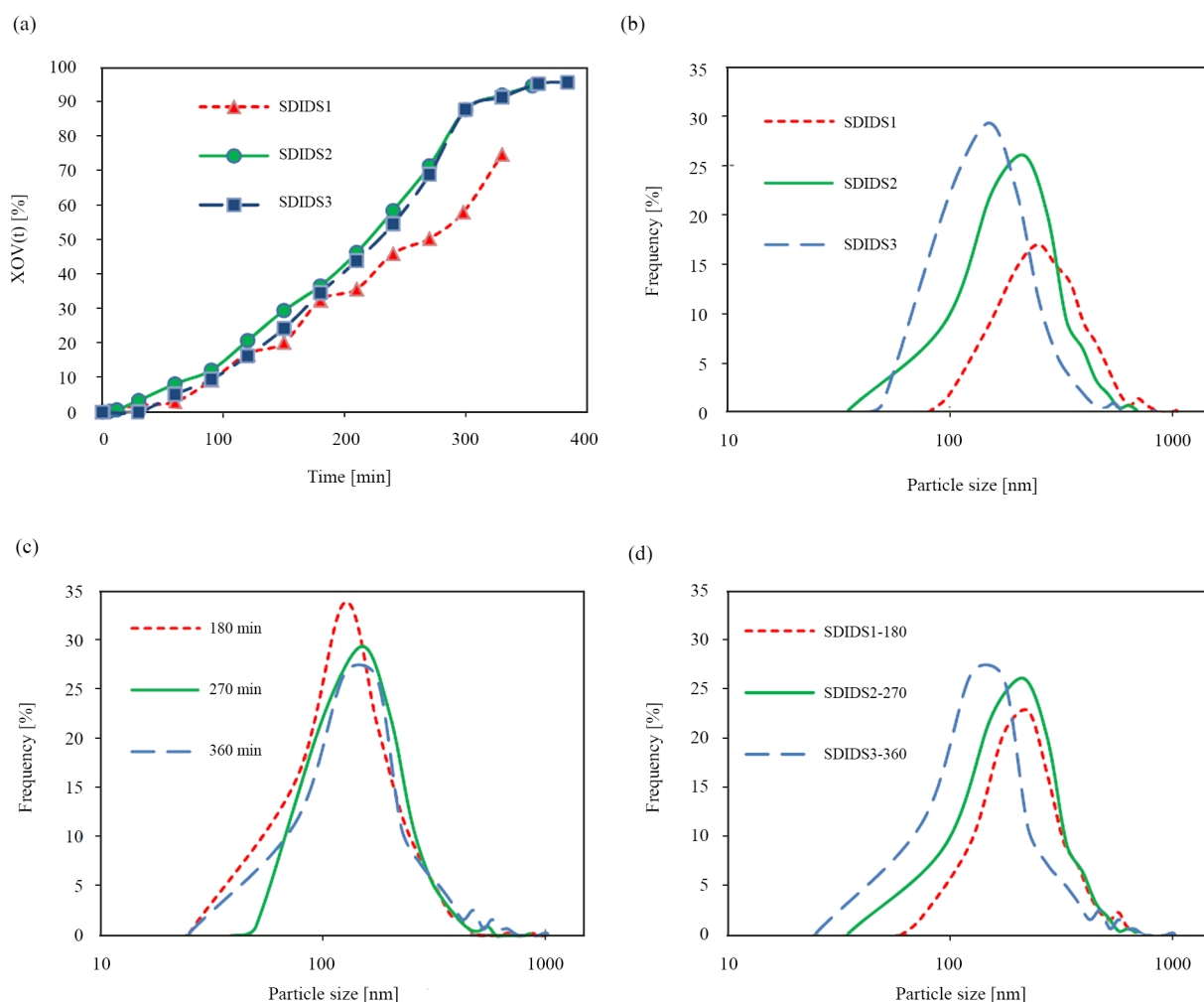| Sample	SDIDS1	SDIDS2	SDIDS3
CMC [a] by Conductometry [mg L^{-1}]	6.17 & 10.32	8.45 & 11.85	8.77 & 10.81
CMC by Tensiometry[mg L^{-1}]	9.41	9.37	10.58
Electrophoretic Mobility [μmcm/Vs] [b]	-7.30	-5.11	-5.37
Zeta Potential [mV] [b]	-92.7	-65.2	-68.5

[a] Differential conductivity method (CMC$_L$ and CMC$_H$)
[b] Determined by Zetasizer

potential for production of oligo-micelles with very small aggregates in each period of time which do not qualify them as micelles for particle nucleation but act more as available emulsifier supplier with higher mobility. Actually, when an alcohol exists in an emulsifier micellar solution, it disrupts the three dimensional network structures of the water and water molecule replaces with isopropyl alcohol molecule [18, 20], so the amphiphilicity of the emulsifier decreases and it does not have the ability to form micelles in the alcohol dominant media, and as a result the fraction of monomeric emulsifier increases in the media [18], ultimately, equilibrium is reached between the micellar and alcohol phases [18, 20]. Actually, with increasing alcohol concentration, the electrostatic repulsions between the head group of emulsifier in micellar core is shown to be decreased [19]. Also, it is reported that micelles could even disappear when enough alco-

hol is added to the emulsifier solution [17]. By consumption of emulsifier molecules for stabilizing the growing particles, although emulsifier concentration in reaction media decreases, the alcohol concentration remains constant. Hence, the ratio of alcohol to emulsifier gradually reaches to a new condition for re-construction of oligo-micelle with small aggregate. Therefore, in each equilibrium state, the new balance between the required free emulsifier for both polymer particle stability and series of oligo-micelles, which are saturated by alcohols, are formed due to new thermodynamic condition. The step-like behavior in the conversion curve for SDIDS1 (Figure 2a) could be attributed to the successive equilibrium time reached for emulsifier molecules partitioning between the oligo-micelle, polymer particles and free emulsifier in the media.

Table 4 shows that R_p values differ for the three sam-

Figure 2. Batch results of the three SDIDS samples: SDIDS1, SDIDS2, SDIDS3: (a) conversion vs. time, (b) PSD curves of the latex at 270 minutes, (c) PSD curves of SDIDS3 at 180, 270 and 360 minutes, (d) PSD curves of SDIDS1 at 180, SDIDS2 at 270, and SDIDS3 at 360 minutes.

ples and with supposing a trend, it is increasing from SDIDS1 to SDIDS3. Similar trends are observed for anion content, while the opposite trend is reported for isopropyl alcohol content (Table 1). The overall conversions are nearly the same for all three samples at time 180 minutes of the reactions however at time 270 minutes, the SDIDS1 shows about 20% lower conversion in comparison to the SDIDS2 and SDIDS3. R_p for SDIDS1 is about 21% and 27% lower than its amounts for SDIDS2 and SDIDS3, respectively.

Samples removed at 180 and 270 minutes, within the interval II for all the three runs and also at 360 minutes in the interval III for SDIDS3, were analyzed for their particle size which was further used to calculate the kinetic parameters such as, $\bar{n}$, N_p and N_{pm}. PSD curves (Figure 2b) in accordance with SEM images (Figure 3), clearly show that the particle sizes are the biggest for SDIDS1, the medium for SDIDS2 and the minimum for SDIDS3.

The $\bar{n}$ data in Table 4 show that the polymerization obeys Smith-Ewart kinetic case 3 with $\bar{n}$ >0.5 for SDIDS1 and case 1 with $\bar{n}$ <0.5 for SDIDS2 and SDIDS3 [40]. It also shows that $\bar{n}$ and R_p/N_p increase by increasing the alcohol content in the SDIDS samples. For VCM, the average number of growing radicals per particle, $\bar{n}$, is reported to be much less than 0.5 [32, 33]. So, the radical desorption from polymer particles into the water phase is, thus, important [3, 41]. The results in Table 4 indicate that shows agreement with its reported value in literature for SDIDS2 and SDIDS3. However, for SDIDS1, where the size of particles is bigger, $\bar{n}$ is higher due to lower radical desorption from polymer particles into the water phase [1].

Increase in $\bar{n}$ with increasing of alcohol content means that alcohol content influences the mass transfer phenomena. The probable reason that explains the decrease in free radical desorption by increasing of alcohol content might be related to the size of particles. The higher size of particles causes the decrease in desorption rate of free radicals from the particle phase. When particles' diameter increases with increasing in alcohol content (with respect to decrease in N_p), the surface area per particle will decrease as a result for SDIDS1. This would cause the increase in entrance efficiency of radicals to each particle, where $\bar{n}$ increases. And also the high solubility and mobility of the newly formed monomeric radicals in media with rich alcohol content and more oligo-micelle formation

promote entrance efficiency. Generally, the number of particles created is determined by the balance between the rate of nucleation and the rate of coagulation [25]. Noteworthy that lower N_p and N_{pm} for SDIDS1 in comparison to the other two at 180 minutes have shown lower number of particles initiated at nucleation period in interval I. It seems that emulsifier molecules in SDIDS1 do not have the ability to form spate of micelles in the alcohol dominant media which is qualified for particle nucleation [17, 18, 20].

Also significant reduction of N_{pm} for SDIDS1 in comparison to the other two in conversion range of 32 to 50% at growth stage at in interval II is a sign for observing coagulation at higher rates in comparison to nucleation, leading to a drop in both N_p and N_{pm} and increase in particle size is completed. It is known that the formation of primary particles by homogenous nucleation during polymerization favors the growth of particles via association of small and large particles. The primary particles are colloidally unstable due to shortage of free emulsifiers which are being used for oligo-micelle formation. Hence, they undergo coagulation with large polymer particles and polymerize very slowly [1]. Coalescence of particles increases the particle size and decreases the particle concentration. On the other hand, a drop in the number of particles simultaneously contributes to a slower overall reaction rate, R_p and higher polymerization rate per particle, R_p/N_p [29, 30] (Table 4).

It could be concluded that SDIDS1 with higher alcohol content potentially has higher mobility (Table 3) at the equal mass concentration in comparison with SDIDS2 and SDIDS3. It manipulates more coagulation as a result, by the higher collision of the particles.

For SDIDS2, from conversion 37 to 71%, the reduction in N_{pm} is less than its amount for SDIDS1 and also N_p is increased. This increase in N_p indicates the appearance of new particles [5]. It means that both coagulation and nucleation have happened simultaneously. But for SDIDS3, from conversion 35 to 69%, the N_{pm}, and also N_p are increased with a higher rate in comparison with those for SDIDS2. This indicates that the nucleation rate is higher and very low coagulation is formed which is supported by lower particle size for SDIDS3. By considering similar alcohol contents for both SDIDS2 and SDIDS3 (Tab. 2), the difference in N_p and N_{pm} for these two samples could be related to the higher anion and lower water contents in SDIDS3.

K-value quantities in Table 4 show that polymer

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Table 4. Kinetic results and latex properties of batch runs of the SDIDS samples: (a) SDIDS1, (b) SDIDS2, (c) SDIDS3.

Sample	SDIDS1		SDIDS2		SDIDS3		
% $X_{ov}(t)$ final [a]	74.65		94.44		95.48		
d $X_{ov}(t)$ /dt [min⁻¹]× 1E 3	2.34		2.83		3.00		
R_p [mol L⁻¹ s⁻¹]× 1E 4	4.94		5.98		6.31		
Time [min]	180	270	180	270	180	270	360 [c]
% $X_{ov}(t)$	32.47	50.30	36.59	71.34	34.57	68.83	95.07
$\overline{d_v}\,[nm]$	316	386	247	289	238	237	302
$\overline{d}_{pswol}\,[nm]$	377	461	295	341	284	283	309
N_p [per liter aqueous phase] × 1E -16	0.66	0.56	1.57	1.97	1.65	3.32	3.52
$\overline{n}$	0.728	0.856	0.373	0.311	0.374	0.186	1.067
N_{pm}, [per g polymer] × 1E-13	4.39	2.40	9.14	5.74	10.20	10.50	5.03
R_p / N_p [mol s⁻¹] × 1E 20	7.45	8.76	3.88	3.02	3.83	1.90	1.79
K-value	68.1	67.5	66.7	68.7	65.3	69.0	67.3
Coarse matter [a] [% wt]	Over [b] (more than 10 %wt)		Medium (about 2 - 5 % wt)		Nil (less than 0.05 %wt)		

[a] At the final conversion

[b] Runaway observed at this run

[c] Available due to very low coarse matter content

chains can grow more for SDIDS1 in comparison to the small particles of SDIDS2 and SDIDS3 because the higher particle sizes reduce radical desorption rate from particles. Generally, desorption events are very operative in small particles while the formation of occluded or buried radicals or the fraction of less reactive radicals is more operative in large particles [1].

It is observed that R_p/N_p and   increase with increasing $\overline{d}_{pswol}$ (Table 4), which is consistent with classical emulsion polymerization kinetics. It is expected that for SDIDS sample with higher alcohol content, diameter of polymer particles and the polymerization rate per particle increase with increasing the mobility of SDIDS monomers due to the higher oligo-micelle formation. Our results indicate that alcohol content has higher effect on particle growth (R_p/N_p) and has inverse effect on the nucleation process and the particle number.

Particle Growth History
Figure 2c compares PSD of SDIDS3 latexes removed at different time intervals. The PSD at time 180 minutes shows almost a skewed bell type distribution and two distinguished districts of particle sizes. The first district is very low in size distribution almost 75 nm with a frequency of % 15.6. The second one which is the main peak at almost 125 nm with a frequency

of % 33.7. The PSD at time 270 minutes shows one main bell type curve with its peak shifting about 25 nm to higher particle sizes relative to the main peak of PSD at time 180 minutes. The interesting point is that the increase in the average particle sizes has been occurred by the cost of vanishing the smaller particles peak at 75 nm, and finally a small peak at 550 nm has formed. The PSD at time 360 minutes shows a distinguish district in size as skewness at 75 nm with a frequency of % 11.4 which confirmed the new particle formation. At higher particle size, the PSD curve is shifted to higher sizes around 475 nm which could be under the effect of coagulation at high conversions [5]. By the cost of formation of high particle sizes, the N_p decreases and the condition would prepare for secondary particle formation [25].

It seems the oligo-micelle formation can vary particle growth history. Generally, according to the emulsion polymerization theory, the number of particles remains constant after the interval I for VCM [2, 3] unless the conditions change toward particle coagulation [23] or secondary particle formation [25]. Based on the N_{pm} values listed in Table 4, an optimized number of latex particles per unit mass of the polymer equal to 5×10^{13} particles is assumed as a criterion N_{pm} for a normal emulsion polymerization of VCM latex in the current study. This optimum is almost obtained at 180
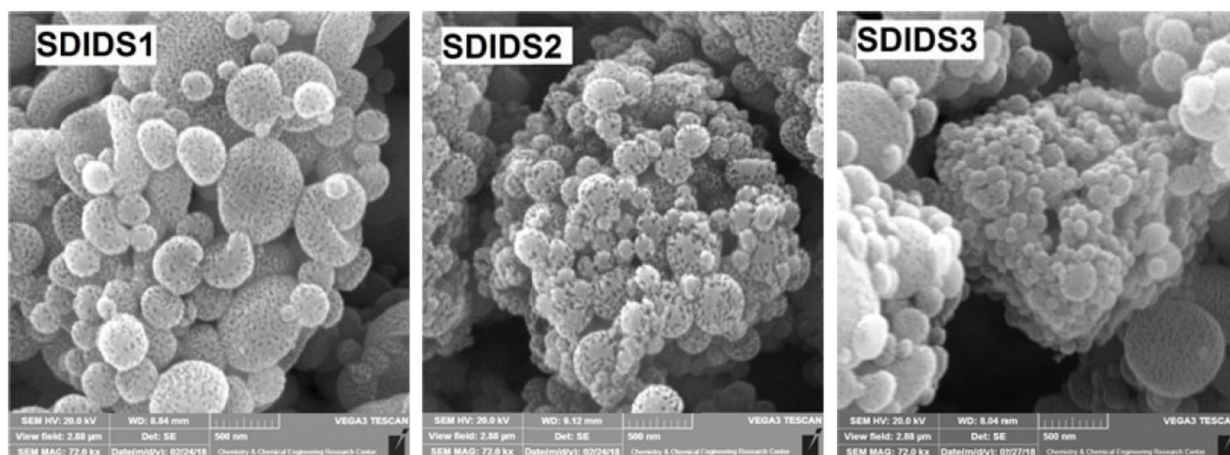
Figure 3. SEM images (with scale bar 500 nm) of the three SDIDS samples at 270 minutes of polymerization.

min for SDIDS1, at 270 min for SDIDS2 and at time 360 min for SDIDS3. Figure 2d compares the PSD curves of the mentioned times for the three samples. Almost, similar trends with the least difference in particle sizes are obtained. It could be observed that the criterion particle growths are formed with a delay time from SDIDS1 to SDIDS3. The observed behavior matches the trends observed for isopropyl alcohol content which promotes oligo-micelle formation, while an opposite trend is observed for anion content which promotes micelle formation from SDIDS1 to SDIDS3(Table 1). It could be concluded that different condition of oligo-micelle formation would lead to different particle growth history.

Latex Stability

Latex stability for the polymerization used SDIDS1 could not exceed more than 75% conversion. The main parameter responsible for this observation is believed to be the high concentration of alcohol. As discussed earlier when alcohol concentration is high, size of particles increases while the number of particles decreases. In this condition, termination reaction rate decreases while at the same time the viscosity in the particles increases due to a decrease in the value of C'_{MP} [3, 4]. Another possibility is the decrease in radical desorption rate from particles by promoting the polymerization auto- acceleration rate [7], which is observed as experimentally runaway. Also, the big coarse particles are settled as a separated phase at the reactor bottom. However, in the case of the other two samples, it was possible to convert VCM to $X_{ov}(t)$ up to about 95% due to their regular particle contents. SDIDS3 with more anions and less isopropyl alcohol content shows the highest stability with the least %

wt coarse matter among the three studied samples. Although SDIDS2 in nearly all the parameters behaves more similar to SDIDS3, however, the main reason for the differences in coagulation behavior and coarse matter content for these two samples is not exactly understood. Although due to the results from Table 1, higher anion content of SDIDS3 seems to provide conditions leading to more coverage of the particles. Higher isodecyl alcohol content (0.6 %wt from Table 1) of SDIDS3, is believed to act as a nonionic emulsifier and to increase the stability of emulsion system by decreasing the repulsion forces between the hydrophilic parts of the emulsifier [8, 21, 37-39].

In addition, the pH of the reaction media as a witness to track electrolyte change remained approximately constant all the times at around 7 during the polymerization course for all three runs. However, when a runaway occurred (batch SDIDS1), a reduction in pH of the end aliquot was observed from 7 to 3–4 as an exception which probably related to PVC degradation, leading to the hydrochloric acid formation.

CONCLUSION

It was revealed that isopropyl alcohol as co-solvent in the three SDIDS samples effects distinctly on their performances. In the series of studied samples, the highest isopropyl alcohol concentration and the lowest anionic content in the SDIDS samples (i.e., the sample SDIDS1) might be the reasons for the following observations:

1- Sooner and better promotion potential for oligo-micelles formation due to higher isopropyl alcohol content

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2- Greater particle size due to the lower particle nucleation after the disappearance of the micellar emulsifier (end of the interval I)

3- Higher particle growth rate ($\overline{n}$ and R_p/N_p) due to an increase in the particle size and the emulsifier mobility which results in the step-like behavior

4- Slower overall rate due to the lower N_p and its reduction by the coalescence of particles because of less strength of latex stabilization

5- Higher chain growth rate (K-value) due to the greater particle size and particle growth rate ($\overline{n}$ and R_R/N_p).

SYMBOLS AND ABBREVIATION

Symbols used

C_E	concentration of emulsifier in water
C_{MP}	overall monomer concentration in the polymer particles at interval II
C'_{MP}	overall monomer concentration in the polymer particles at interval III
$C_{M,0}$	initial monomer concentration (moles per unit volume of the continuous phase)
d_i	diameter of particle with index i.
$\overline{d}_{pswol}$	particles diameter swelled with the monomer
$\overline{d}_V$	volume average particle diameter
K_p	propagation rate constant
K-value	a measure of molecular weight for PVC
M_M	molecular weight of the monomer
M/W	weight ratio of monomer to water
$\overline{n}$	average number of growing chain per particle
n_i	number of particles with diameter d_i.
N_p	number of latex particles per unit volume of the aqueous phase
N_{pm}	number of latex particles per unit mass of the polymer
N_{av}	Avogadro's number
P/W	weight ratio of polymer to water
R_p	polymerization rate per unit volume of the continuous phase
SC	solid content
SC (initial)	solid content at the beginning of reaction
SC (final)	solid content at the end of reaction
SC (t)	solid content at time t
X_c	critical conversion
$X_{ov}(t)$	overall mass conversion at time t

Greek symbols

κ	conductivity
ρ_P	average density of the polymer
ρ_W	density of water
ρ_M	density of monomer
$\theta(t)$	overall molar conversion at time t

Abbreviations

CMC	critical micelle concentration
CMC_L	first minimum of CMC region
CMC_H	first maximum of CMC region
DM water	demineralized water
E-PVC	PVC produced by emulsion polymerization
K-value	a measure of molecular weight for PVC
PSD	particle size distribution
PVC	poly (vinyl chloride)
SDBS	sodium dodecylbenzenesulfonate
SDIDS	sodium di-isodecyl sulfosuccinate
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SPS	sodium pentadecan-sulfonate
VCM	vinyl chloride monomer

REFERENCES

1. Capek I (1995) Kinetics of the free-radical emulsion polymerization of vinyl chloride. Adv Polym Sci 120: 135-205

2. Peggion E, Testa F, Talamini G (1964) A kinetic study on the emulsion polymerization of vinyl chloride. Makromol Chem 71: 173-183

3. Ugelstad J, Mork P C, Dahl P, Rangnes P(1969) A kinetic investigation of the emulsion polymerization of vinyl chloride. J Polymer Sci C 27: 49-68

4. Boieshan V (1990) The rate of batch emulsion polymerization of vinyl chloride. Acta Polym. 41: 303-306

5. Boieshan V (1990) Formation of latex particles during the batch emulsion polymerization of vinyl chloride. Acta Polym 41: 298-303

6. Alvarez AE, Ressia JA, Aparicio LV, Sarmoria C, Valles EM, Brandolin A (2001) Batch emulsion polymerization of vinyl chloride: Effect of operating variables on reactor performance. Lat Am Appl Res 31: 317-323

7. Pakdel AS, Behbahani MR, Saeb MR, Khonakdar HA, Abedini H, Moghri M (2015) Evolution of vinyl chloride conversion below critical micelle concentration: a response surface analysis. J Vinyl & Addit Technol 21: 157-165

8. Jalilian SM, Ziaee F (2011) Vinyl chloride emulsion polymerization reaction: Effect of various formulations. Iranian J Polym Sci Technol 24: 205-214

9. Rangnes P, Palmgren O (1971) Particle size of poly (vinyl chloride) latices and rheology of poly (vinyl chloride) pastes. J Polym Sci Polym Symp 33:181-192

10. Ash M, Ash I (2010) Handbook of industrial surfactants. In: Trade name reference, 5th ed, Synapse Information Resources, U.S.A, Vol. 1, Part 1, pp 502

11. Breuer W, Höfer R (2003) Sulfosuccinates for emulsion polymerization. Tenside Surf Det 40: 208-214

12. Deepika, Tyagi VK (2006) Sulfosuccinates as mild surfactant. J Oleo Sci 55: 429-439

13. Manabe M, Kawamura H, Kameyama K (2011) Premicelle formation of double-chain surfactants and bile salts in the neighborhood of the CMC region: Application of a differential conductivity technique to the determination of micellization parameters. J Oleo Sci 60: 15-525

14. Miqan SN, Farshchi-Tabrizi F, Abedini H (2015) Study of several approaches for predicting electrical conductivity of sodium-dodecyl-sulfate solution in the presence of Na_2CO_3 and KPS. J Mol Liq 201 :59-67

15. Miqan SN, Farshchi-Tabrizi F, Abedini H; Atashy-Kashi H (2013) Estimation of micellization parameters of sds in the presence of some electrolytes for emulsion polymerization systems. J Surfact. Deterg. 16: 271-278

16. Rao IV Ruckenstein E (1986) Micellization behavior in the presence of alcohols. J Colloid Interface Sci 113 :375-387

17. ZANA R (1995) Aqueous surfactant-alcohol systems: A Review. Adv Colloid Interface Sci 57: l- 64

18. Aramaki K, Olsson U, Yamaguchi Y, Kunieda H (1999) Effect of water-soluble alcohols on surfactant aggregation in the C12EO8 system. Langmuir 15:6226-6232. http://doi.org/ 10.1021/la9900573

19. Rafatia A A, Gharibi H, Rezaie-Sameti M (2004) Investigation of the aggregation number, degree of alcohol attachment and premicellar aggregation of sodium dodecyl sulfate in alcohol–water mixtures. J Mol Liq 111: 109-116

20. Javadian S, Gharibi H, Sohrabi B, Bijanzadeh H, Safarpour MA, Behjatmanesh-Ardakani R (2008) Determination of the physico-chemical parameters and aggregation number of surfactant in micelles in binary alcohol–water mixtures. J Mol Liq 137: 74-79

21. Javadian S, Gharibi H, Fallah HT (2010) Adsorption and micellar properties of binary ionic/nonionic surfactant mixtures in Ethylene Glycol + Water. J Chem Eng Data 55: 1122-1130

22. Civera C, Arias C, Elorza MA, Elorza B, García-Blanco F, Galera-Gómez P A (2014) Hydrophobicity enhancement inmicelles of Triton X-165 by the presence of the cosolvent 2,2,2 trifluoroethanol (TFE). J Mol Liq 199: 29–34

23. Vidottoa G, Crosato-Arnaldi A, Talamini G (1970) Kinetic study of emulsion polymerization of vinyl chloride. Die Makrormol Chem 134: 41-55

24. Karakag G, Orbey N (1989) An experimental investigation of poly(vinyl chloride) emulsion polymerization Effect of initiator and emulsifier concentrations on polymerization kinetics and product particle size. British Polym J 21: 399-406

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IPPI

25. Vale HM, McKenna TFL (2008) Particle formation in vinyl chloride emulsion polymerization. experimental study. Ind Eng Chem Res 47: 8107-8118

26. Shahbazian A, Navarchian AH, Pourmehr M (2009) Application of Taguchi method to investigate the effects of process factors on the performance of batch emulsion polymerization of vinyl chloride. J Appl Polym Sci 113: 2739-2746

27. Pourmehr M, Navarchian AH (2009) Batch emulsion polymerization of vinyl chloride: application of experimental design to investigate the effects of operating variables on particle size and particle size distribution. J Appl Polym Sci 111: 338-34

28. Pakdel AS, Saeb MR, Abedini H, Khonakdar HA, Boldt R (2014) A combinatorial approach to evaluation of monomer conversion and particle size distribution in vinyl chloride emulsion polymerization. Polym Bull 71: 2487-2506

29. Mahdavian AR, Abdollahi M (2004) Investigation into the effect of carboxylic acid monomer on particle nucleation and growth in emulsifier-free emulsion copolymerization of styrene–butadiene–acrylic acid. Polymer 45: 3233-3239

30. Abdollahi M, Sharifpour M (2007) Effect of carboxylic acid monomer and butadiene on particle growth in the emulsifier-free emulsion copolymerization of styrene-butadiene-carboxylic acid monomer. Polymer 48: 035-2045

31. Zadhoush A, Alsharif MA, Esmailzadeh-Boukany P (2004) The influence of k-value and plasticizer type on the rheological behaviour of plastisol used in coated fabrics. Iranian Polym J 13: 371-379

32. Mahmud F, Atiqullah M, Jarrah N, Hussain I (1992) Measurement of shape and size distributions of PVC resin particles by scanning electron microscopy and image analysis. Eur Polym J 28: 1039-1043

33. Friis N, Hamielec AE (1975) Kinetics of vinyl chloride and vinyl acetate emulsion polymerization. J Appl Polym Sci 19: 97-113

34. Vale HM, McKenna TF (2009) Particle formation in vinyl chloride emulsion polymerization: reaction modeling. Ind Eng Chem Res 48: 5193-5210

35. Chen LJ, Lin SY, Chern CS, Wu SC (1997) Critical micelle concentration of mixed surfactant SDS/NP(EO)40 and its role in emulsion polymerization. Colloids and Surface A: Physicochemical and Engineering Aspects 122: 61-168

36. Unzueta E, Forcada J (1995) Semicontinuous emulsion copolymerization of methyl methacrylate and n-butyl acrylate: 1. Effect of mixed emulsifiers in seeded polymerization. Polymer 36:1045-1052

37. Tomas A, Gil M H, Bordado J C, Goncalves P, Rodrigues P (2009) Preparation of poly(vinyl chloride) latexes using a dual surfactant system: the effect in the particle size distribution. J Appl. Polym Sci 112: 1416-1424

38. Pham VH, Lee YH, Lee DJ, Chung JS (2009) Influence of emulsifiers on particle size and particle size distribution of PVC latex synthesized by miniemulsion polymerization. Korean J Chem Eng 26:1585-1590

39. Najjar R (2012) Microemulsions _ an introduction to properties and applications. In Tech, Croatia

40. Smith WV, Ewart RH (1948) Kinetics of emulsion polymerization. J Chem Phys 16: 592-599

41. Xie TY, Hamielec AE, Wood PE, Woods DR (1991) Suspension, bulk, and emulsion polymerization of vinyl chloride-mechanism, kinetics, and reactor modelling. J Vinyl Technol 13: 2-25