

Versatic Acid/Vinyl Acetate의 비닐 에스테르를 가지는 α,ω -Diacrylate Poly(dimethylsiloxane)의 에멀션 공중합 연구

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A Study on Emulsion Copolymerization of α,ω -Diacrylate Poly(dimethylsiloxane) Containing Vinyl Ester of Versatic Acid/Vinyl Acetate

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Abstract : The α,ω -diacrylate poly(dimethylsiloxane) (DA-PDMS) containing vinyl ester of versatic acid/vinyl acetate (Veova-10/VAc) was prepared by emulsion copolymerization of (DA-PDMS), Veova-10 (with VAc), and auxiliary agents at 85 °C in the presence of ammonium peroxodisulfate (APS) as an initiator. Sodium dodecyl sulfate (SDS) and nonylphenol ethylene oxide-40 units (NP-40) were used as anionic and nonionic emulsifiers, respectively. The resulting copolymers were characterized by using Fourier transform infrared spectroscopy (FT-IR). Thermal properties of the copolymers were studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology of copolymers was also investigated by scanning electron microscopy (SEM) and then the effects of variables such as temperature, agitation speed, surfactant kinds, molecular weights, initiator, and DA-PDMS concentrations on the properties of the silicone-containing Veova-10/VAc emulsions were examined. The calculation of monomer conversion versus time histories indicates that by increasing the DA-PDMS concentration the polymerization rate and the number of polymer particles decrease, respectively.

Keywords : emulsion copolymerization, silicone containing emulsions, α,ω -diacrylate poly(dimethylsiloxane), vinyl ester of versatic acid, vinyl acetate.

Introduction

Water-based adhesives have become increasingly important as the range of applications of polymer materials widens. Currently, worldwide efforts are aimed at reducing the volatile organic solvent content of most adhesive materials. This has promoted the search for a new generation of high performance water-based adhesives to replace the conventional solvent-based technology.^{1–3}

Due to their potential industrial application (exterior and

interior architectural coatings, adhesives and paints),^{3,4} the poly(vinyl acetate) (PVAc) based latexes are particularly attractive. Moreover, the copolymerization of VAc with other monomers (such as vinyl chloride,⁵ vinyl versate,⁶ acrylate,^{7–12} vinyl propionate, methacrylate, maleate acid, ethylene or acrylonitrile² provides useful latexes with a wide range of properties. The Veova-10/VAc emulsion copolymer is one of the most important industrial latexes, widely used in architectural coatings market. This copolymer can be dried at room temperature or under heated conditions, which has a relatively good durability. Therefore, aqueous Veova-10/VAc polymer emulsions have been widely used as a resin

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for aqueous paints. However, the Veova-10/VAc and/or acrylate copolymers, when exposed to UV lights and environmental conditions its quality, is deteriorated. As a result, it loses its gloss retentivity.¹³

In order to solve these difficulties, it was proposed to add silicone to an aqueous Veova-10/VAc and acrylate polymer emulsions to increase the coating resistance to UV light, oxygen, water and various types of solvents. These will improve the durability of the coating.¹⁴⁻¹⁷ Also, Yamaya and coworkers¹⁸ emphasized that silicone resins, resulting from hydrolytic condensation of silane compounds, could be used since they are able to form films having high hardness, water, and heat resistance.

In this work, the influence of DA-PDMS co-monomer on the emulsion copolymerization of Veova-10/VAc with sodium dodecyl sulfate and nonylphenol ethylene oxide-40 units as mixed emulsifiers were investigated. The stability and the copolymerization kinetics of the Veova-10/VAc emulsion modified by DA-PDMS were compared with Veova-10/VAc. Also, the effects of temperature, agitation speed, surfactant kinds and their weights and also initiator and (DA-PDMS) concentrations on the properties of the copolymers were examined. The properties of the latexes including heat stability and (T_g) were measured and evaluated. In addition, the structure of the terpolymers was also clarified.

Experimental

Materials and Equipment. Reagent grade VAc (Fisher Scientific Co) was further purified by distillation in a rotary evaporator at reduced pressure of 30 mmHg to remove inhibitor. The Veova-10 provided by Achema (Lithuania) was also distilled under vacuum and stored at 0 °C to avoid thermal polymerization. The DA-PDMS was a commercial product of Goldschmidt Chemical Corp., Germany (Tegomer V-Si 2150 with $M_n = 1298 \pm 70$ g/mol). It was dried at 70 °C in a vacuum oven for 48 h before using. NaHCO₃ (Merck) was analytical grade and used directly without further purification. Sodium lauryl sulfo acetate (SLSA), sodium methyl cocoil torat (SMCT) and sodium dodecyl sulfate (SDS) were purchased from Hoechst AG Germany and used directly without further purification. Sodium dodecyl benzene sulfonate (SDBS) and dioctyl sodium sulfosuccinate (DSS) provided by Henkel KGaA Germany and used as received. Sodium lauryl ether sulfate (SLES) and sodium cocoil isotionate (SCI) were kindly supplied from Akzo Chemicals BV, Netherlands and used also as received. Nonylphenol ethylene oxide-40 units (NP, Iconol NP-40, BASF), Germany and initiator APS (Fisons), were used as received. Hydroxyethyl-cellulose

(HEC) was supplied from Fluka and used without further purification. Water was distilled and deionized. All of the solvents such as *N,N*-dimethylformamide (DMF), dimethyl-sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and dimethylacetamide (DMAC) were purchased from Merck and distilled before using for reactions.

Polymerization Procedure. Continuous emulsion copolymerization was carried out using a 500 mL, 5-necked round bottom flask equipped with a reflux condenser, stainless steel stirrer, sampling device and two separate feed streams. The first feed stream was a solution of VAc, Veova-10, DA-PDMS, and anionic surfactant. The other feed was the initiator solution with 3.0×10^{-3} molL⁻¹ concentration. Before emulsion copolymerization start-up, the reaction vessel was first charged with the desired amounts of water, emulsifier, NaHCO₃ and initiator solution respectively. During polymerization process the reaction mixture was stirred at a rate of 200 rpm and the temperature was maintained at 60 °C. After 5 min a small portion of the monomer mixture was added to the flask at a period of 20 min. Then, the temperature was kept at 85 °C until the end of polymerization. The polymerization was performed under air atmosphere to investigate the effect of temperature, agitation speed, initiator and DA-PDMS concentration on monomer conversion. A typical recipe for the preparation of a 52% solid product and the process is given in Table 1 and Scheme 1, respectively.

In order to determine the conversion percentage during the polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples are relatively small so that the overall composition in the reactor is not seriously affected. Once a sample is removed and put in a watch glass, polymerization is terminated by the addition of 7 ppm hydroquinone. Then two drops of ethanol is added to the sample as a coagulant agent and the contents of the watch glass were evaporated at room temperature, and then dried to a constant weight in a vacuum

Table 1. Polymerization Recipe at 85 °C

Compound	Initial charge	Feed	Total
Veova-10(g)	1.00	8.86	9.86
VAc(g)	3.86	34.74	38.60
DA-PDMS(g)	10% w	90% w	Variable (0-5)
Protective colloid : HEC	0.26	-	0.26
Buffer: NaHCO ₃ (g)	0.75	-	0.75
Initiator : (NH ₄) ₂ S ₂ O ₈ (g)	0.10	0.40	0.50
Demineralized water(g)	126	-	126
Nonionicemulsifier : Nonylphenol Ethylene oxide-40 units, NP-40(g)	5.00	-	5.00
Anionic emulsifier : SDS(g)	0.50	4.50	5.00

Scanning electron micrographs were taken on a JEOL-JXA 840 A SEM. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying on a gold coating of approximately 300 Å on an Edwards S 150 B sputter coater. FT-IR spectra of the copolymers were taken using a Nicolet Impact 400 D Model spectrophotometer.

Results and Discussion

Agitation Effects on Polymerization Rate. In heterogenous reaction systems, mass transfer is one of the important factors that affects polymerization rate.²² In order to investigate the mass transfer effect on the polymerization rate, experiments were carried out under conditions of different impeller speeds. Experimental results are presented in Figures 1 and 2 where the conversions of monomer to polymer are plotted against reaction time and impeller speeds at different agitation speeds. In these experiments, initiator concentration was $3.0 \times 10^{-3} \text{ molL}^{-1}$ in H_2O and the concentration of total monomer added per unit volume of aqueous phase, M_0 was 5.0 molL^{-1} in H_2O . In Figure 1 agitation speeds show the highest polymerization

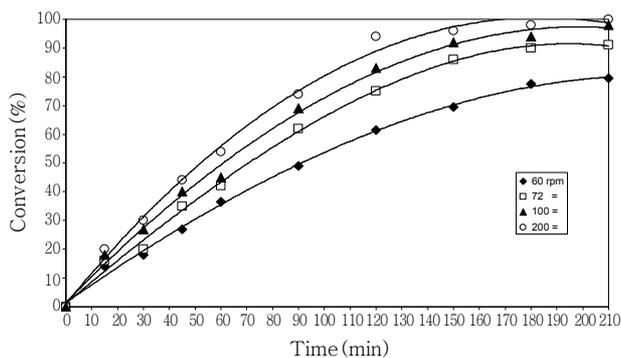


Figure 1. The effect of agitation speed on monomer conversion with polymerization time at (◆) 60, (□) 72, (▲) 100, and (○) 200 rpm. $[M]_0 = 5.0 \text{ molL}^{-1}$, DA-PDMS = 0.05 molL^{-1} , $T = 85 \text{ }^\circ\text{C}$, $[I]_0 = 3.0 \times 10^{-3} \text{ molL}^{-1}$.

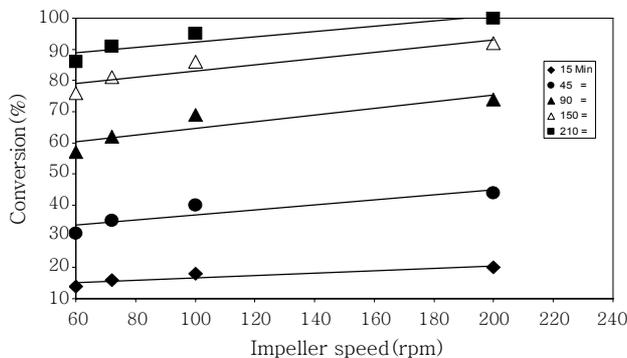


Figure 2. The effect of agitation speed on monomer conversion with impeller speed at (◆) 15, (●) 45, (▲) 90, (△) 150 and (■) 210 min. $[M]_0 = 5.0 \text{ molL}^{-1}$, DA-PDMS = 0.05 molL^{-1} , $T = 85 \text{ }^\circ\text{C}$, $[I]_0 = 3.0 \times 10^{-3} \text{ molL}^{-1}$.

rate at 200 rpm and the lowest polymerization rate at 60 rpm. Figure 2 confirms an increase in the polymerization rate by increasing the agitation speed and also the experimental results at agitation speeds between 72 and 100 rpm do not show any difference in polymerization rate. It is worth mentioning that Zhang *et al.*²³ have reported the same variation in the organosilicon composite emulsion polymerization. However, an increase in impeller speed to 200 rpm leads to delayed attainment of acceleration in the polymerization rate. Accordingly, the reaction time required to attain high conversion is longer at 200 rpm than at the other impeller speeds. Song and Poehlein²⁴ observed similar tendency for emulsion polymerization in the absence of a solid phase and explained it by a consideration of monomer mass transfer from monomer droplets to the polymer particles formed in the aqueous phase.

Effects of Initiator Concentration. Figure 3 shows the results of different initiator concentrations on the polymerization reaction rate. Upon increase in initiator concentrations at both the initial and intermediate stages of reaction leads to an enhancement of the polymerization rate. The rate increase at the intermediate stage suggests the existence of more than one radical in a polymerization locus. Thus, the polymerization mechanism is different from that of an ideal emulsion polymerization,^{25,26} in which only one radical can exist and no gel effect appears.

Effects of Temperature. The effects of temperature of maximum conversion and initial rate of emulsion copolymerization of DA-PDMS modified Veova-10/VAc is shown in Figure 4. The temperature range studied at fixed concentration of monomers and initiator was between 65 to 90 °C. It was observed that both the initial rate of polymerization and maximum conversion increased by increasing temperature. Figure 4 also shows that there is a conversion percentage around 60 onset at 65 °C and it means that polymerization started.

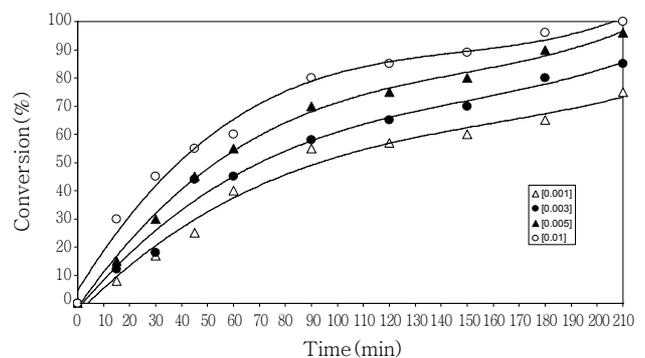


Figure 3. The effect of initial initiator concentration on monomer conversion with time at $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = (\triangle) 0.001$, (●) 0.003, (▲) 0.005 and (○) 0.01 molL^{-1} , $[M]_0 = 5.0 \text{ molL}^{-1}$, DA-PDMS = 0.05 molL^{-1} , $T = 85 \text{ }^\circ\text{C}$, 200 rpm.

After this temperature it has been observed that there is an increase in the polymerization rate by increasing temperature. The temperatures 85 and 90 °C are suitable for these systems but at 85 °C the highest conversion percentage is obtained. Actually, very high temperature such as 90 °C and more is dangerous for these systems, because the polymer may turn to gel point.

Effects of the DA-PDMS Concentration. Addition of DA-PDMS in Veova-10/VAc and acrylic emulsion provides beneficial effects by improving various mechanical properties such as water and weather ability and good acid and alkali resistance.¹⁶ In addition to this, the incorporation of silicone plays the roles of coupling agent and softener²⁷ and it is enriched on surface of the film. On the other hand, Zhang *et al.*¹⁷ demonstrated that silanes can be bonded with hydroxyl groups on the surface of substrate to increase the adhesion and also FT-IR analysis indicated that organic functional silanes can be polymerized with other monomers. Figure 5 shows the effect of DA-PDMS concentration on the conversion versus time histories where the initial initiator and total monomer concentrations were constant at $[I]_0 =$

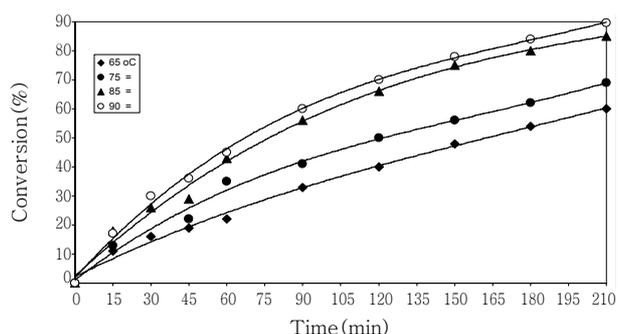


Figure 4. The effect of reaction temperature on monomer conversion with time at (◆) 65, (●) 75, (▲) 85, and (○) 90 °C, $[M]_0=5.0 \text{ molL}^{-1}$, DA-PDMS=0.05 molL⁻¹, T=85 °C, 200 rpm, $[I]_0=3.0 \times 10^{-3} \text{ molL}^{-1}$.

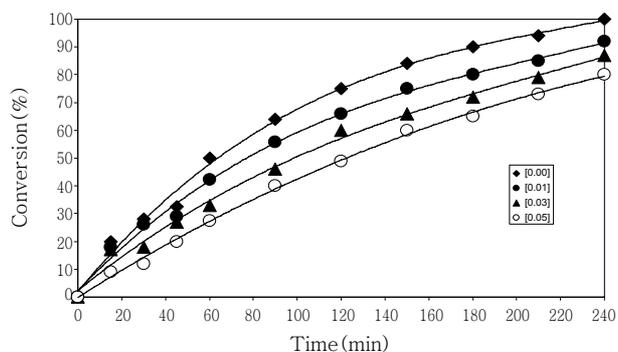


Figure 5. The effect of initial DA-PDMS concentration on monomer conversion with time at (◆) 0.00, (●) 0.01, (▲) 0.03, and (○) 0.05 molL⁻¹, $[M]_0=5.0 \text{ molL}^{-1}$, T=85 °C, 200 rpm, $[I]_0=3.0 \times 10^{-3} \text{ molL}^{-1}$.

$3.0 \times 10^{-3} \text{ molL}^{-1}$ and $[M]_0=5.0 \text{ molL}^{-1}$. It has been observed that the rate of reaction decreases by increasing the amount of DA-PDMS. Figure 6 confirms a decreasing in the reaction rate with increasing DA-PDMS concentration. Kan *et al.*²⁸ also observed the same behavior in the acrylate-silicone emulsion.

It is known that the rate of propagation and consequently the rate of copolymerization in a radical copolymerization reaction are inversely related with the termination rate constant. As the amount of DA-PDMS increases it could act as a chain transfer agent and decreases the rate of polymerization reaction.

Effects of the Weights and Kind of Surfactants on the Rate of Polymerization. The plot of monomer conversion versus time at different NP-40/SDS total weight at 85 °C is shown in Figure 7. Based on this figure, increasing of NP-40/SDS weight will increase the rate of copolymerization reaction which is carried out in the presence of DA-PDMS. The comparisons of the effects of some of the different surfactants on the monomer conversion are shown in Figure 8. These surfactants are NP-40/SMCT, NP-40/SCI, NP-40/SLES, NP-

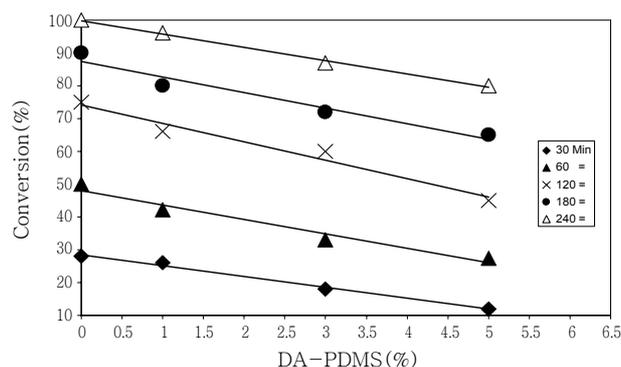


Figure 6. The effect of initial DA-PDMS concentration on monomer conversion with silicone percent at (◆) 30, (▲) 60, (×) 120, (●) 180, and (△) 240 min. $[M]_0=5.0 \text{ molL}^{-1}$, T=85 °C, 200 rpm, $[I]_0=3.0 \times 10^{-3} \text{ molL}^{-1}$.

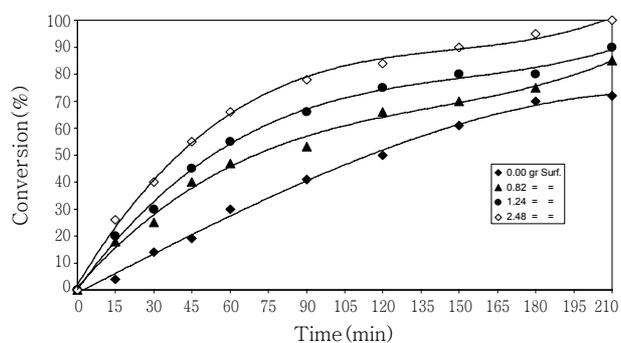


Figure 7. The effect of surfactant weights on monomer conversion with time at (◆) 0.00, (▲) 0.82, (●) 1.24, and (◇) 2.48 gr, $[M]_0=5.0 \text{ molL}^{-1}$, DA-PDMS=0.05 molL⁻¹, T=85 °C, 200 rpm, $[I]_0=3.0 \times 10^{-3} \text{ molL}^{-1}$.

40/SLES, NP-40/DSS, NP-40/SLSA, NP-40/SDBS and NP-40/SDS in the copolymerization of Veova-10/VAc which takes place in the presence of DA-PDMS. According to the above mentioned figure it has been observed that the rate of copolymerization reaction changes by variations of the kinds of surfactant systems. Also shown in Figure 8, the surfactant kind will have the most effect on copolymerization rate. This belongs to the curve of NP-40/SDS and the lowest copolymerization rate. This belongs to the curve of non surfactant. Therefore, this is the logical reason for choosing the NP-40/SDS emulsifier system for the whole copolymerization reactions.

Solubility and FT-IR Studies. The emulsion copolymers basically have low solubility or have not solubility in any solvents at all. These copolymers which have been synthe-

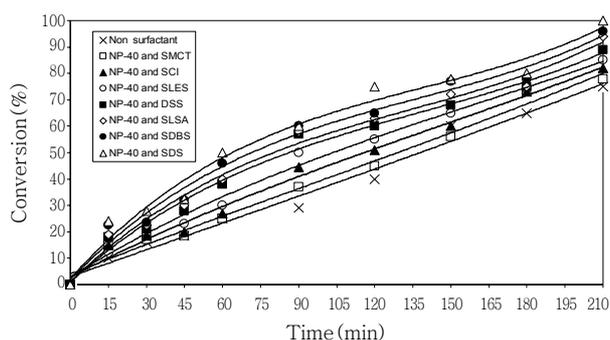


Figure 8. The effect of surfactant kinds on monomer conversion with time at (x) non surfactant, (□) NP-40 and SMCT, (▲) NP-40 and SCI, (○) NP-40 and SLES, (■) NP-40 and DSS, (◇) NP-40 and SLSA, (●) NP-40 and SDBS and (△) NP-40 and SDS, $[M]_0=5.0 \text{ molL}^{-1}$, DA-PDMS=0.05 molL^{-1} , $T=85 \text{ }^\circ\text{C}$, 200 rpm, $[I]_0=3.0 \times 10^{-3} \text{ molL}^{-1}$.

sized from VAc, and Veova-10, with or without DA-PDMS are not exceptions. They are not soluble even in aprotic polar solvents such as NMP, DMSO, DMF or DMAC. This insolubility could be due to conversion of the polymer samples to gelation immediately during of drying under air atmosphere or vacuum. Different procedure for the preparation, purification and drying of the polymer samples were carried out. For example, the product was isolated by filtration after precipitation with a large amount of methanol and was dried under vacuum at 60 $^\circ\text{C}$. After 48 h it was observed that it is insoluble in all of the above mentioned solvents. It is worth mentioning that these copolymers will turn to gel in ethanol after dissolving in little water. Consequently, it is very difficult to investigate the characteristics of the terpolymers by solving them in any solvents. For example, NMR study of these copolymers is nearly impossible to perform, however, FT-IR spectra in the region from 4000 to 500 cm^{-1} were recorded with a sample prepared by making a film of the latex on the surface of a glass and drying it, then removing the film from the glass. Figure 9 shows the FT-IR spectra of (A) VAc, Veova-10 (B) with 0.01, (C) with 0.03 and (D) with 0.05 molL^{-1} of DA-PDMS added to the copolymers, respectively. The comparison of A spectra with B, C, or D spectra has not shown any differences between two different samples of copolymers. The same analyses were repeated for each sample three times and from the FT-IR data it was concluded that this method is not able to show the presence of DA-PDMS moiety in these kinds of copolymers.

Determination of Particle Size of Latexes at Dfferent DA-PDMS Concentrations. The particle sizes of 0.00, 0.01, 0.03 and 0.05

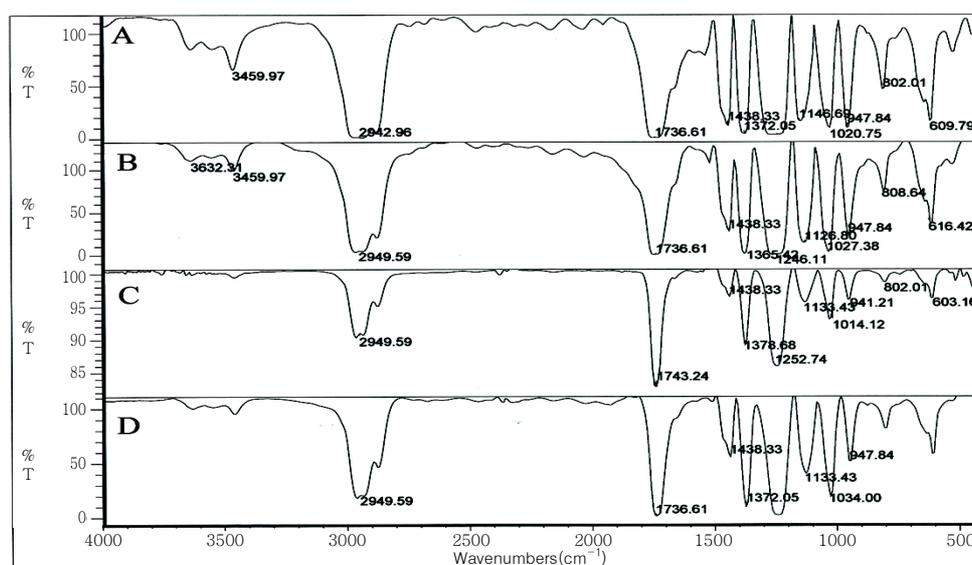


Figure 9. FT-IR spectra of Veova-10/VAc copolymer with (A) 0, (B) 0.01, (C) 0.03, and (D) 0.05 molL^{-1} DA-PDMS. $[M]_0=5.0 \text{ molL}^{-1}$, $T=85 \text{ }^\circ\text{C}$, 200 rpm, $[I]_0=3.0 \times 10^{-3} \text{ molL}^{-1}$.

Table 2. Particle Size of Latexes at Different DA-PDMS Concentrations

Run	DA-PDMS (molL ⁻¹)	d_p^3 (nm)	Time (min)	X_M (%)	M_0 (g/cm ³ H ₂ O)	$M_T \times 10^{-4}$ (nm)
1	0.00	1.5×10^3	60	50	0.50	267
2	0.00	1.5×10^3	90	64	0.50	342
3	0.00	1.5×10^3	120	75	0.50	400
4	0.00	1.5×10^3	150	84	0.50	449
5	0.00	1.5×10^3	240	100	0.50	534
1	0.01	2×10^3	60	42	0.50	168
2	0.01	2×10^3	90	56	0.50	220
3	0.01	2×10^3	120	66	0.50	260
4	0.01	2×10^3	150	75	0.50	300
5	0.01	2×10^3	240	92	0.50	360
1	0.03	2.7×10^3	60	33	0.50	98
2	0.03	2.7×10^3	90	46	0.50	136
3	0.03	2.7×10^3	120	60	0.50	178
4	0.03	2.7×10^3	150	66	0.50	196
5	0.03	2.7×10^3	240	87	0.50	250
1	0.05	3.5×10^3	60	27.50	0.50	63
2	0.05	3.5×10^3	90	40	0.50	91
3	0.05	3.5×10^3	120	49	0.50	112
4	0.05	3.5×10^3	150	60	0.50	137
5	0.05	3.5×10^3	240	80	0.50	183

$\rho_p = 1.19 \text{ g/cm}^3$, 200 rpm, $T = 85 \text{ }^\circ\text{C}$, $[I]_0 = 3.0 \times 10^{-3} \text{ molL}^{-1}$.

molL⁻¹ DA-PDMS containing Veova-10/VAc emulsions were examined by SEM and the data are given in Table 2. According to these data the numbers of average particle diameter were found to be 1500, 2700, 3500 and 5000 nm, respectively. Also it is observed that the number of polymer particles decrease by increasing the DA-PDMS concentration. In addition, it is obvious that the number of polymer particles for the emulsions obtained increases by increasing the time and conversion monomers to copolymers. These results suggest that Veova-10 and VAc monomers were completely polymerized in the presence of DA-PDMS.

Thermal Properties. The thermal properties of Veova-10/VAc and DA-PDMS modified Veova-10/VAc copolymers were evaluated by means of TGA/DTG and DSC under nitrogen atmosphere. The Veova-10/VAc emulsion copolymers (Figure 10(a)) shows a stable situation up to 275 °C. The chemical decomposition will start after this temperature and the maximum decomposition is at around 425 °C. On the other hand, the DA-PDMS modified Veova-10/VAc copolymers (Figure 10(b)) demonstrated thermal decomposition similar to the above, but the maximum decomposition was around 475 °C. Based on these results, it is concluded that the existence of DA-PDMS moiety in the copolymers causes some thermal stability and by increasing the amount of DA-PDMS thermal stability increases.

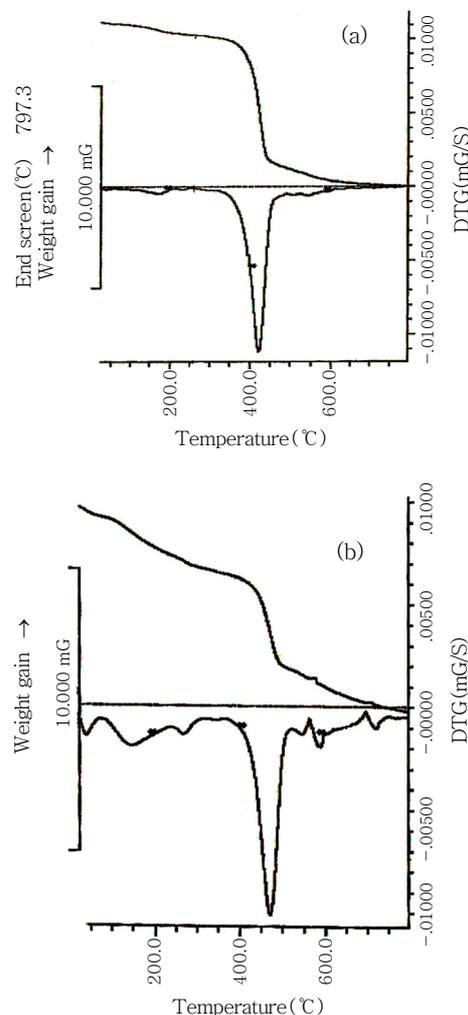


Figure 10. TGA/DTG thermograms of Veova-10/VAc copolymers (a) without and (b) with 0.05 molL⁻¹ DA-PDMS in N₂ atmosphere. $[M]_0 = 5.0 \text{ molL}^{-1}$, $T = 85 \text{ }^\circ\text{C}$, 200 rpm, $[I]_0 = 3.0 \times 10^{-3} \text{ molL}^{-1}$.

The DSC curve of the copolymers is shown in Figure 11 (a) and 11 (b) for Veova-10/VAc and DA-PDMS modified Veova-10/VAc copolymers, respectively.

Figure 11 (a) reveals an endothermic shift around 25 °C, which corresponds to T_g of unmodified copolymers, and Figure 11 (b) shows a T_g around -55 °C for DA-PDMS modified copolymers. According to these results it is found that the presence of DA-PDMS moiety causes the change in thermal behavior and it particularly affects T_g .

Effects of the DA-PDMS on Stability of Latex. The effect of DA-PDMS on stability of latex was investigated and the results were presented in Figure 12. The coagulum increased gradually as the content of DA-PDMS increased and resulted in instability of the emulsion in the course of polymerization as the content of DA-PDMS reached 5%. Moreover, the emulsion would be demulsified in 27 days.

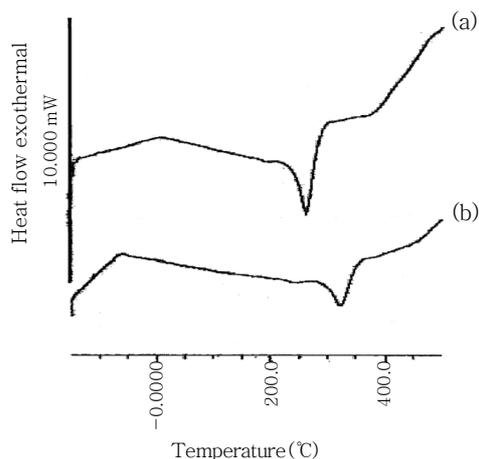


Figure 11. DSC thermograms of Veova-10/VAc copolymers (a) without and (b) with 0.05 molL^{-1} DA-PDMS. $[M]_0 = 5.0 \text{ molL}^{-1}$, $T = 85 \text{ }^\circ\text{C}$, 200 rpm, $[I]_0 = 3.0 \times 10^{-3} \text{ molL}^{-1}$.

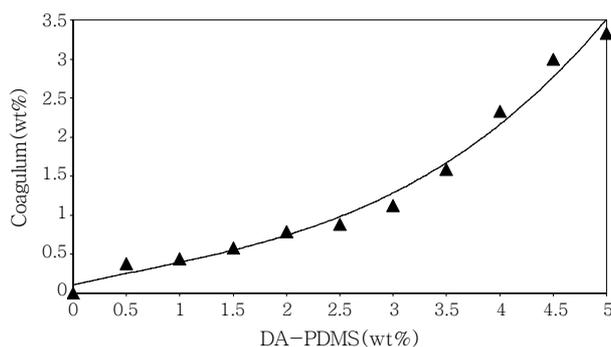


Figure 12. The effect of the content of DA-PDMS on the polymerization stability.

Conclusions

The continuous emulsion copolymerization of DA-PDMS modified Veova-10/VAc resin initiated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was evaluated. The experimental conditions consisting of impeller speed, initiator concentration, temperature, and DA-PDMS concentration were varied and the following results were obtained:

- 1) The prepared copolymers have high solid content (52%) and can be used in the emulsion paints as a binder.
- 2) The presence of DA-PDMS in the Veova-10/VAc copolymer caused an increase in the heat stability while the T_g decreased.
- 3) An increase in initiator concentration at both initial and intermediate stages of the polymerization resulted in an increase in the polymerization rate.
- 4) Initial rate of polymerization and maximum conversion increase by increasing temperature.

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