PVC 성장핵을 사용한 스티렌의 유화중합

조 의 환 · 이 경 우

한국과학기술원 화학과

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PVC-Seeded Emulsion Polymerization of Styrene

Iwhan Cho and Kyung-Woo Lee

Department of Chemistry, Korea Advanced Institute of Science and Technology

P. O. Box 150 Chongyangni, Seoul 131, Korea

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Abstract: The polymerization kinetics and the morphology of PVC-seeded styrene emulsion polymerization were investigated. Batch polymerization technique was employed and transmission electron microscopies coupled with OsO_4-, RuO_4- staining methods were used for the morphological studies. The rate of polymerization was found to be independent of the swelling time and the initiator concentration ($K_2S_2O_8$), but it increased along with the agitation speed. The strong acidic condition of polymerization medium and the addition of isoprene, DVB or $CHBr_3$ slowed down the rate of polymerization. The PVC-PS composite latexes had constant morphology regardless of the change in polymerization parameters. The "off-centered core-shell (PVC-core, PS-shell)" morphology was thought to be originated from the low swelling of PVC with styrene. Crosslinking agent made the morphology "concentric core-shell" and a common solvent to PVC and PS made the smooth composite particles.

1. INTRODUCTION

Composite polymer latexes have been widely studied by many authors[1~8]. Besides the academic curiosity, the successful endeavor in this area of research could lead to the polymeric materials of potential engineering properties.

The major research areas are; 1) The seed polymer is soluble to the second monomer (or monomers) and the two polymers are miscible, e.g., PS/PS, PEA/PMMA, etc., and 2) the seed polymer is soluble (swellable) to the second monomer(s) but two polymers are immiscible, e.g., PEA/PS, PS/poly (styrene-co-butadiene), etc. Another characteristics com-

posite system is that the polymers are rubbery-glassy pair. The morphology of the final composite latexes depend upon the polymerization methods, the molecular weights of the polymers, the hydrophilicity of polymers and the ratio of the polymers. And in our previous study[11] we showed that the initiator concentration and species are important factors for determining the particle morphology of composite latex.

Poly(vinyl chloride) (PVC) is not soluble in vinyl chloride. Thus, the particle nucleation mechanism becomes different from that of the standard emulsion polymerization mechanism (PS). According to Liegeois[9], the particle grows via PVC-core/vinyl chloride-shell morphology. Generally when a polymer is not soluble in its monomer, the polymer will form surface layers like "onion skins"[7]. Sperling and his coworkers[4,5] suggested that the morphology of composite latex particle prepared by PVC/poly (butadiene-co-acrylonitrile) was a graded composition within the latexes, in which PVC formed a core that was partially penetrated by poly (butadiene-co-acrylonitrile), yielding increased amounts of poly (butadiene-co-acrylonitrile) in the shell of the latex particles.

In this article we describe the morphology and polymerization kinetics of PVC-seeded styrene polymerization system. PVC is swellable by styrene but PVC is immiscible with polystyrene, thus the morphology and the kinetics of this system becoming different from other systems.

2. EXPERIMENTAL SECTION

Apparatus and experimental procedure used in this study have been described in previous papers[10,11].

PVC latex : Vinyl chloride is considerably soluble in water and the polymerization mechanism is different from other monomers so that it was impossible to prepare the monodispersed PVC latex. The specifications of the PVC seed
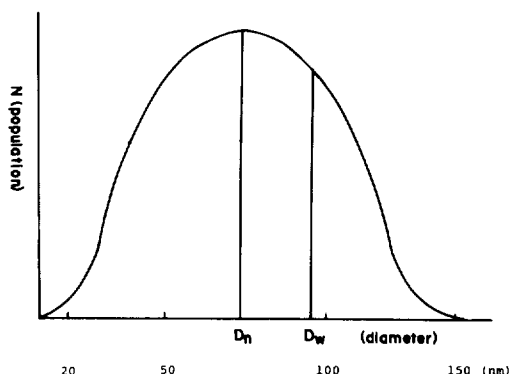

Fig. 1. Particle size distribution of PVC seed latex.

latex used in the present study are as follows:

Total Solid Content(%)	43.3
pH	10.4
Surface Tension (dyne/cm)	58.5
Particle Size	
D_n (nm)	74.5
D_w (nm)	97.6
$U \ (= \dfrac{D_w}{D_n})$	1.31

Surface tension of PVC latex was sufficiently above CMC (critical micelle concentration), so that in PVC-styrene systems the new particle formation was almost improbable. The particle size of PVC latex was measured from latex TEMs[11] and the particle size distribution is plotted in Fig. 1.

The basic polymerization recipe and the polymerization conditions are as follows :

Recipe		
H_2O	475	part
Styrene	75	"
PVC latex (dry base)	25	"
$K_2S_2O_8$	0.5	"
etc.		

Conditions	
Polymerization Temperature	60±1°C

Agitation Speed	200 rpm
Atmosphere	N$_2$
Swelling Time	ca. 1 hour
Post Heat-treating Time	ca. 2 hours

3. RESULTS AND DISCUSSION

3-1. Kinetics

Unlike to PMMA-styrene system, PVC is only swellable in styrene and the equilibrium swelling ratio of PVC latex by styrene was very small (below 0.1g styrene/1 g PVC). Therefore the monomer droplets remain until weight fraction of PS in each polymerizing particle become large enough to absorb all the styrene phase (stage II in Smith-Ewart theory). Under this circumstance the gravimetric method for the determination of the monomer conversion becomes erroneous. Accordingly the rate of polymerization was estimated indirectly from the peak time of the polymerization reaction.

3-1-1. Swelling Time

The effect of swelling time are shown in Table 1. These results demonstrate that the rates of polymerization of styrene is not affected by the swelling time. Probably these results are the consequence of the low equilibrium swelling ratio of PVC latex.

3-1-2. Agitation Speed

The effect of agitation speed on the rate of polymerization are shown in Table 2. With the increasing speed of agitation the rate of polymerization also increased. It is well known that the rate of polymerization is usually not affected by the agitation speed regardless of monomers (hydrophilic or hydrophobic), if the stability of dispersion is good enough to retain the size of monomer droplets (1 μm) through the emulsion polymerization. But in the present system the monomer droplets are dependent on

Table 1. Effect of Swelling Time on the Rate of Polymerization of PVC-Styrene System at 60℃

Experimental Number	Swelling Time (hrs)	pH	Peak Time (min.)
PCS-5	86	7.3	138
PCS-3	–	7.1	133

* Comonomer (isoprene, 0.906 pphm) was used.

Table 2. Effect of Agitation Speed on the Rate of Polymerization of PVC-Styrene System at 60 ℃

Experimental Number	Agitation Speed (rpm)	pH	Peak Time (min.)
PCS-16	200	6.8	16.2
PCS-18	100	2.5	525

*Comonomers (isoprene, 0.906; DVB (divinyl benzene), 1 pphm) were used.

the agitation speed due to the insufficient emulsifier, and the low swelling ratio make the polymerization system in monomer-starved state. Therefore, the increase of agitation speed should increase the surface area of the monomer droplets and the diffusion rate of monomer into the polymerizing particles. Consequently the rate of polymerization will increase with the agitation speed in these systems. But the effect will be decreased because the latex is coagulated gradually under high shear stress.

3-1-3. pH

The rate of polymerization under strong acidic condition was studied. Because PVC seed latex was under the basic condition, aqueous HCl solution was added to make the system acidic.

As shown in Table 3, the polymerization was slowed down in acidic medium. This trend is same to that observed in PMMA-styrene system[11]. The reason could not be explained accurately, but it could be caused by the retardation effect by oxygen, generated by K$_2$S$_2$O$_8$ hydrolysis in acidic medium.

3-1-4. Initiator Concentration

The effect of initiator concentration are shown in Table 4. Regardless of comonomers the rate of polymerization was not affected by the change in initiator concentration within experimental error, when pH of latex was greater than 3. In case of PCS-4 the low pH value of the medium after the post heat treatment was resulted from the decomposition of $K_2S_2O_8$. It can be assumed that the actual pH during the polymerization should be much higher than 3. Therefore, the rate of polymerization remained constant, 3. This is in good agreement with Smith-Ewart theory, since PVC particle works only as a nucleus for polymerization and almost all the polymerization of styrene took place in PS-styrene phase and it did not affect the polymerization system.

However, when the media of polymerization systems were strongly acidic (below 2.5), the rate of polymerization would increase along with the initiator concentration. These results were similar to that of PS-styrene system[12]. In these two cases pH of the polymerization medium was not affected by the decomposition of $K_2S_2O_8$ because of the added HCl solution. The reasons for the increase in the rate of polymerization with the increase of initiator concentration under acidic condition has been already discussed (vide supra)[13].

3-1-5. Comonomer

A Small amount of isoprene was used as a comonomer to introduce OsO_4-staining site in the polymer backbone and its effect on the rate of polymerization was checked. The results are

Table 3. Effect of pH on the Rate of Polymerization of PVC-Styrene System at 60℃

Experimental Number	HCl (0.1 N)* (g)	K₂S₂O₈* (g)	pH	Peak Time (min.)
PCS-13	10	0.01	2.2	− [a]
PCS-11	−	0.01	8.6	180
PCS-12	10	0.1	1.9	210
PCS-9	−	0.1	7.3	138

* The weight is based on 100 g of H_2O in polymerization system.

a; Because of the slow reaction the peak time was not appeared.

Table 4. Effect of Initiator Concentration on the Rate of Polymerization of PVC-Styrene at 60 ℃

	PCS-3	PCS-4	PCS-11	PCS-9	PCS-12	PCS-14
Isoprene (pphm)	0.906	0.906	−	−	−	−
HCl (0.1 N)[a] (g)					10	10
K₂S₂O₈[a] (g)	0.1	0.4	0.01	0.1	0.1	0.4
pH	7.1	3.1	8.6	7.3	1.9	2.0
Peak Time (min)	133	126	130	138	210	130

a; The quantities are based on 100g of H_2O in polymerization system.

Table 5. Effect of Isoprene on the Rate of Polymerization

Experimental Number	Isoprene (pphm)	pH	Peak Time (min.)	Remarks
PCS-2	−	7.1	130	
PCS-7	0.906	7.1	140	
PCS-1	−	7.3	52	PVC/Styrene=1/1 (weight ratio)
PCS-6	0.906	7.2	79	
PCS-10	−	2.6	50	Polymerization Temperature, 80℃
PCS-8	0.906	2.4	64	
PCS-14	−	2.0	130	HCl (0.1N)[a], 10g
PCS-15	0.906	1.9	156	

a; The weight is based on 100 g of H_2O in these system.

Table 6. Effect of Additives on the Rate of Polymerization in PVC-Styrene at 60℃

Experimental Number	CHBr₃ (pphm)	DVB-55 (ppmh)	pH	Peak Time (min.)
PCS-7	−	−	7.1	140
PCS-25	0.67	−	3.3	267
PCS-12	−	6.67	6.8	162

shown in Table 5. the rate of polymerization of styrene was decreased by the addition of isoprene as expected. According to the data reported in the literature[15], isoprene is copolymerized with styrene preferentially. Therefore the slow rate of polymerization is caused by the slow rate of isoprene polymerization.

3-1-6. Other Additives

Effects of chain transfer agent, $CHBr_3$, and crosslinking agent, DVB, are shown in Table 6. Addition of $CHBr_3$ and DVB decreased the rate of polymerization. As explained in previous report[11], a chain transfer agent facilitates the escape of the transferred radicals from the polymerizing particle, thus reducing the rate of polymerization. In the case of DVB the rate of polymerization was gradually retarded by the increase of crosslinking.

The latex containing DVB was not coagulated. This phenomenon proved that the crosslinking of PS occured in each particle.

3-1-7. Polymerization Temperature

As expected, the rate of polymerization was increased with polymerization temperature. The results are shown in Table 7.

3-2. Morphology

The morphology of PVC-PS composite latexes was studied with the samples prepared under the various polymerization conditions. In Table 8 the additional variations on polymeri-

Table 7. Effect of Polymerization Temperature on the Rate of Polymerization

Experimental Number	Polymerization Temperature (℃)	Isoprene (pphm)	pH	Peak Time (min.)
PCS-9	60	–	7.3	138
PCS-10	80	–	2.6	50
PCS-7	60	0.906	7.1	140
PCS-8	80	0.906	7.1	64

zation conditions are noted. However, these PVC-PS composite latexes, being different from the case of PMMA-PS composite latexes[10], were not affected significantly by the polymerization parameters. As discussed in Kinetics Section, PVC was slightly swellable in styrene. Therefore, PVC particles acted only as nuclei for styrene polymerization and the post-polymerization of styrene took place at the surface of the nuclei. The high interfacial tension of PVC to H_2O (37.8 dyne/cm)[16] compared with that of PS (32.7 dyne/cm)[16] contributed further to surface polymerization. Thus, PVC-PS composite latexes exerted "core-shell" (PVC-core, PS-shell) morphology regardless of the polymerization conditions. Besides the core-shell morphology, the PVC-PS composite latexes had the following characteristics:

a) The particle morphology is not "concentric" but "off-centered" core-shell type. The formation mechanism has not identified.

Table 8. Polymerization Conditions and Results of PVC-Styrene System

	PCS-1	-2	-15	-16	-21	-26	-27
Ingredients[a]							
Water	95	100	100	100	100	95	100
PVC (dry)	5	5	5	5	5	5	5
Styrene	5	15	15	15	15	15	15
$K_2S_2O_8$	0.1	0.1	0.4	0.1	0.1	0.1	–
AIBN	–	–	–	–	–	–	0.1
HCl (0.1 N)	–	–	10	–	–	–	–
Isoprene	–	–	0.136	0.136	0.136	5	–
DVB	–	–	–	1	–	–	–
$CHBr_3$	–	–	–	–	0.1	–	–
Cyclohexanone	–	–	–	–	–	5	–
Polymerization Temperature (℃)	60	60	60	60	60	85	60
Peak time (min.)	52	130	156	162	_b	_b	258
pH	7.3	7.1	1.9	6.8	3.2	3.4	9.3

* Charge factor is 5.
a; Quantities are in weight parts.
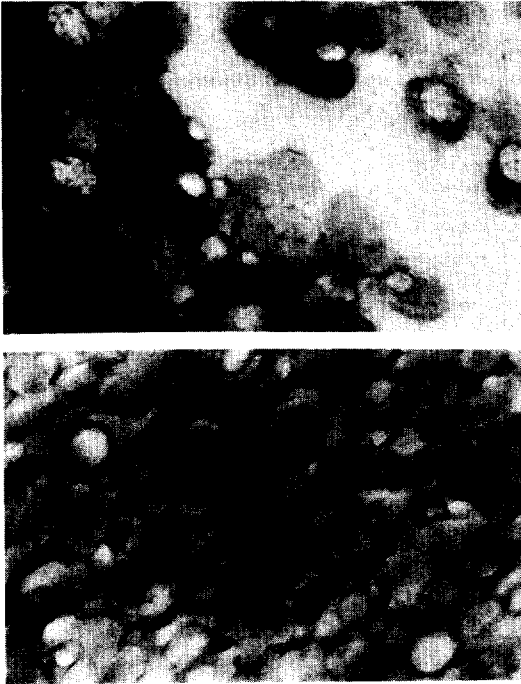b; Because of the slow reaction the peak time was not detected.

Fig. 2. The internal morphologies of PCS-2 &
-15. PCS-2 was stained with RuO_4 and
PCS-15 with OsO_4. In PCS-2, PS-
rich region was dark and PVC-rich
region was bright but in PCS-15 the
interface of PS and PVC was stained
with OsO_4.

Fig. 3. Apparent latex shape of various PVC-
PS composite latexes. The character-
istics of each latex are shown in Table
8. (magnification, a, b, d · x38,000, c; x
58,000).

b) If the crosslinking agent was used, the
particle morphology would have changed
(Fig. 3-c). Probably the morphology
would be "concentric core-shell" because
the crosslinking of PS absolutely restricts
the mobility of polymer molecules.

c) The particle size distributions become
narrower as the polymerization proceeds.
It could be identified from the opalescence
of the dialyzed PVC-PS composite latex.

d) If the polymerizing particles were swollen
with a solvent common to PVC and PS
(e.g. cyclohexanone), the particle surface
became smooth (Fig. 3-d). Although PS
was polymerized mainly on the surface of
the PVC seed particles, small amount of
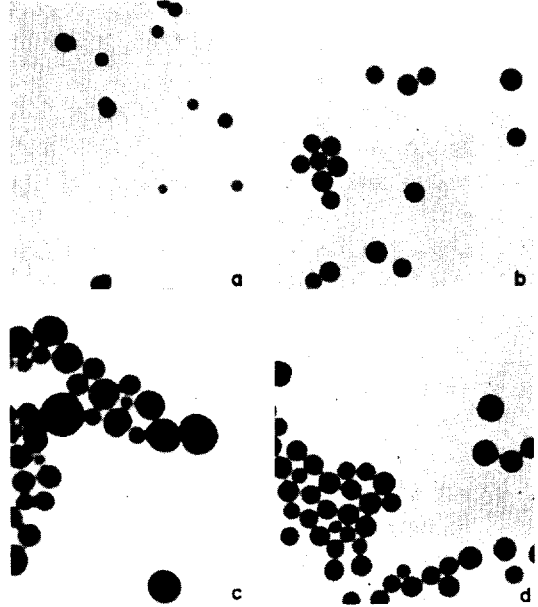PS was polymerized in PVC region and it

Fig. 4. The internal morphology of PCS-27
stained with RuO_4. The dark region is
PS-rich region and the bright region
is PVC-rich region. (mag., x58,000).

contracted the PVC-rich region irregularly.
However, if the particles were swollen with
a common solvent, the phase separation

took place easily. And the morphology of smooth surface and good phase separation resulted.

e) The anchoring effect of terminal SO_4^- groups was not observed in PVC-PS composite latex particles, because of the surface polymerization of styrene. And the oil-soluble initiator, AIBN, also gave the "off-centered core-shell" morphology based on the same reasons to that described above (cf. Fig. 4).

f) During the seeded polymerization, PVC was grafted by PS, but the loci of grafting, surface of the particle or inner part, were not identified. The grafted quantity of PS onto PVC was 0.23g per 1g in PCS-10. It was determined by the solvent extraction method.

4. CONCLUSION

The rate of polymerization, R_p, which was indirectly estimated by the peak time, was independent of the swelling time and of the initiator ($K_2S_2O_8$) solution. Under the strong acidic condition R_p was slowed down. R_p was increased along with the increase of agitation speed. Addition of isoprene, DVB and $CHBr_3$ decreased R_p. These results were caused by the facts that PVC latex particles acted only as the polymerization nuclei and did not affect the polymerization mechanism. The morphology of PVC-PS composite latex particles was the "off-centered core-shell (PVC-core, PS-shell)" regardless of the polymerization conditions, e.g., swelling time, pH, agitation speed, $K_2S_2O_8$ concentration and oil-soluble initiator (AIBN). The particle size distribution was changed gradually to the narrower distribution by the increase of the PS/PVC ratio. If crosslinking agent was used, the "concentric core-shell" morphology was formed. Addition of a common solvent, cyclohexanone, to PVC seed latex made the phase separate easily

during polymerization so that the morphology of smooth surface and good phase separation was observed. There was no notable anchoring effect of terminal-SO_4^- groups.

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