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# Catalytic Emulsion Copolymerization of Styrene and Ethylene by Neutral Nickel (II) Complex

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Catalytic copolymerization of styrene and ethylene by neutral nickel(II) complex has been performed in emulsion. The influences of the ratio of styrene to ethylene, polymerization temperature and time, ethylene pressure and polymerization procedure on the activity of catalyst and the composition of polymer were investigated in detail. The morphology of the polymer latex was observed by TEM, and the polymer was also characterized by NMR and GPC. The results showed that the latex particle was spherical, and the latex up to 10% solid content and the high-molecular-weight poly(styrene-*b*-ethylene) was obtained. The content of the ethylene in the copolymer was evidently enhanced by the addition of the styrene decreasing, addition of the toluene and introduction of the procedure without prepolymerization. The styrene incorporated in the copolymer were in the range of 72 mol% to 100 mol%.

**Keywords:** Catalytic polymerization, emulsion, styrene, ethylene

## 1 Introduction

The radical polymerization in aqueous system has been commercialized to produce coatings and adhesives. Nevertheless, the structure of the polymer prepared in water cannot be controlled by the radical polymerization. With the development of late transition metal catalysts for olefin polymerization, the catalytic polymerization has been carried out in water as a dispersing medium for the catalyst of low oxophilicity (1, 2). The well-regulated structure of polymer could be achieved in aqueous polymerization. Recently, Claverie (3–5) and Mecking (6–11) have presented catalytic ethylene polymerization in a water medium, respectively. The catalytic systems used in these studies were based on nickel and palladium, such as Brookhart's cationic Pd(II)  $\alpha$ -diimine (I, Fig. 1) (6, 7), Klabunde's neutral Ni(II) with sulfonated P,O-chelate (II, Fig. 1) (10), and Grubbs' neutral Ni(II) salicylaldimine (IV, Fig. 1) (10, 11) for Mecking and neutral Ni(II) with fluorinated P,O-chelate(III, Fig. 1) for Claverie. Claverie (3–5) has presented the ethylene polymerization in emulsion using a novel family of P,O-chelated Ni(II) catalysts. The linear PE latices up to 10% solid content can be obtained using a mini-emulsion tech-

nique. However, colloidal stability was hampered by very high crystallinity of the polyethylene and by the presence of hexadecane (cosurfactant) (3). The polymer crystallinity was reduced through ethylene copolymerization with  $\alpha$ -olefins, functionalized  $\alpha$ -olefins, and high comonomer incorporation and stable latex of 30% solid content could be achieved (3). Whereas, the materials obtained by this catalytic system were low molecular weight products. Mecking (10–12) has presented the suspension polymerization of ethylene in water using neutral Ni(II) salicylaldimine complex IVa (Fig. 1), and the high molecular weight PE was obtained. In addition, ethylene polymerization was performed in minemulsion by single-component catalyst IVb (see Fig. 1) (11).

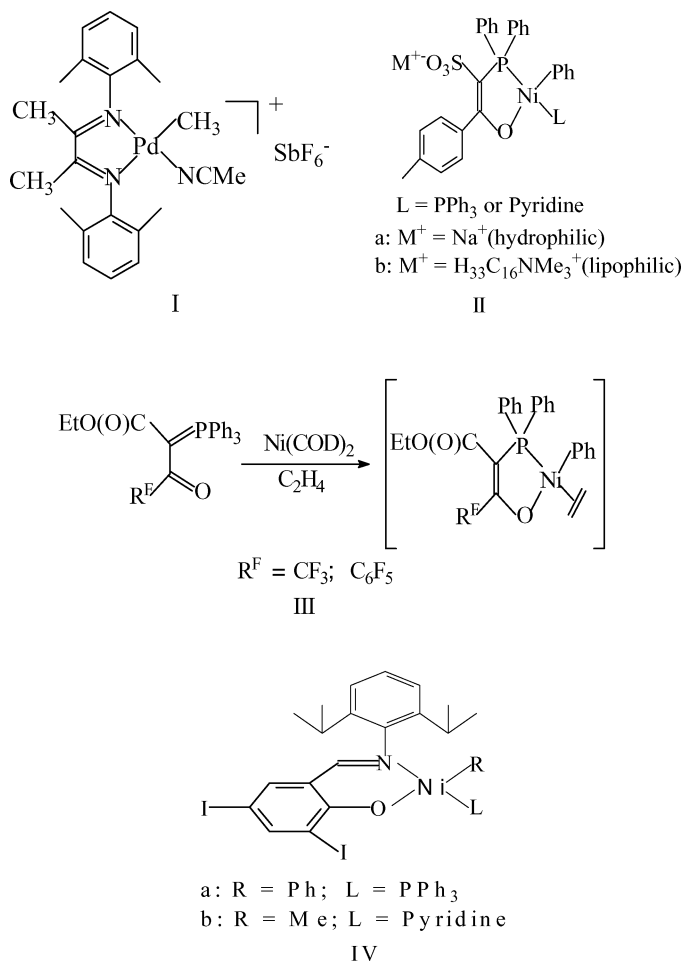
In our investigation, the neutral Ni(II) salicylaldimine complex, activated by Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> or Ni(COD)<sub>2</sub>, was used to implement the copolymerization of styrene and ethylene in water. The composite system of non-ionic and anion surfactant was utilized as emulsifier, and the stable latex was achieved.

## 2 Experimental

### 2.1 General Procedures

Complexes were manipulated by standard Schlenk techniques under argon. Toluene was freshly distilled on sodium benzophenone under argon prior to use. Polymerization-

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**Fig. 1.** Schematic molecular formula of precatalysts for ethylene polymerization in aqueous systems.

grade ethylene was dried through a 4Å molecular sieves column before introduced into the vessel. Styrene was treated by 10% NaOH solution, dried by anhydrous CaCl<sub>2</sub>, and distilled in vacuum. Water was redistilled twice and heavily degassed with argon. Sodium dodecyl sulfate (SDS) and PVA (98% hydrolysis, Mn = 85,000~124,000) were purchased from Sigma-Aldrich Company. OP-10 was purchased from Shanghai Additive Company.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were characterized by a Bruker AVANCE instrument at 500 and 125 MHz, respectively. MS spectra were recorded on a HP 5989A instrument. Elemental analyses were performed on an EA-1106 type analyzer. Gel permeation chromatography (GPC) was performed on a Waters 1515 instrument equipped with a Waters 2414 refractive index detector, THF as solvent, eluent rate 1 mL/min. Transmission electron microscopy (TEM) was used to observe the morphology of latex on a JEOL JEM-1200EX II.

The salicylaldimine ligands and their Ni(II) complexes (IVa, Fig. 1) were synthesized according to the literature (13). The salicylaldimine Ni(II) complexes IVa was charac-

terized by NMR, EA and MS-EI. <sup>1</sup>H-NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.32(b, 3H, Ar-H); 6.74–6.98 (b, 15H, Ar-H); 7.64 (s, 8H, Ar-H and CH=N); 3.94 (s, 2H, CH); 1.32 (s, 6H, CH<sub>3</sub>); 0.99 (s, 6H, CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 26.4 (s). Anal. Calcd. for C<sub>43</sub>H<sub>40</sub>NOI<sub>2</sub>PNi (930.26): C, 55.52; H, 4.33; N, 1.51. Found: C, 56.02; H, 4.56; N, 1.32. MS-EI: 532.9 (M<sup>+</sup>-PPh<sub>3</sub>-Ph-Ni, 4.0%), 262.1 (PPh<sub>3</sub>, 100%), 77.0 (Ph, 14.3%). The phosphine scavenger Rh(acac) (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (14) and Ni(COD)<sub>2</sub> (15) were synthesized according to the literature, respectively. The Rh(acac) (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> was characterized by EA and NMR. Anal. Calcd. for C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>Rh: C, 41.88; H, 5.86. Found: C, 41.80; H, 5.79. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 5.33 (s, 1H, C<sub>2</sub>H<sub>4</sub>); 2.91 (b, 8H, CH); 1.97 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 186.51, 99.10, 59.64, 59.53, 2.25.

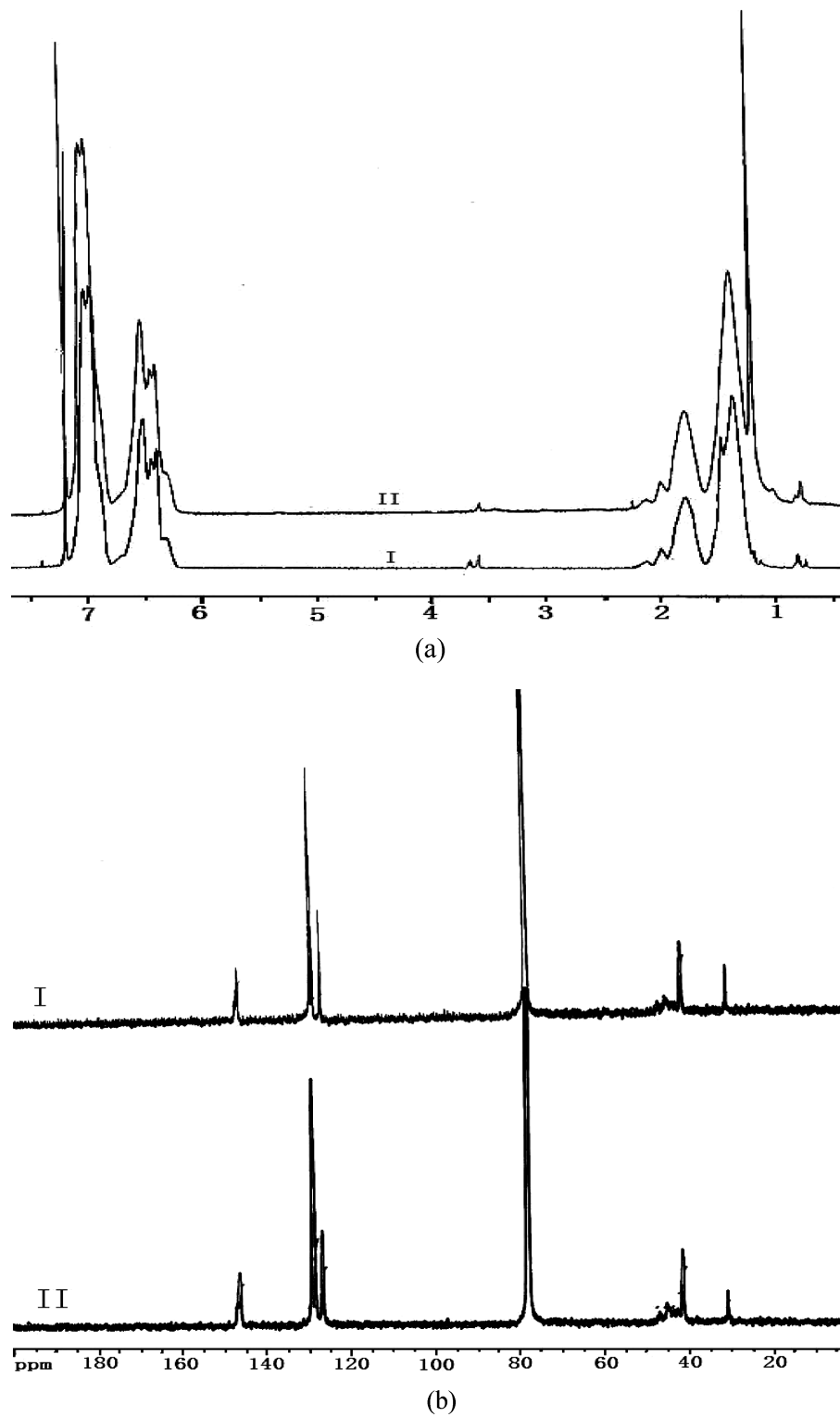
## 2.2 Typical Polymerization Procedure in Emulsion

Polymerization was carried out in a 150 mL pressure vessel. The catalyst precursor and activator were dissolved separately in a small amount of toluene. Both solutions were transferred into the Schlenk tube containing the required amount of water, SDS, OP-10 and styrene under quickly stirring. The mixture was transferred simultaneously into the vessel at a specified temperature under mild stirring. Ethylene was immediately introduced at a constant pressure. After the specified reaction time, the reaction was stopped by cooling and releasing the ethylene to reduce the pressure. The polymer latex was filtered through a nylon sieve. The solid contents of latex were determined by gravimetry at 120°C. For the characterization of polymers, the latices were added to an excess of ethanol. The precipitated polymers were isolated, washed with ethanol, and dried in a vacuum.

## 3 Results and Discussion

The NMR spectra of polystyrene and poly(styrene-co-ethylene) were shown in Figure 2. In contrast to the <sup>1</sup>H-NMR spectrum of polystyrene, there existed a signal for ethylene at δ 1.2 ppm in the <sup>1</sup>H-NMR spectrum of poly(styrene-co-ethylene). The styrene incorporated in the copolymer was calculated according to the area of this peak, and the incorporation of styrene varied from 72 mol% to 100 mol%. The <sup>13</sup>C-NMR spectra of the copolymers indicated that their structures were identical whether the Rh(acac) (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> or Ni(COD)<sub>2</sub> was used as activators. There were signal peaks for SSS sequence at δ 40 and 45 ppm, and the signal peak was broad at δ 45 ppm, which indicated polystyrene segment was random. Furthermore, there was a signal peak for the EEE sequence at δ 30 ppm. This was characteristic of PS-b-PE (16).

In order to investigate the influence of polymerization conditions on the activities of catalyst and structures of



**Fig. 2.** The NMR spectra of polymers (a)  $^1\text{H-NMR}$  for polystyrene (I, entry 7 in Table 1) and poly(styrene-ethylene) (II, entry 11 in Table 2); (b)  $^{13}\text{C-NMR}$  for poly(styrene-ethylene) catalyzed by  $\text{IVa/Rh(acac)(C}_2\text{H}_4)_2$  (I, entry 11 in Table 2) and  $\text{IVa/Ni(COD)}_2$  (II, entry 17 in Table 2), respectively.

**Table 1.** Representative results of catalytic copolymerization of Styrene and Ethylene in Emulsion (catalysts in styrene)

Entry <sup>#</sup>	St/mL	t/h	Pressure/ MPa	Solid content/%	pH	St/ mol%
1	2	2	5.0	3.63	7.08	93.29
2	4	2	5.0	6.30	7.41	96.50
3	6	2	5.0	8.80	7.02	98.03
4 <sup>a</sup>	8	2	5.0	10.2	7.01	98.20
5	6	1	5.0	7.27	7.25	98.73
6	6	4	5.0	8.80	7.15	97.48
7	6	2	0.04 <sup>b</sup>	7.79	7.31	100.00
8	6	2	3.0	8.16	7.14	97.90
9	6	2	6.0	8.87	7.05	97.24

<sup>#</sup>catalyst: 50  $\mu$ mol, Ni/Rh = 2:1; OP-10: 3.0 g, SDS: 0.5 g, H<sub>2</sub>O: 50 mL; prepolymerized 5 min at 80°C, then copolymerized at 65°C. <sup>a</sup>sediment 0.21 g; <sup>b</sup>Ar filled only.

polymer, the polymerization were first carried out by the prepolymerization procedure that the styrene was used as a solvent to dissolve the catalyst and polymerized in 5 min at 80°C, then copolymerized with ethylene at 65°C. The volatile organic compound (VOC) in latex could be reduced by the above procedure. The solid contents of latex and the styrene incorporation in the copolymer were changed with the different styrene concentration, polymerization time and ethylene pressure (Table 1). The results showed that the solid contents of latex and the styrene incorporation increased with increase of the styrene concentration. When the dosage of styrene increased to 8 mL, there was slight flocculation in latex. Polymerization experiments with a different time were performed using 6 mL styrene at 5.0 MPa ethylene pressure. With the increase of reaction time, the solid contents of latex increased. However, overtime has no strong effect on the solid contents after 2 h, and the ethylene incorporation in the copolymer continued to increase a little. Increasing the ethylene pressure (entries 8, 3 and 9, Table 1), the solid contents of latex increased, and ethylene

incorporation slightly changed. The pH values of latices were in the range of 7.0–7.5.

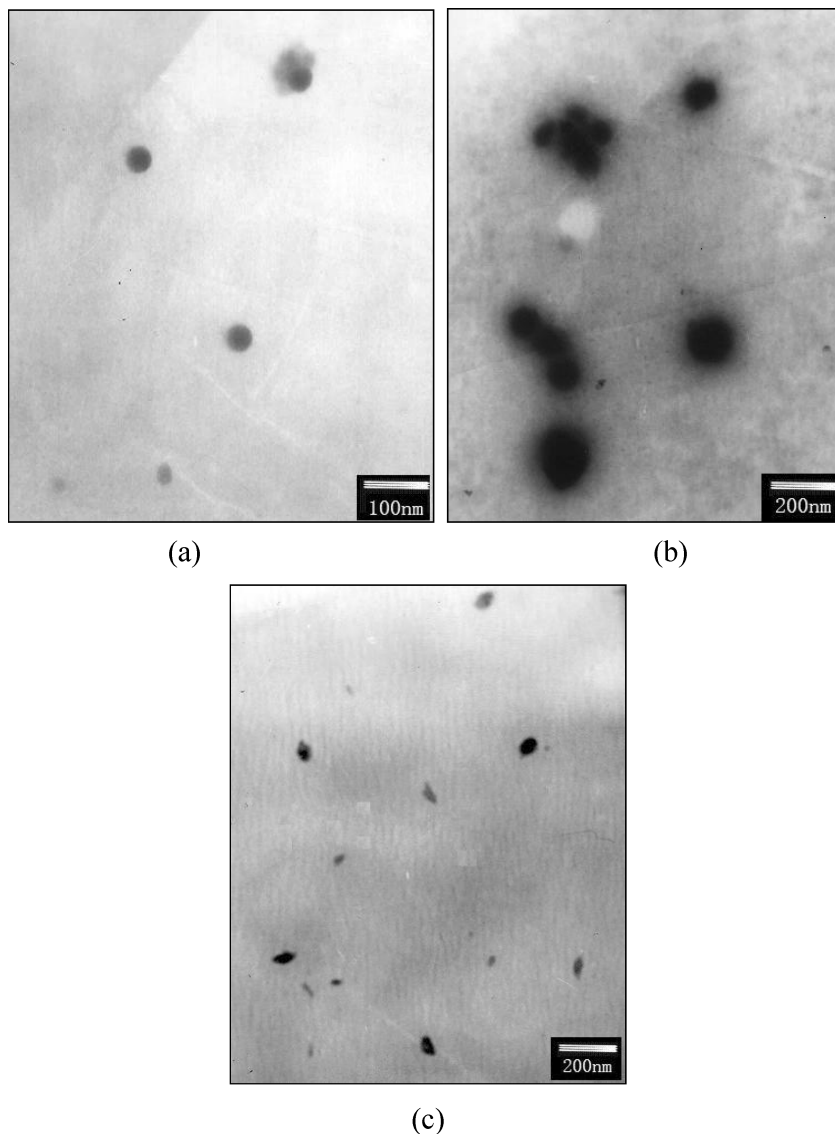
Some methods were adopted to increase ethylene incorporation in the copolymer, such as reducing styrene concentration and adding a few of toluene to increase ethylene solubility in aqueous system and the procedure without prepolymerization used. The results of the catalytic polymerization in water were shown in Table 2, and the stable latex of poly(styrene-*co*-ethylene) was obtained. In comparison with the results in Table 1, the ethylene incorporations in the copolymer were distinctly higher with the addition of toluene (entry 1 in Table 1, entry 10 in Table 2). The copolymerization of styrene and ethylene in emulsion were carried out at different temperatures (entries 10, 11 and 12, Table 2). The catalytic activity and solid content of latex were both lower at 25°C. As the polymerization temperature was enhanced to 50°C, the catalytic activities of ethylene and styrene increased, that is, the solid content of latex and the ethylene incorporation were correspondingly enhanced. However, the molecular weight of copolymer greatly decreased, and the particle size of latex reduced as well. As the temperature continued to enhance to 65°C, the solid content of latex and the ethylene incorporation slightly decreased. This influence attributed to the decomposing of catalyst and the reduction of the solubility of ethylene in the toluene. Thus, the aqueous catalytic copolymerization of ethylene and styrene was appropriate at 50°C. The absolute zeta potential of the latex particle was more than 35 mV, the data elucidated that the latex was stable.

Using the styrene prepolymerization procedure or reducing the quantity of catalyst in aqueous polymerization (entries 13 and 14, Table 2), the solid content of latex and the ethylene incorporation in copolymer both reduced, but the molecular weight of the copolymer increased. With the increase of the solvent quantity, the ethylene solubility in polymerization system increased, thus, the ethylene incorporation largely enhanced (entry 15, Table 2). However, the solid content of latex decreased, and the latex was

**Table 2.** Representative results of catalytic copolymerization of styrene and ethylene in emulsion (catalysts in styrene/toluene)

Entry <sup>#</sup>	T/°C	Solid content/%	pH	St/mol%	Particle size/nm	Zeta/mV	Mn $\times 10^{-4}$	Mw $\times 10^{-5}$	Mw/Mn
10	65	3.30	7.56	86.47	n.d.	n.d.	9.5	2.1	2.2
11	50	3.31	7.90	84.70	21.4	-61.8	9.0	9.9	11.1
12	25	1.10	8.25	87.95	42.3	-35.2	170	38	2.3
13 <sup>a</sup>	50	2.42	8.54	97.13	21.6	-52.6	29	12	4.3
14 <sup>b</sup>	50	2.26	7.71	93.55	35.8	-47.2	110	27	2.4
15 <sup>c</sup>	50	1.21	7.89	71.67	n.d. <sup>h</sup>	n.d.	n.d.	n.d.	n.d.
16 <sup>d</sup>	50	3.01	7.25	88.37	18.0	-56.9	n.d.	n.d.	n.d.
17 <sup>e</sup>	50	2.03	8.38	81.97	24.9	-49.3	13	4.6	3.4
18 <sup>f</sup>	50	0.72	7.36	0.00	25.0	-64.4	n.d.	n.d.	n.d.
7 <sup>g</sup>	65	7.79	7.31	100.00	41.9	-42.0	56	25	4.5

<sup>#</sup>Catalyst: 50  $\mu$ mol, Ni/Rh = 2:1; St = 2 mL; toluene = 2 mL; OP-10: 3.0 g; SDS: 0.5 g; H<sub>2</sub>O: 50 mL. t = 2 h; P = 5.0 MPa; Not prepolymerized. <sup>a</sup>prepolymerized 5 min at 80°C; <sup>b</sup>cat: 25  $\mu$ mol; <sup>c</sup>toluene: 4 mL; <sup>d</sup>PVA added: 0.5 g; <sup>e</sup>IVa/Ni(COD)<sub>2</sub> = 1:2; <sup>f</sup>not adding styrene; <sup>g</sup>polystyrene emulsion in Table 1; <sup>h</sup>n.d.: not determined.



**Fig. 3.** Transmission electron microscopy (TEM) images of polymer latex (a) polystyrene (entry 7 in Table 1); (b) poly(styrene-*co*-ethylene) (entry 11 in Table 2); (c) polyethylene (entry 17 in Table 2).

unstable. The results showed that the addition of excess toluene had a detrimental effect on the stability of latex and the catalytic activity. These phenomena were consistent with Mecking's work (10) that the increase of organic solvent in water led to a decrease in polyethylene yield during the aqueous polymerization. The catalytic activity of IVa/Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> to poly(styrene-*co*-ethylene) was superior to polyethylene (entries 11 and 18, Table 2) in aqueous system. As Ni(COD)<sub>2</sub> was used as an activator in the aqueous copolymerization of styrene and ethylene (entry 17, Table 2), the solid content of latex slightly decreased due to its higher sensitivity to moisture. However, the ethylene incorporation in the copolymer increased, which indicated this catalytic system had higher selectivity and activity to ethylene. Whether Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> or Ni(COD)<sub>2</sub> was utilized as activator, the pH values of latex

were in the range of 7.0~8.5. In contrast to the absent of toluene, the pH for poly(styrene-*co*-ethylene) latex slightly enhanced in the presence of toluene.

The compounding of non-ionic and anion surfactant had the functions of the steric and static stabilization in emulsion polymerization, which was advantageous to achieve the stable latex. The results also showed that the particle sizes of polymer latex were in the range of 20~50 nm in Table 2. The particle size of polystyrene latex and poly(styrene-ethylene) latex obtained at room temperature were larger. The PVA was added to the emulsion polymerization system as a protection colloid (entry 16, Table 2), and the result revealed that the particle size of the polymer latex decreased. The hydrophilic PVA could lower the critical micelle concentration in emulsion and had the steric protection on latex particles. Meanwhile, the protection

also kept the ethylene from entering the latex particles to implement copolymerization, thus ethylene incorporation in the copolymer and the solid content of latex decreased.

The molecular weights of polymers prepared by catalytic polymerization in aqueous system and determined by GPC were higher, and Mw varied from  $2 \times 10^5$  to  $4 \times 10^6$ . Under the same conditions, the Mw of poly(styrene-co-ethylene) was lower than that of polystyrene (entries 10 and 7, Table 2). The molecular weight of copolymer obtained at 25°C was higher than that at 65°C, and the polydispersity of both copolymers were narrower. With the addition of the catalyst decreasing (entry 14, Table 2), the molecular weight of the polymer increased and the polydispersity of the polymer became narrow since the chain transfer in catalytic polymerization reduced. As IVa/Ni(COD)<sub>2</sub> was used as catalysts in place of IVa/Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>, the Mw of poly(styrene-co-ethylene) obtained was decreased, and the polydispersity of the copolymer became narrow (entries 11 and 17, Table 2).

The latex particles were visualized by transmission electron microscopy (TEM, Fig. 3). The polyethylene particles were quasi-spherical, which was related to the crystallinity of polyethylene. While the particles of polystyrene and poly(styrene-co-ethylene) were spherical.

#### 4 Conclusions

The salicylaldehyde neutral Ni(II) complex, activated by Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> or Ni(COD)<sub>2</sub>, was applied to the catalytic polymerization of styrene, ethylene and their copolymerization in emulsion. Using the combination system of non-ionic and anion surface active agent, the stable polymer latex was achieved. The solid contents of latex were up to 10%, and the latex particles sizes were in the range of 20~50 nm. The results of NMR and GPC indicated that the polymers obtained were a block copolymer with high molecular weight. The ethylene incorporation in copolymer increased evidently by reducing the concentration of styrene and adding toluene, and was up to 28 mol%. The molecular weight of the copolymer catalyzed in aqueous phase at 25°C was distinctly higher than that of the copolymer at 65°C, and the polydispersity of the copolymer was narrower. The catalytic activity of IVa/Ni(COD)<sub>2</sub> to poly(styrene-co-ethylene) was lower than that of IVa/Rh(acac)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>,

but the ethylene incorporation in the copolymer was high. The catalytic copolymerization of styrene and ethylene in emulsion is very important in both academic research and industrial applications, the further research on catalysts and the properties of the copolymer is being carried out.

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