CHAPTER 3

RESULTS AND DISCUSSION

3.1 Result of the products synthesized by a microwave radiation method.

3.1.1 Effect of liquid media

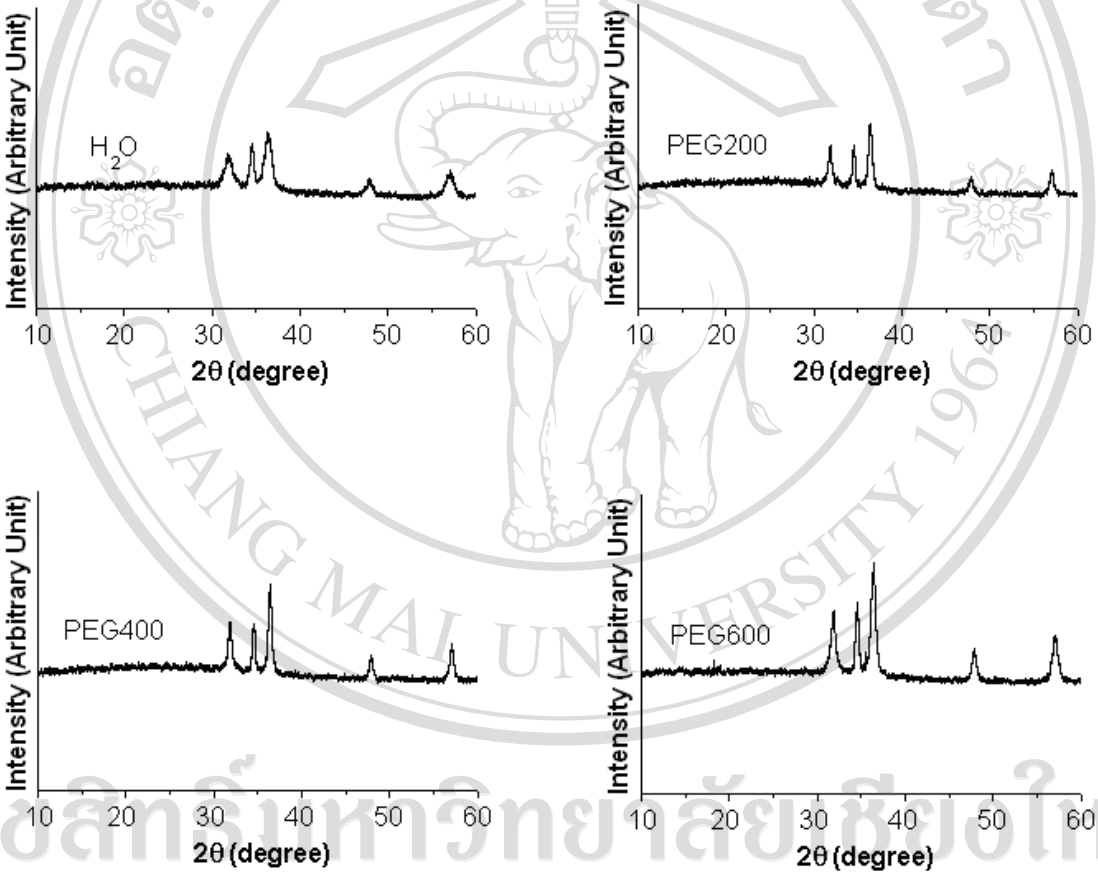


Figure 3.1 XRD patterns of the products synthesized by a microwave radiation using H_2O, PEG200, PEG400, PEG600 as liquid media.

Fig 3.1 shows XRD spectra of the products synthesized using 1:15 molar ratio of $Zn(NO_3)_2$ to NaOH in H_2O and PEG with different MWs as a liquid media. All diffraction peaks can be indexed and specified that the products crystallized as hexagonal structure with no detection of impurities such as metallic zinc. These patterns were consistent with the literature data (JCPDS file no. 075-1526) [65]. Its diffraction peaks were narrow and sharp, specifying that the X-ray radiation reflected and diffracted from atoms in lattice order. The strongest intensity peak was at 2θ = 36.4 degrees belonging to the (101) plane of the products. In addition, we found that the crystallinity of the products strongly depends on liquid media. By using H_2O as a liquid medium, the XRD peak was broad and diffuse, and its intensities was rather low, indicating that the product was composed of a number of nanoparticles and the degree of crystallinity was rather low. When reaction media was changed from H_2O to PEG with different MWs, the XRD peaks became sharper and narrower, and the intensities were stronger. It impels that the degree of crystallinity of the products continuously increased with the MWs of PEG increases. Comparing the intensities of (002) peaks for different products, they became higher when the solvents were changed from H_2O to PEG with different MWs; especially, for higher MW. They were specified that the crystalline products grew along the c axis. Calculated lattice parameters [66] a = 3.23 and c = 5.18 were also in accordance with those of the literature data. It is worth to note that c/a was 1.60, indicating the preferential growth process along the c axis.

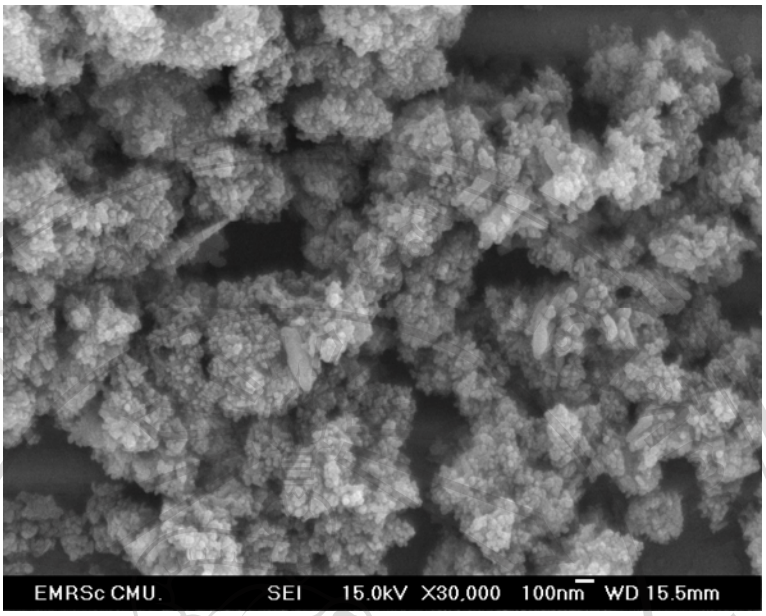


Figure 3.2 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in water solution.

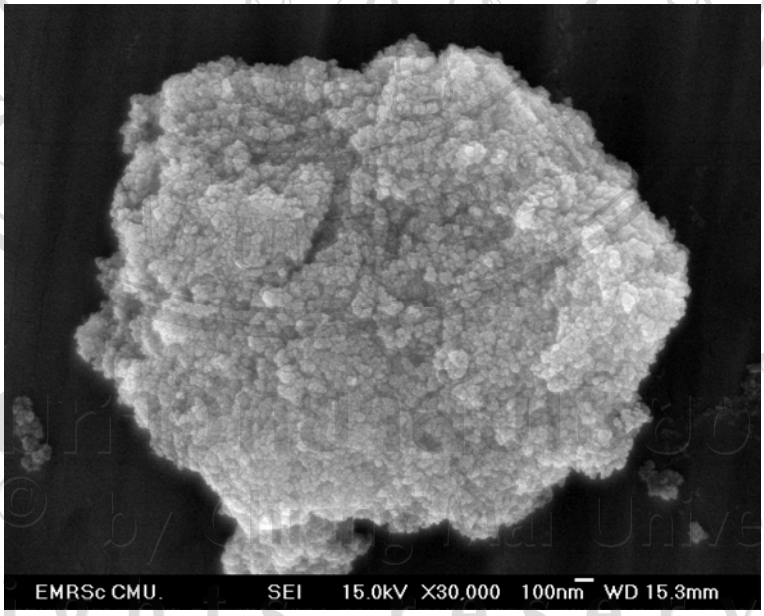


Figure 3.3 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in PEG200 solution.

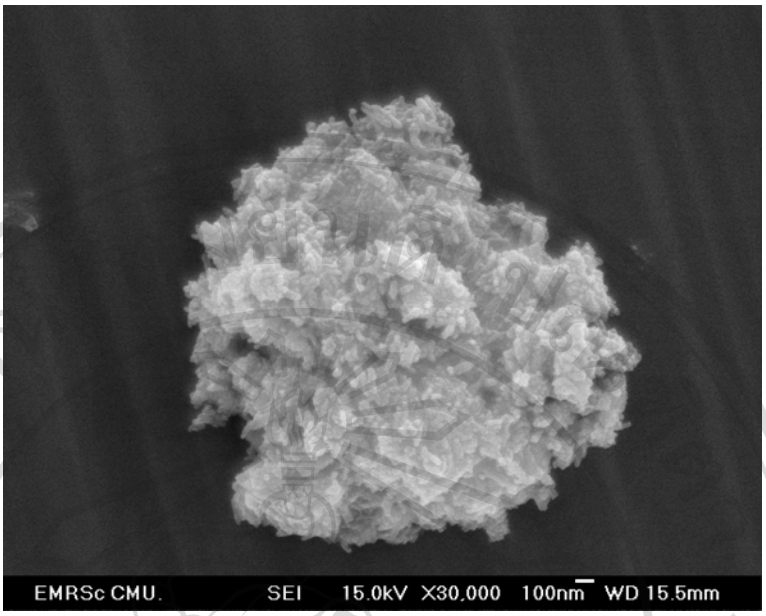


Figure 3.4 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in PEG400 solution.

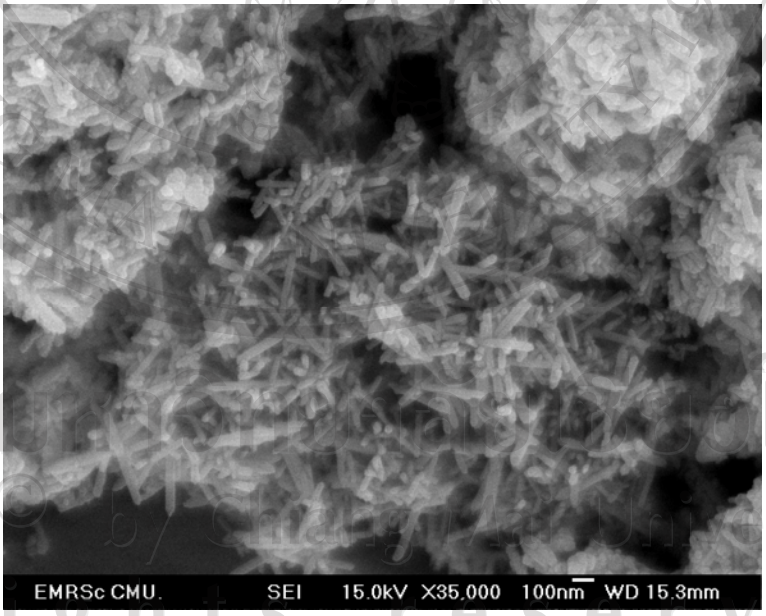
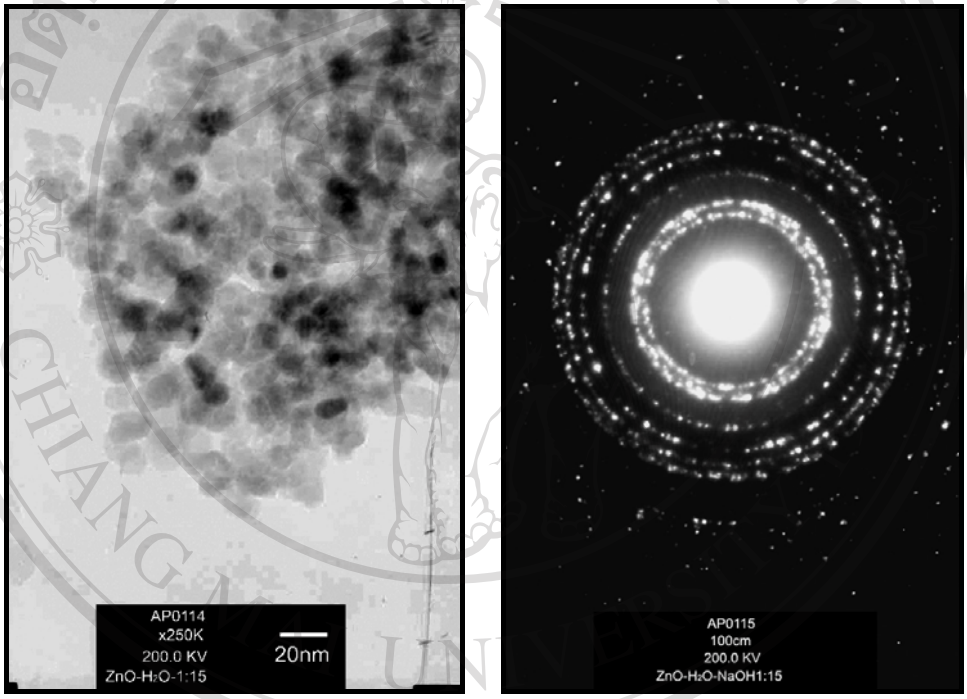


Figure 3.5 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in PEG600 solution.

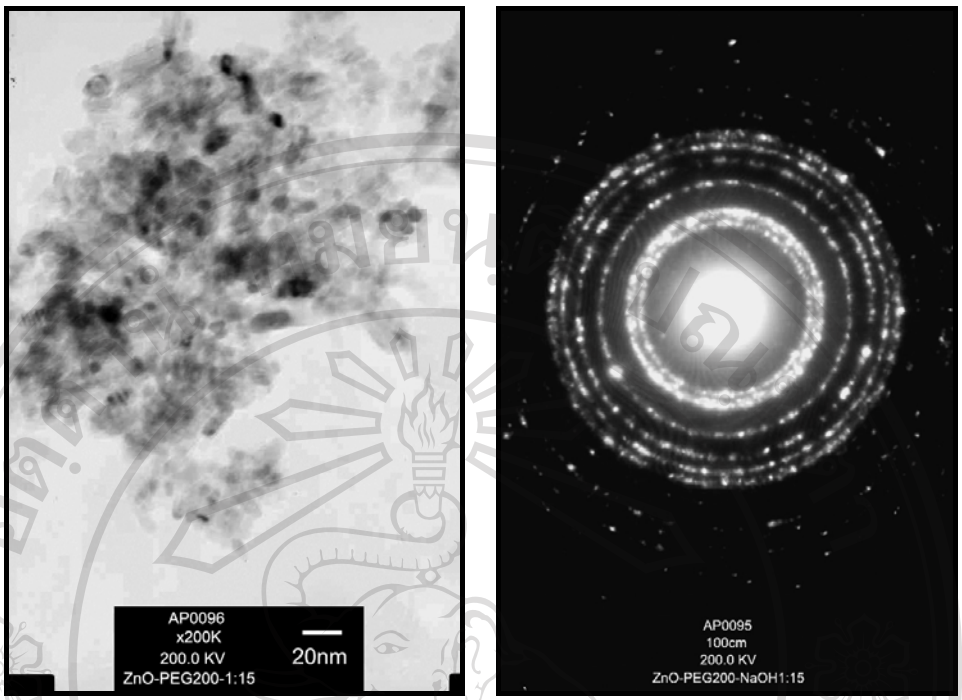
SEM images of the samples (Figures 3.2-3.5) show that morphologies of the products prepared using different liquid media are totally different. In PEG-free solution, a number of nanoparticles were detected. A number of short nanorods were synthesized in PEG200. The length of nanorods was increased when the molecular weight of PEG increased.



(a) (b)

Figure 3.6 TEM images and SAED pattern of the product prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in water solution.

(a) Bright field image (b) SAED pattern



(a) (b)

Figure 3.7 TEM images and SAED pattern of the product prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in PEG200 solution.

(a) Bright field image (b) SAED pattern

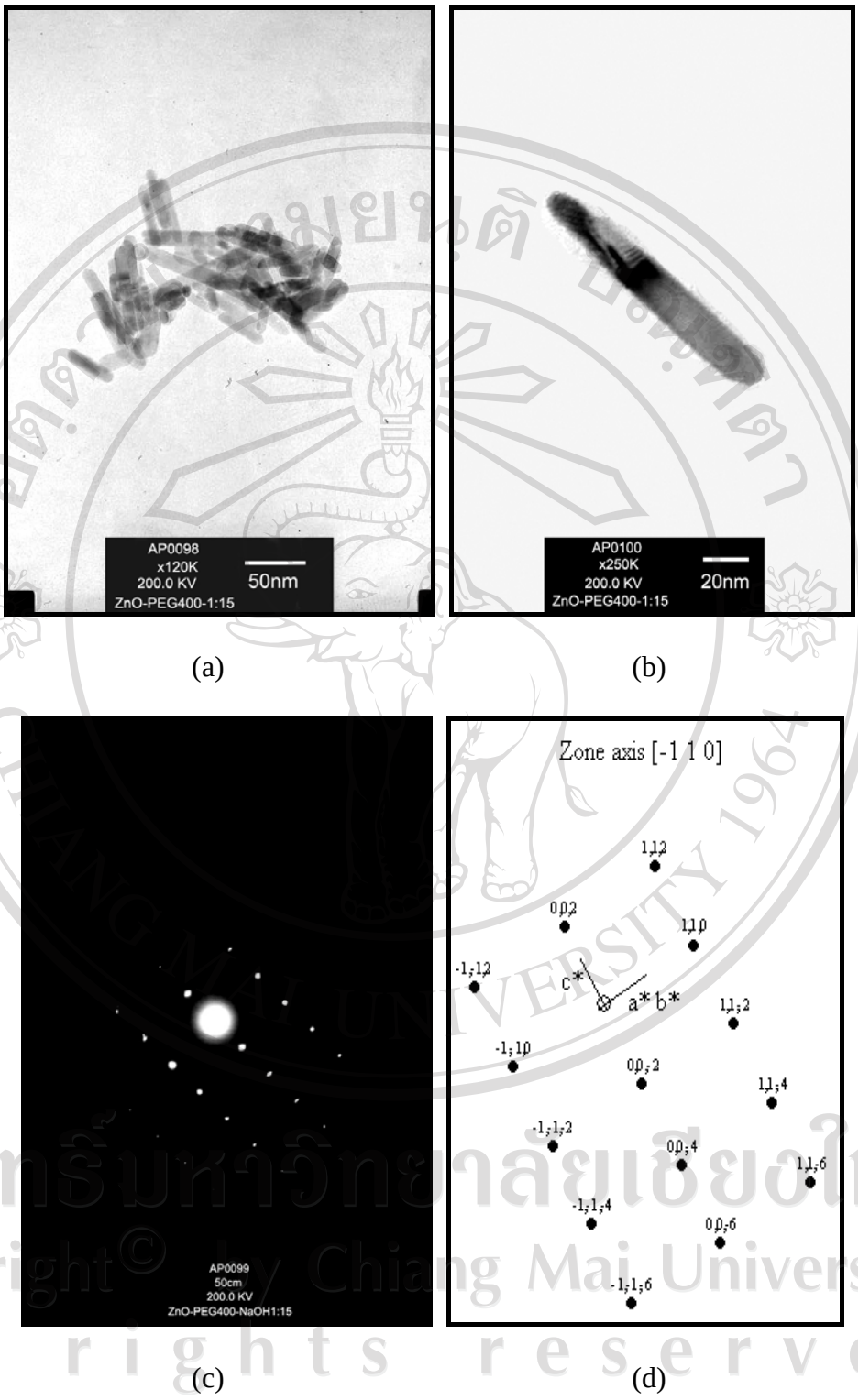


Figure 3.8 TEM images, SAED and simulated pattern of the product prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in PEG400 solution.

(a) and (b) Bright field images (c) SAED pattern (d) simulated pattern

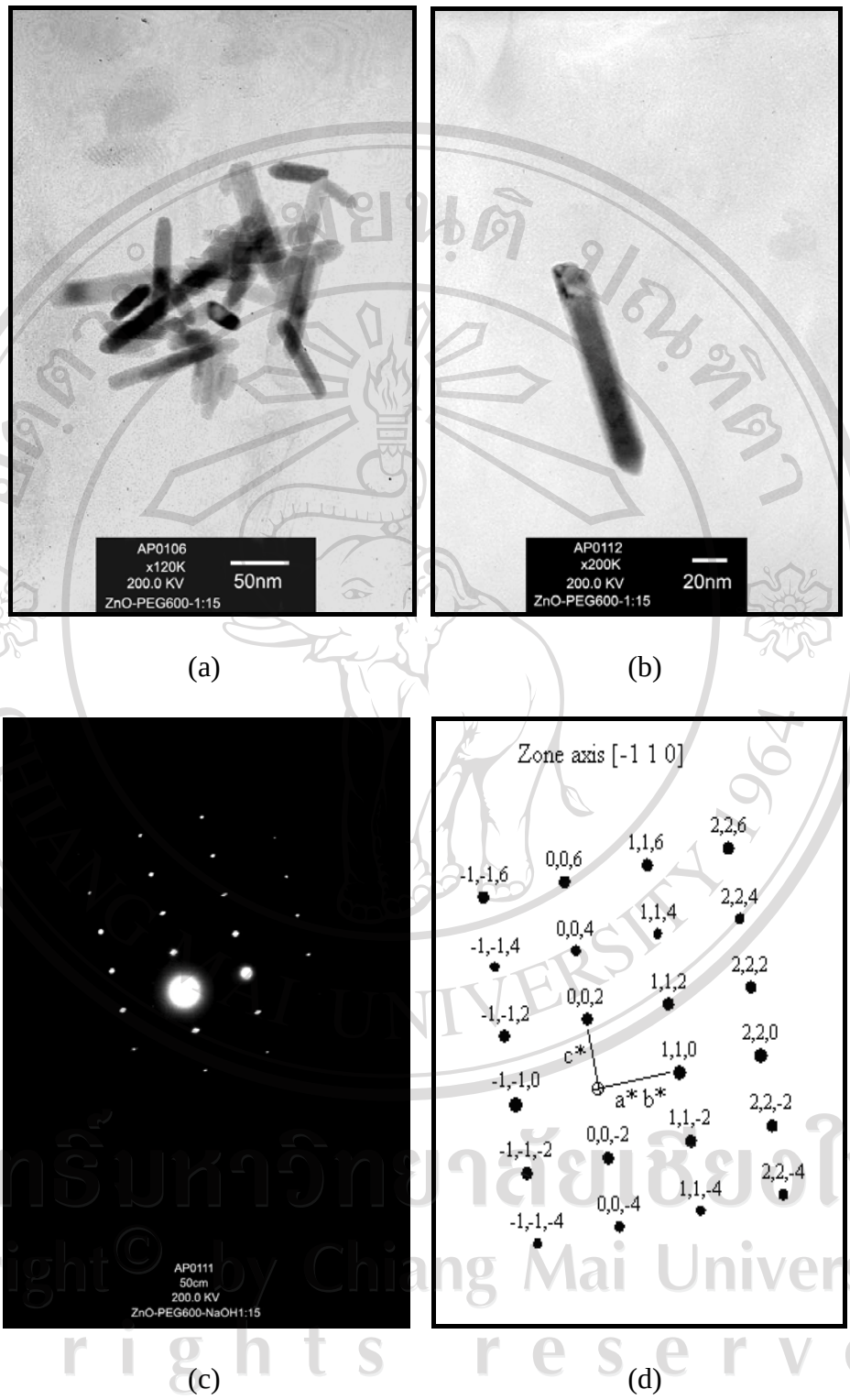


Figure 3.9 TEM images, SAED and simulated pattern of the product prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents in PEG600 solution.

(a) and (b) Bright field images (c) SAED pattern (d) simulated pattern

TEM images of ZnO synthesized using different liquid media are shown in Figures 3.6-3.9. In H_2O solvent, the product was composed of 10 nm nanoparticles which grew at the same rates in all directions. In PEG solvents, the products gradually changed from nanoparticles into nanorods. They were the longest for PEG600. Morphological development shows that the growth of ZnO nanocrystals was inhibited by the selective adsorption of PEG molecules on side walls of the nuclei, which was the same to limit the lateral growth but their tips remain uncovered. Thus, growth in the axial length of the nanorods became faster. When MW of PEG was higher, inhibition of the radial growth became more intense [67]. The nanorods were the longest in PEG600. The SAED patterns of the samples synthesized using water and PEG200 as a liquid media appeared as bright spots arranging in concentric rings. These signify that the products were polycrystalline. The calculated d-spacing of each ring, which shown in table 3.1 and 3.2, corresponded to the (100), (002), (101), (102), (110), (103) and (112) planes in good agreement with the XRD analysis. The diffraction patterns of the samples synthesized using PEG400 and PEG600 as liquid media showed systematic array of diffraction spot with the electron beam in the [-110] direction. These patterns corresponded to a single crystal of hexagonal structure ZnO.

Table 3.1 Ring diffraction pattern values of product prepared using water as a liquid medium.

Ring No.	Diameter (mm)	Radius (mm)	Calculated d-spacing (Å)	d-spacing (JCPDS 075-1526)	Plane hkl
1	17.8	8.90	2.80	2.81	1 0 0
2	19.2	9.60	2.60	2.60	0 0 2
3	20.2	10.10	2.47	2.47	1 0 1
4	25.6	12.80	1.95	1.91	1 0 2
5	30.2	15.10	1.65	1.62	1 1 0
6	32.0	16.00	1.56	1.47	1 0 3
7	36.2	18.10	1.38	1.38	1 1 2

Table 3.2 Ring diffraction pattern values of product prepared using PEG200 as a liquid medium.

Ring No.	Diameter (mm)	Radius (mm)	Calculated d-spacing (Å)	d-spacing (JCPDS 075-1526)	Plane hkl
1	17.7	8.85	2.82	2.81	1 0 0
2	19.2	9.60	2.60	2.60	0 0 2
3	20.1	10.05	2.48	2.47	1 0 1
4	25.9	12.95	1.93	1.91	1 0 2
5	30.5	15.25	1.64	1.62	1 1 0
6	32.2	16.10	1.55	1.47	1 0 3
7	36.2	18.10	1.38	1.38	1 1 2

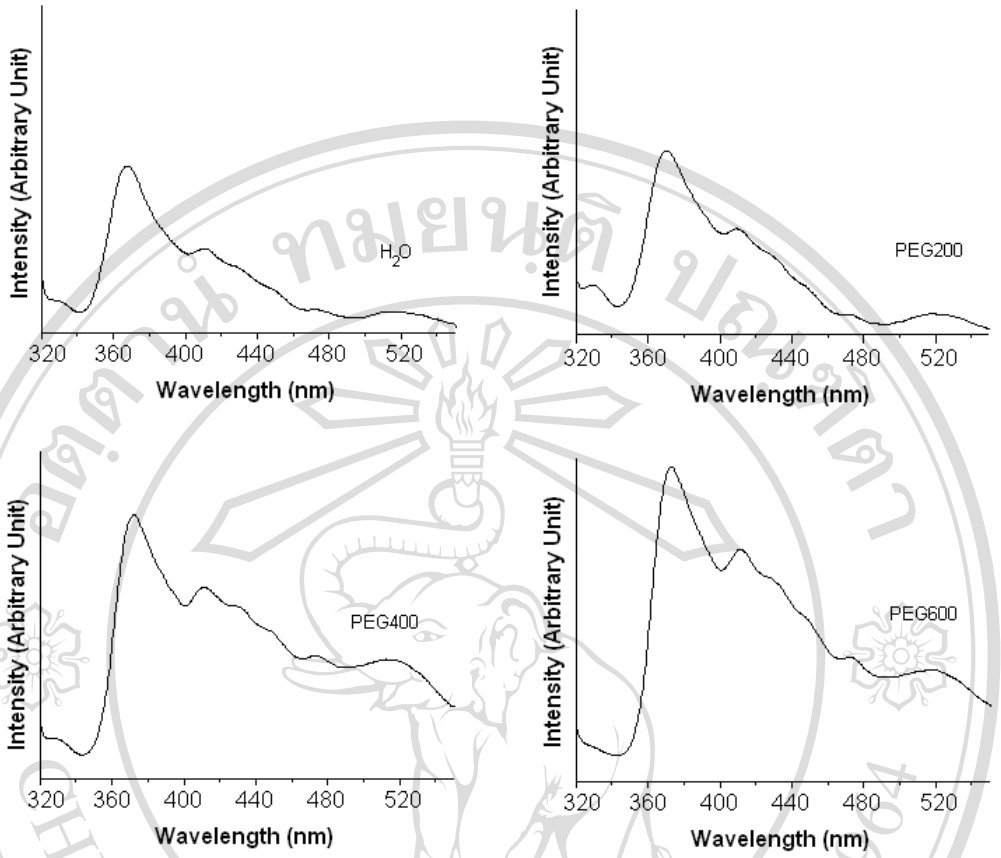


Figure 3.10 PL spectra of the products synthesized using a microwave radiation in H_2O, PEG200, PEG400 and PEG600 solution.

PL spectra with 300 nm excitation wavelengths are shown in Figures 3.10. All spectra show the intrinsic peaks with their surrounding shoulders. An intense, sharp and dominated peak at 370 nm in the UV region was attributed to near band edge emission [68]. The surrounding shoulders at approximately 410 nm were caused by the transition process relating to defects. For the sample synthesized using different liquid media, the intensities for the products synthesized in PEG are higher than that for the product synthesized in water. They were increased with the increase in the MW of PEG to the highest for the product synthesized in PEG600, due to the long nanorods.

3.1.2 Effect of surfactants

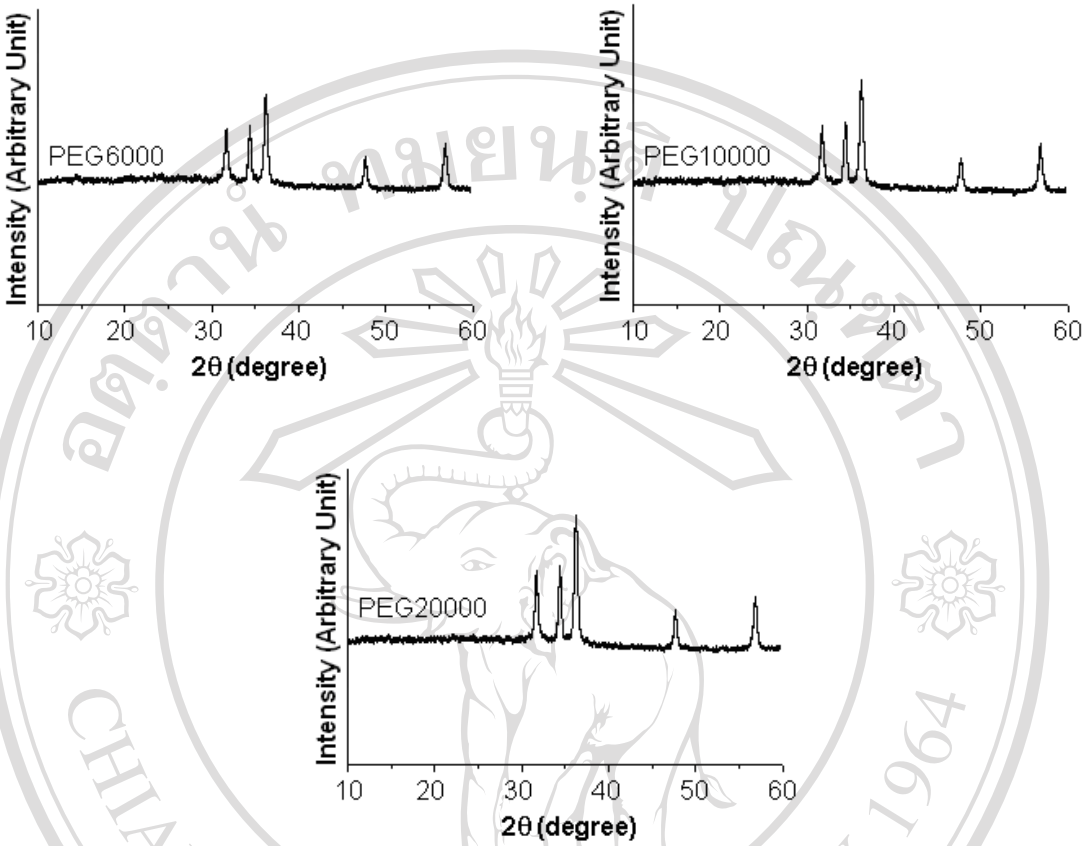


Figure 3.11 XRD patterns of the products synthesized by a microwave radiation using PEG6000, PEG10000, PEG20000 as surfactant.

Figure 3.11 is the representative XRD pattern of samples prepared using PEGs with different MWs as a surfactant. All the diffraction peaks were indexed to be hexagonal structure of ZnO, which are consistent with that of the JCPDS file no. 075-1526. The sharp peaks indicated good crystallization of ZnO. The strongest intensity peak is at 2θ = 36.4 degrees and diffracts from the (101) plane of the products. No peaks of impurities were detected. By using heavier PEG, the intensities of the products became stronger. Thus, we can conclude that the use of heavier PEG resulted in high crystallinity of the products.

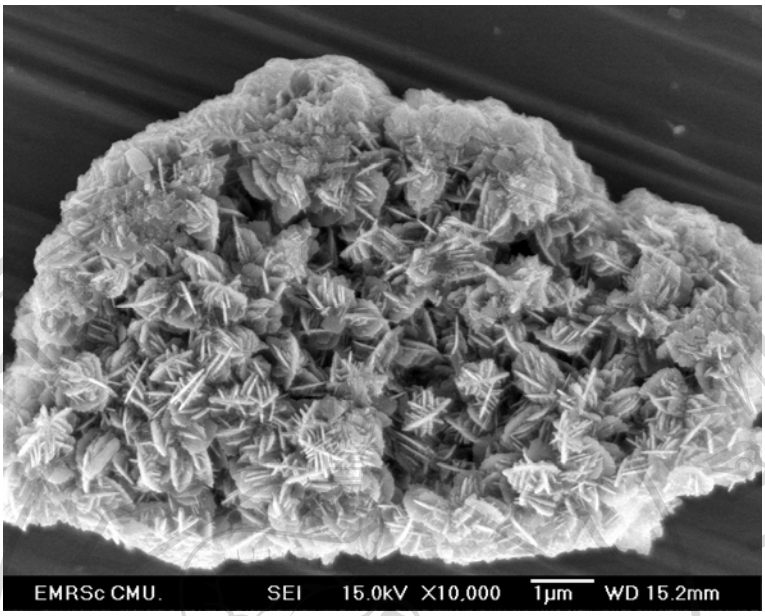


Figure 3.12 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents with PEG6000.

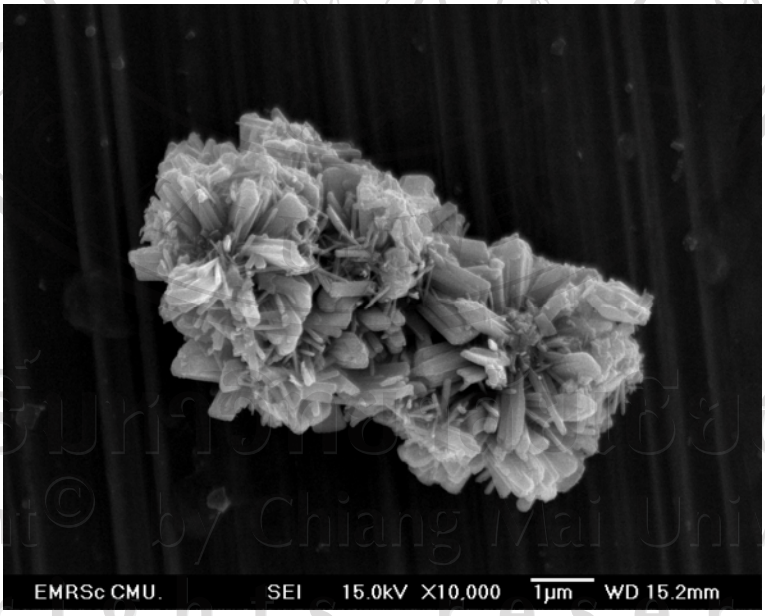


Figure 3.13 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents with PEG10000.

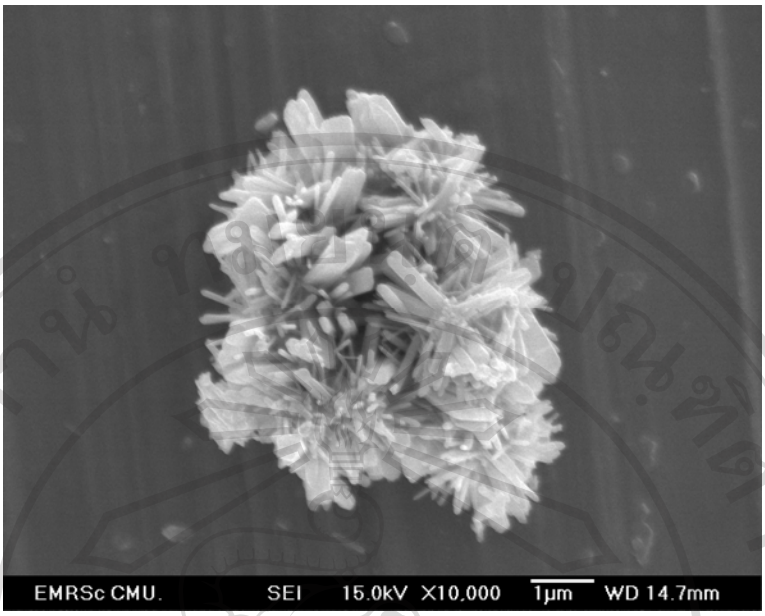


Figure 3.14 SEM image of the sample prepared using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents with PEG20000.

Morphologies of the products synthesized in the solutions containing different molecular weights of PEG are shown in Figures 3.12-3.14. For PEG 6000, plate-shaped particles with different orientations were synthesized. In general, PEG chain molecules become lengthened with their MWs increase. For PEG 10000, their chain molecules were long enough to entangle these nuclei in the solution to form clusters of nuclei with active sites residing on their surfaces. They have different orientation and finally formed clusters of rod-shaped. For PEG20000, these cluster transformed into cluster of rod shape at which the diameter of each rod was decreased in order to reduce their surface areas and to minimize the interfacial free energies. [69]

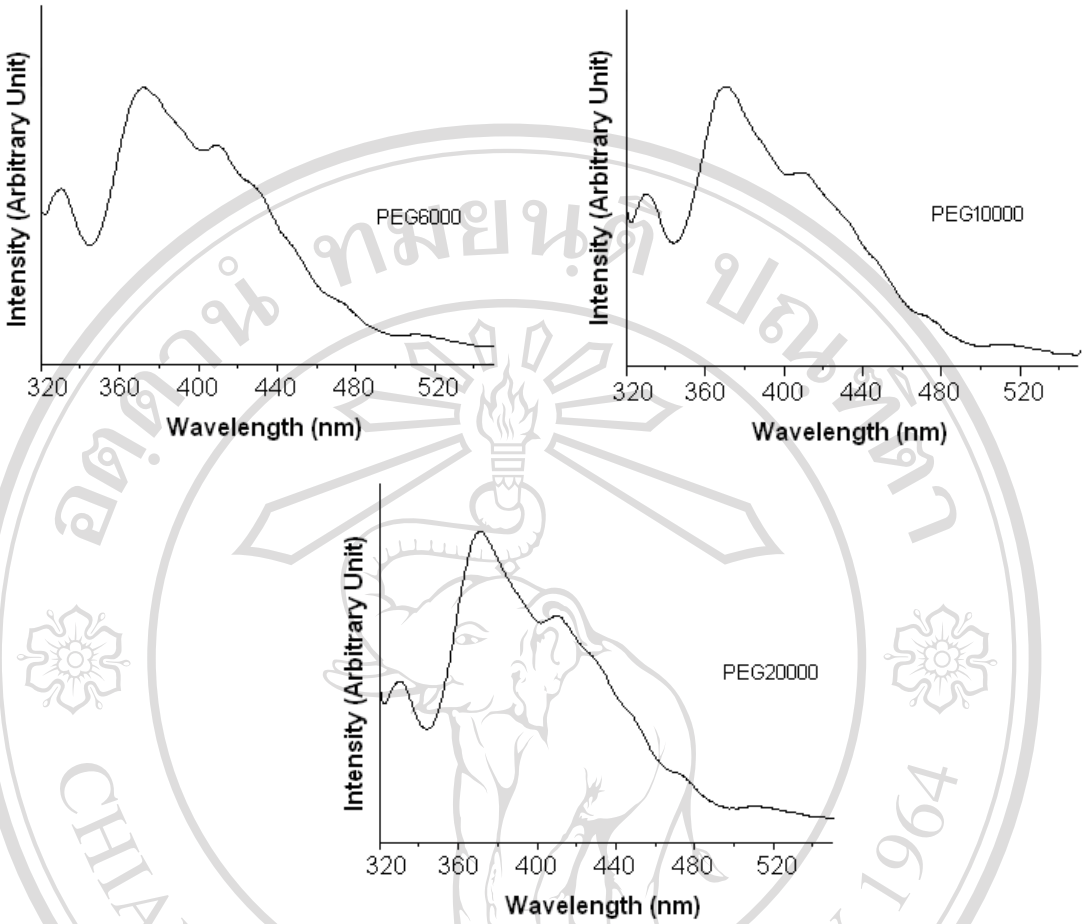


Figure 3.15 PL spectra of the products synthesized by a microwave radiation using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents with PEG6000, PEG10000 and PEG20000 as surfactant.

PL spectra with 300 nm excitation wavelengths are shown in Figures 3.15. Similar to above discussion, all spectra show the intrinsic peaks with their surrounding shoulders. An intense, sharp and dominated peak at 380 nm in the UV region was attributed to near band edge emission [68]. The surrounding shoulders at approximately 410 nm were caused by the transition process relating to defects. The relative intensities of products synthesized in heavier PEG MW are higher than those for lower MWs. It may be due to the longer nanorods.

3.1.3 Effect of the amount of PEG20000

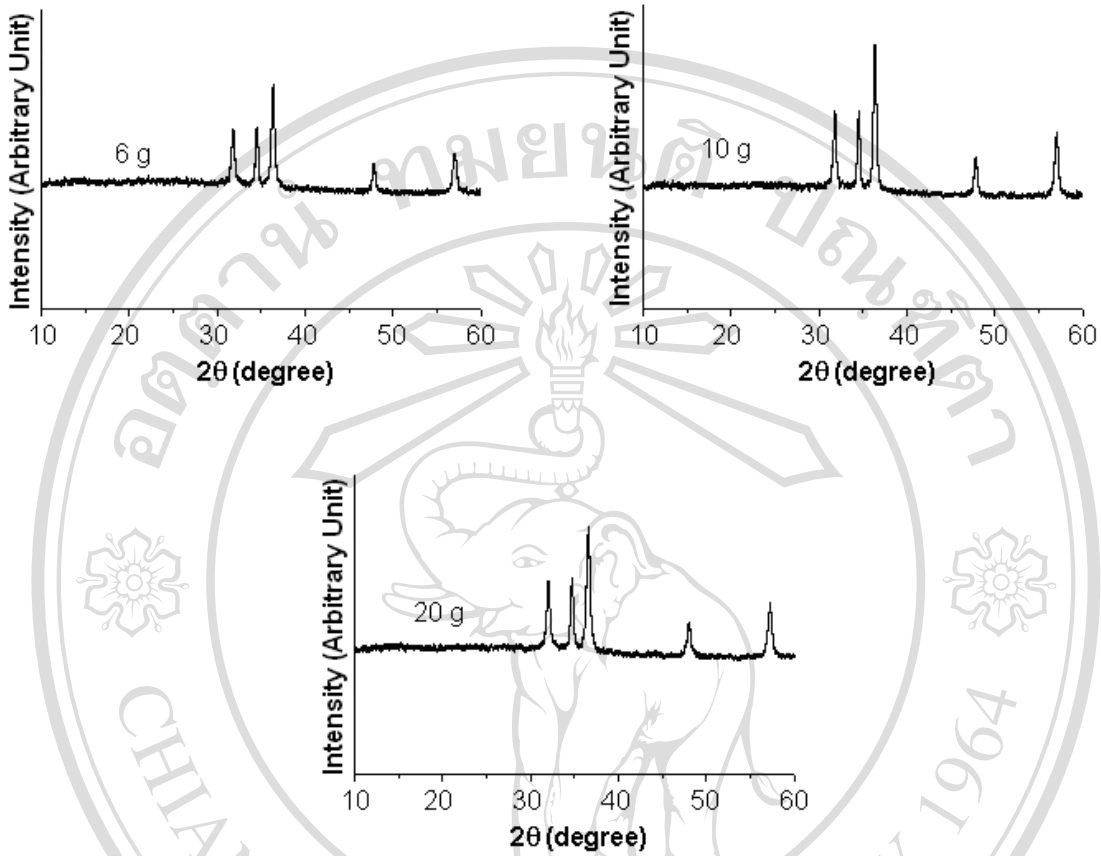


Figure 3.16 XRD patterns of the products synthesized by a microwave radiation using PEG20000 at 6, 10, 20 g as surfactant.

In order to study the effect of amount of PEG20000 on their crystallinity, the samples were prepared using 6 g, 10 g and 20 g PEG20000, respectively. XRD pattern of these samples were shown in figure 3.16. It was found that the crystallinity of the sample was increased when the amount of PEG20000 increased.

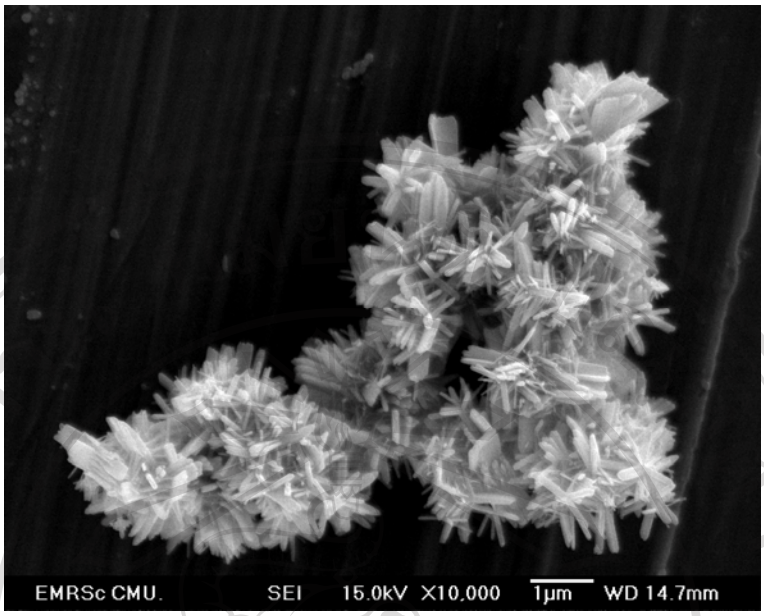


Figure 3.17 SEM image of the product prepared using $Zn(NO_3)$:NaOH = 1:15 as starting reagents using amount PEG 20000.

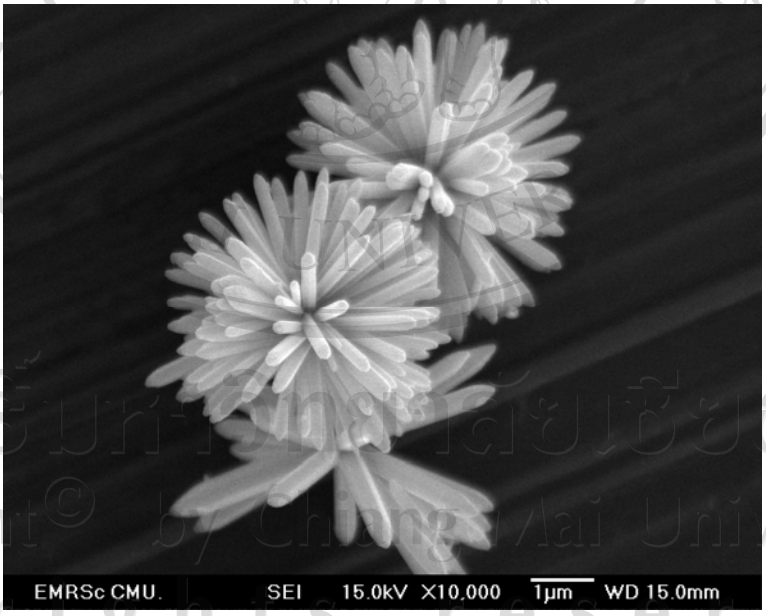


Figure 3.18 SEM image of the product prepared using $Zn(NO_3)$:NaOH = 1:15 as starting reagents using PEG 20000.

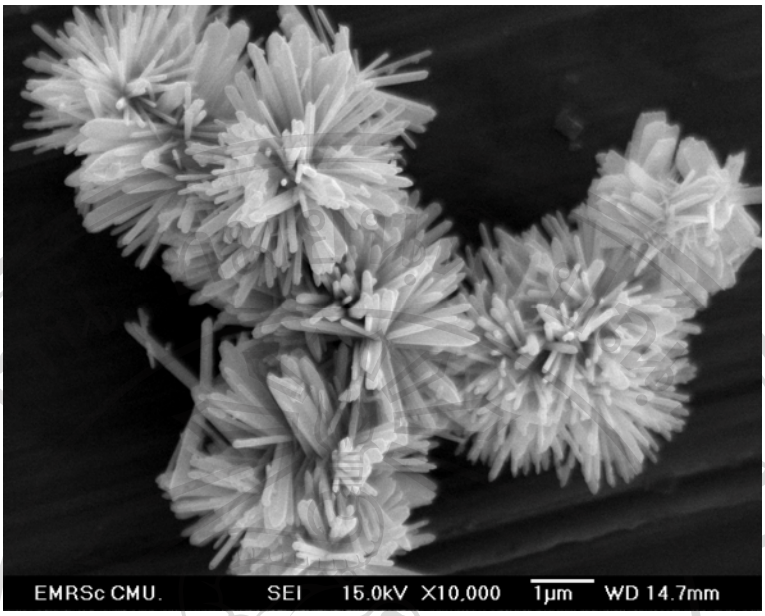
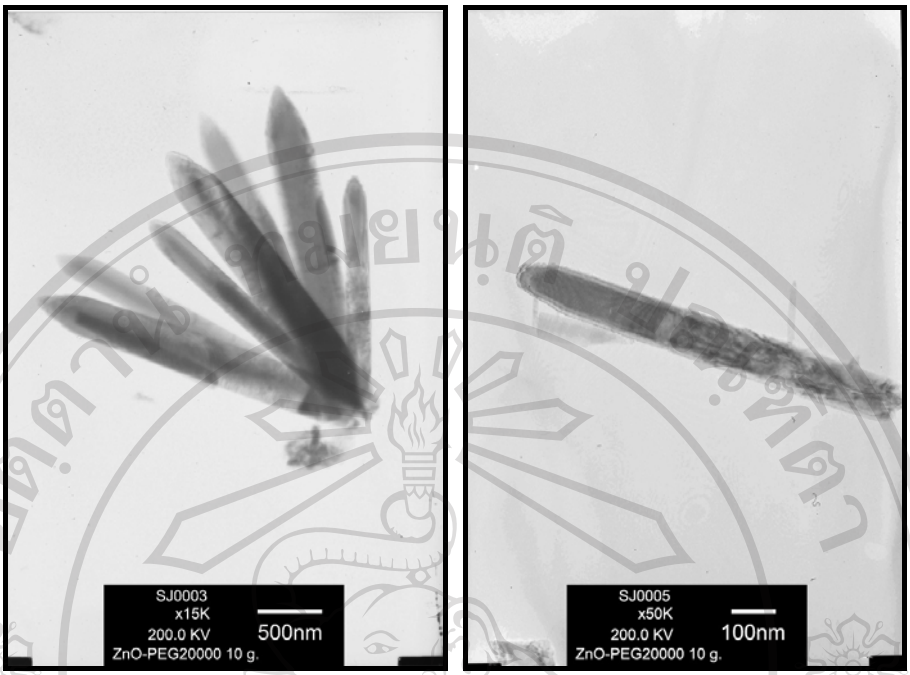
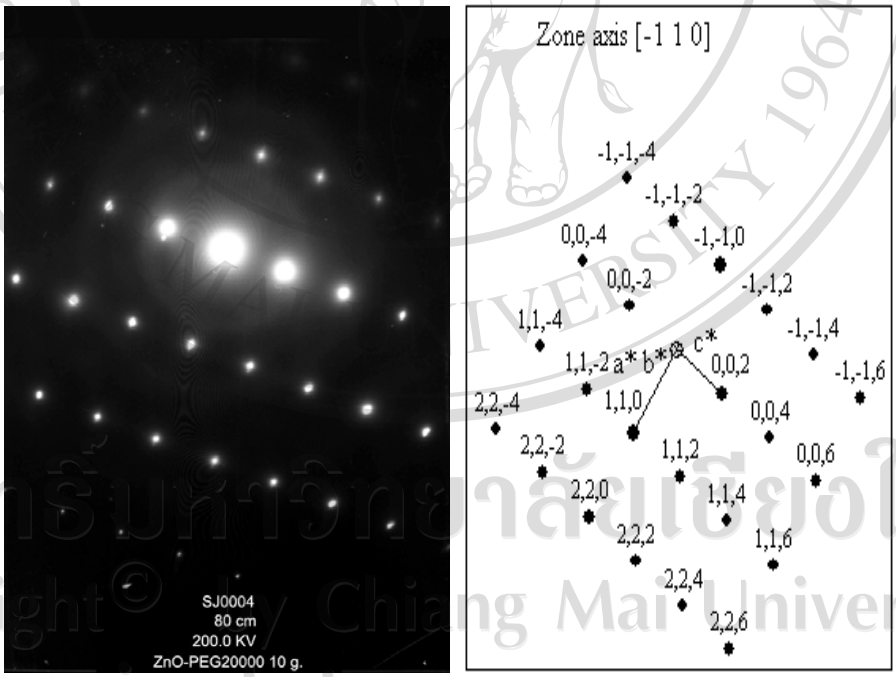


Figure 3.19 SEM image of the product prepared using $Zn(NO_3)$:NaOH = 1:15 as starting reagents using PEG 20000.

Figures 3.17-3.19 shows SEM images of the samples prepared using different amounts of PEG20000. When different amount of PEG20000 with the same precursor ratio were used, different morphologies were synthesized. For 2 g and 6 g PEG20000, the products which using 2 g and 6 g PEG20000 were composed of non-uniform rods and plates, caused by the incomplete capping on the ZnO crystallographic faces. When 10 g PEG20000 was used, flower of nanorods were detected. However, the nanorods flowers still existed in the product prepared using 20 g PEG20000, but the rods were non-uniform. Thus excess PEG20000 was un-necessary.



(a) (b)



(c) (d)

Figure 3.20 TEM images, SAED and simulated patterns of the product synthesized using PEG 20000 as a surfactant.

(a) and (b) Bright field images (c) SAED pattern (d) simulated pattern

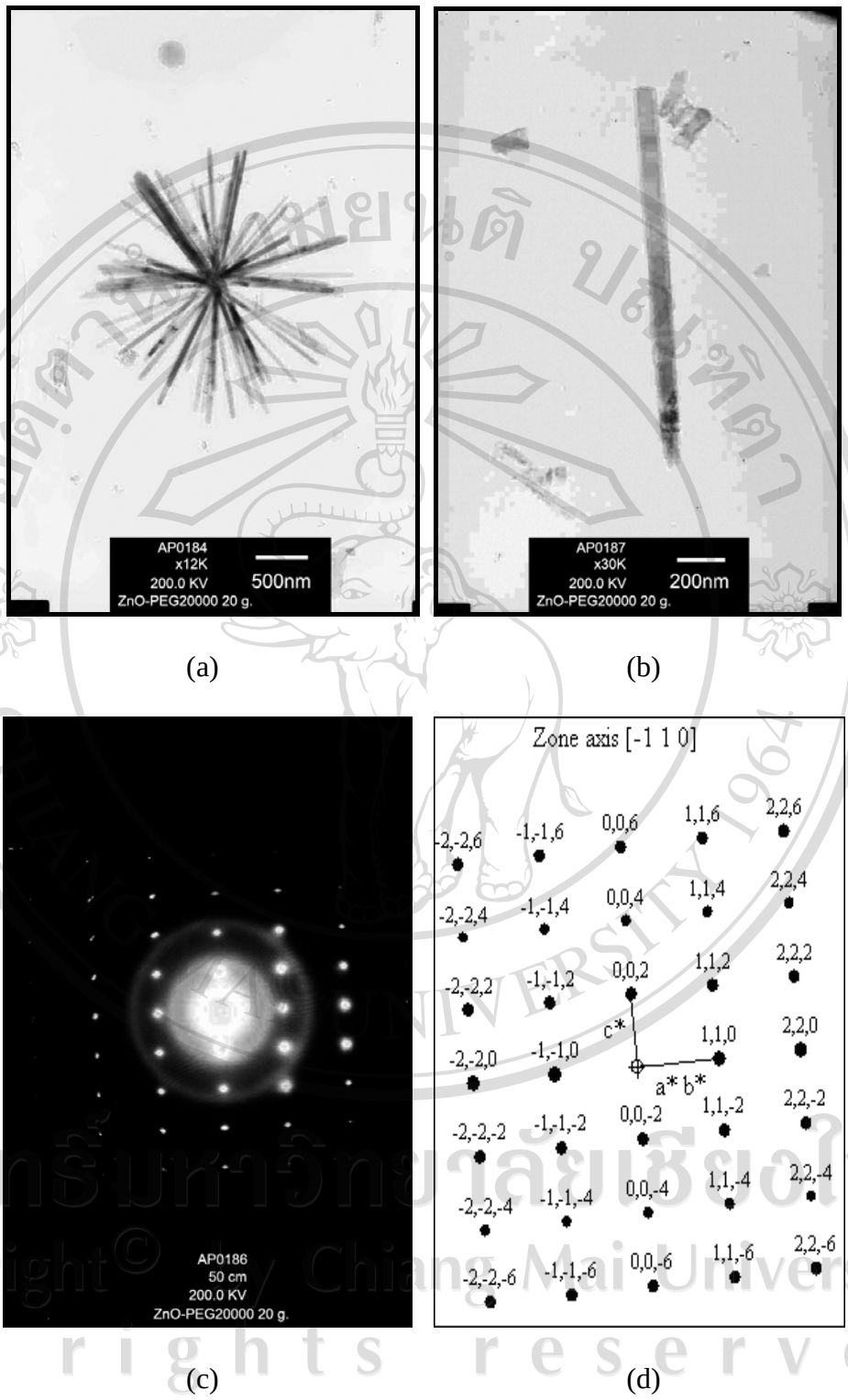


Figure 3.21 TEM images, SAED and simulated patterns of the product synthesized using PEG 20000 as a surfactant.

(a) and (b) Bright field images (c) SAED pattern (d) simulated pattern

Figures 3.20 and 3.21 showed TEM images, SAED and simulated pattern of ZnO nanorods synthesized using 10 g and 20 g PEG20000, respectively. For 10 g PEG20000, ZnO nanorods with the length of 2.3 μm and 274 nm in diameter were synthesized. When 20 g PEG20000 was used, they were 1.2 μm long and 54 nm in diameter. From these results, It was found that diameter of nanorods was decreased when the amount of PEG20000 increased. It was due to the surplus capping of PEG molecule on the side wall of ZnO nanorods which was the cause it inhibit the growing of crystals. As a result, diameter of ZnO nanorods synthesized using 20 g PEG20000 was less than that using 10 g PEG20000. SAED patterns of these samples showed rectangular array of diffraction spots with the electron beam in the [-110] direction. These patterns corresponded to ZnO hexagonal structure. The simulated diffraction patterns showed systematic array of spots, corresponding to the pattern obtained from the experiment.

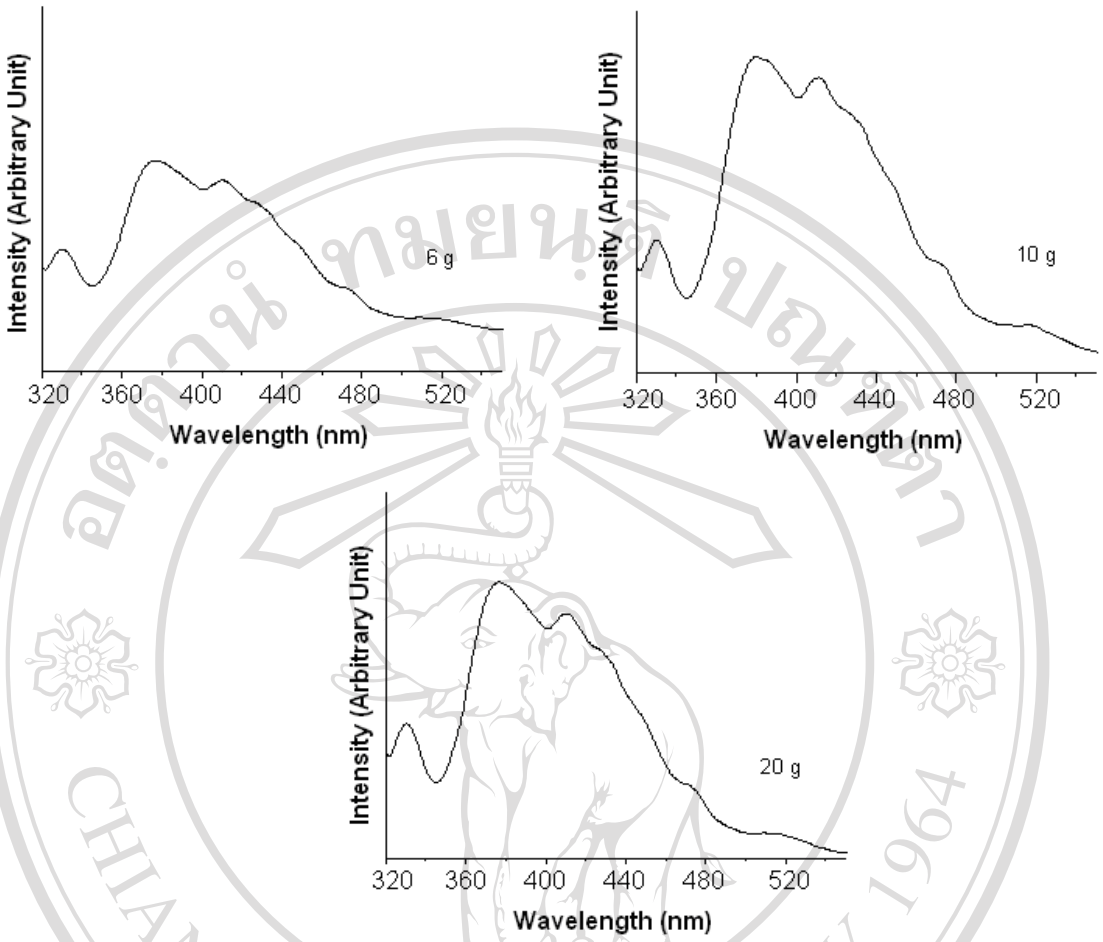


Figure 3.22 PL spectra of the products synthesized by a microwave radiation using $Zn(NO_3)_2$:NaOH = 1:15 as starting reagents with 6 g, 10 g and 20 g PEG20000 as surfactant.

PL spectra with 300 nm excitation wavelengths are shown in Figures 3.22. Similar to above discussion, all spectra show the intrinsic peaks with their surrounding shoulders. An intense, sharp and dominated peak at 380 nm in the UV region was attributed to near band edge emission [68]. The surrounding shoulders at approximately 410 nm were caused by the transition process relating to defects. The relative intensities of products synthesized in 10g PEG20000 are higher than other ones. It may be due to the longer nanorods.

3.2 Result of products synthesized by a ultrasonic radiation method

3.2.1 Effect of $Zn(NO_3)_2$ to NaOH ratios

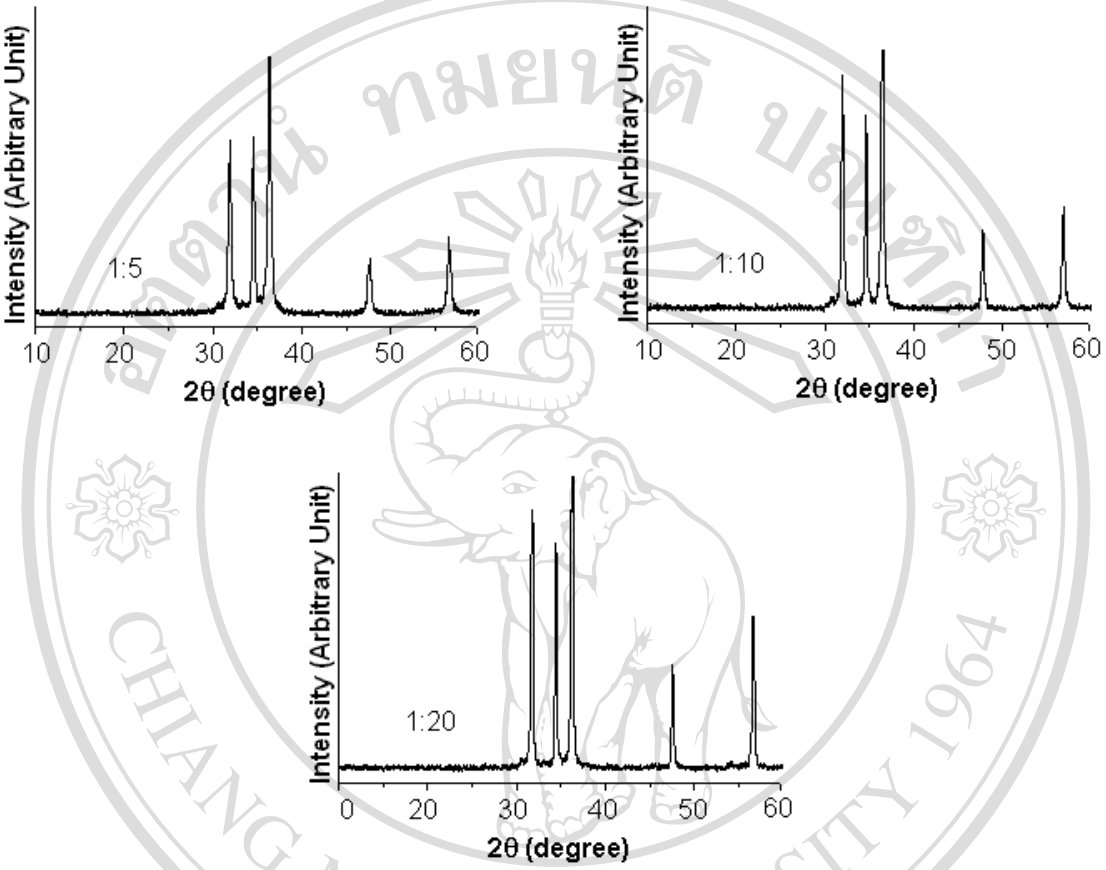


Figure 3.23 XRD patterns of the samples synthesized using different $Zn(NO_3)_2$ to NaOH ratios.

Figure 3.23 shows the XRD patterns of the samples synthesized using different $Zn(NO_3)_2$ to NaOH ratios. All diffraction peaks can be indexed to be ZnO hexagonal structure with P63mc space group with oxygen ions composing a hcp structure and zinc ions in only haft tetrahedral holes. These patterns were in good agreements with that of the JCPDS file no. 075-1526. There were no impurities peaks such as metallic zinc, were detected. The sharp peaks indicated good crystallization of

ZnO nanocystals. The strongest intensity peak was at 2θ = 36.4 degrees and diffracts from the (101) plane of the products.

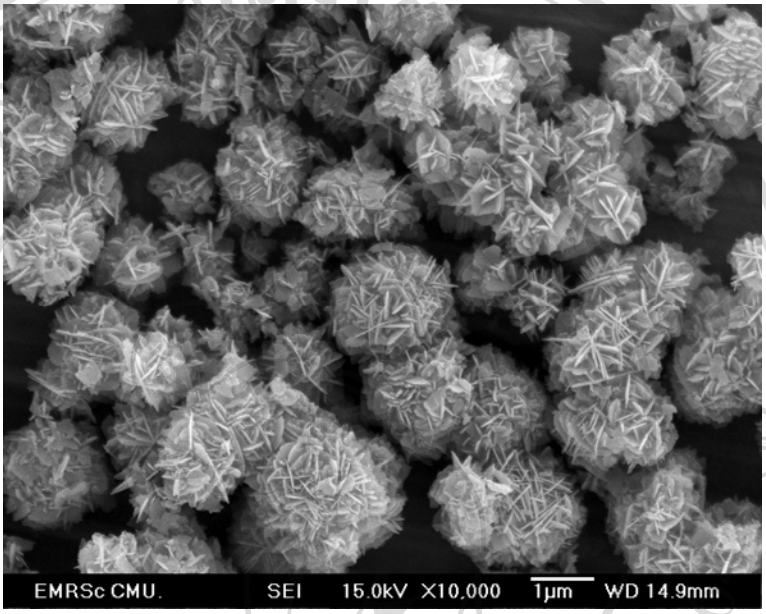


Figure 3.24 SEM image of the product prepared using 1:5 $Zn(NO_3)$ to NaOH ratio.

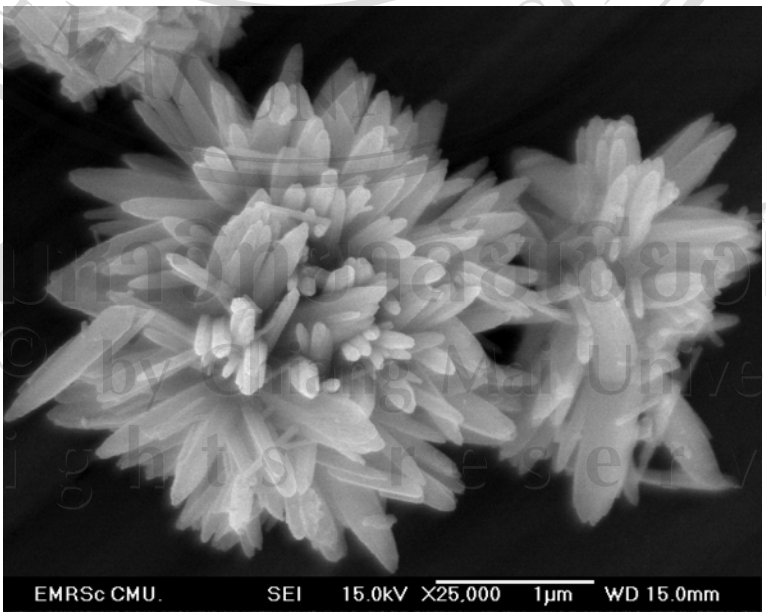


Figure 3.25 SEM image of the product prepared using 1:10 $Zn(NO_3)$ to NaOH ratio.

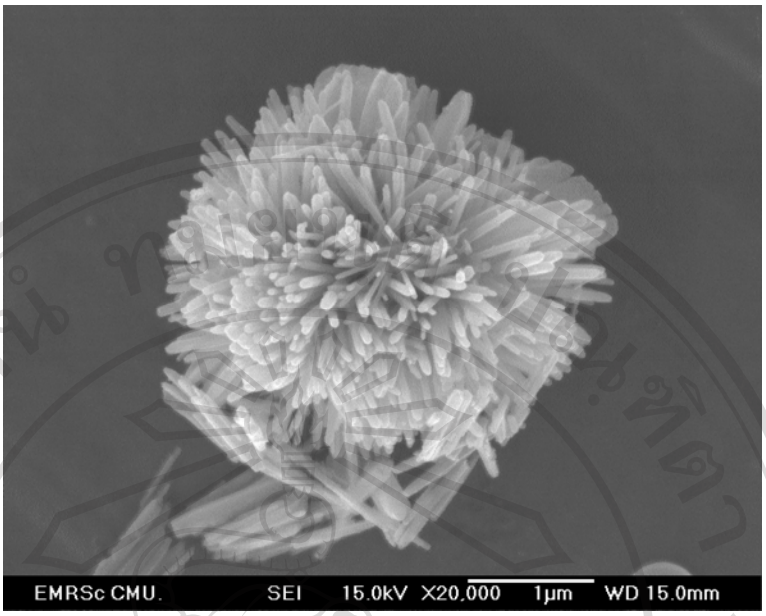


Figure 3.26 SEM image of the product prepared using 1:15 $Zn(NO_3)$ to NaOH ratio.

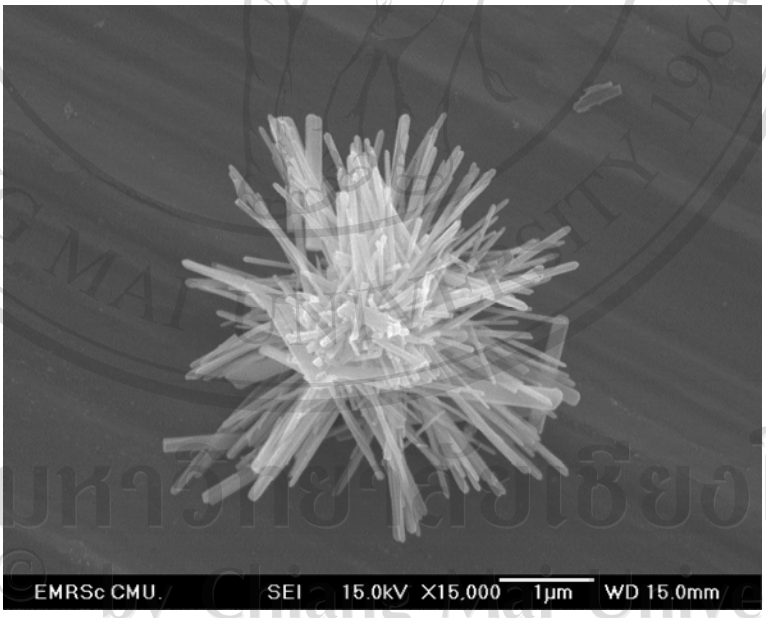


Figure 3.27 SEM image of the product prepared using 1:20 $Zn(NO_3)$ to NaOH ratio.

Figures 3.24-3.27 shows the morphologies of the samples synthesized using different $Zn(NO_3)_2$ to NaOH ratios. At 1:5 mol ratios, they were plate shaped-particles with different orientations and sizes, composing flower-like clusters. When more

NaOH was added to achieve 1:10, 1:15 and 1:20 ratios, they were changed into nanorods in flower-like clusters. The reasonable mechanism of formation of ZnO under different $Zn(NO_3)_2$ to NaOH ratios is explained as follows. Firstly, Zn^{2+} reacted with OH^- to form $Zn(OH)_2$ species.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \quad \text{.....(1)}$$

The above process were at dynamic equilibrium a reversible pathway between solid phase ($Zn(OH)_2$) and solution phase (Zn^{2+} and OH^-) was able to proceed. At the present stage, ZnO nuclei stared to form

$$Zn(OH)_2 \longleftrightarrow ZnO + H_2O$$

Simultaneously, $Zn(OH)_2$ remaining in the solution reacted with OH^- to form $[Zn(OH)_4]^{2-}$ growth unit.

$$Zn(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-} \quad \text{.....(2)}$$

The growth units played the important role in crystal growing. They incorporated into the crystal lattice by a dehydration reaction

$$[Zn(OH)_4]^{2-} \longrightarrow ZnO + 2H_2O + 2OH^- \quad \text{.....(3)}$$

According to the previous work [70], the number of growth units increased with the increase of the pH value. At 5 mol NaOH, growth units in the solutions were insufficiently produced. Only plate-shaped particles were produced. When the amount of NaOH in the solution increased, growth units were sufficient enough to form rod-shaped particles. Their lengths were increased with the amount of NaOH increase. They were the longest at 20 mol NaOH. However, yield of the product synthesized using 20 mol NaOH was low. The products were no longer produced when the excess NaOH was used.

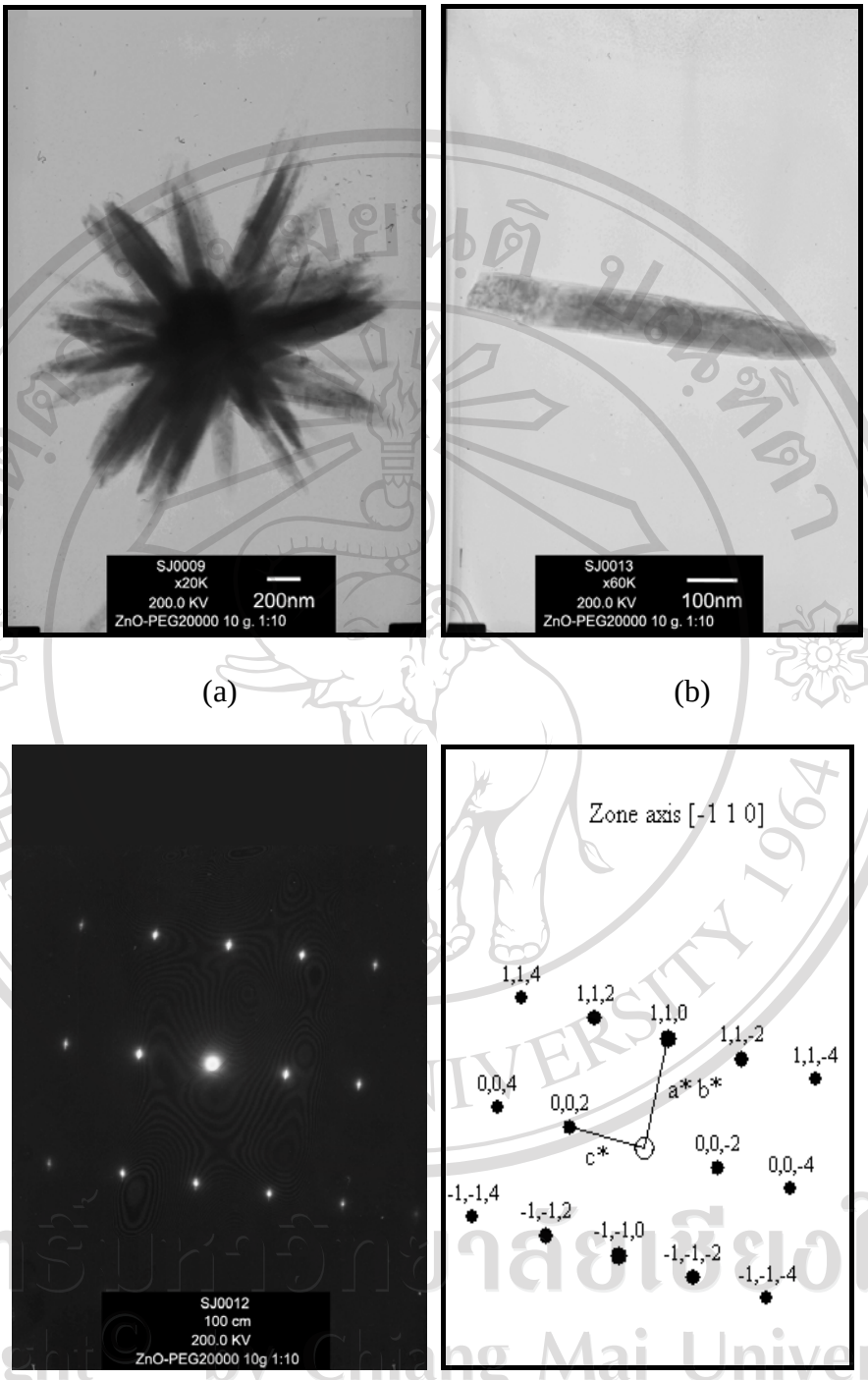


Figure 3.28 TEM images, SAED and simulated patterns of the product synthesized using $Zn(NO_3)_2$ to NaOH ratio.

(a) and (b) Bright field images (c) SAED pattern (d) simulated pattern

TEM image of the product is shown in the Figure 3.28. It was found that each rod is 1.0 μm long and 147 nm in diameter. SAED pattern of a single nanorod with electron beam in the [-1 1 0] direction confirmed that the nanorod was composed of high cystallinity in nature. The diffraction pattern can be index to be hexagonal ZnO.

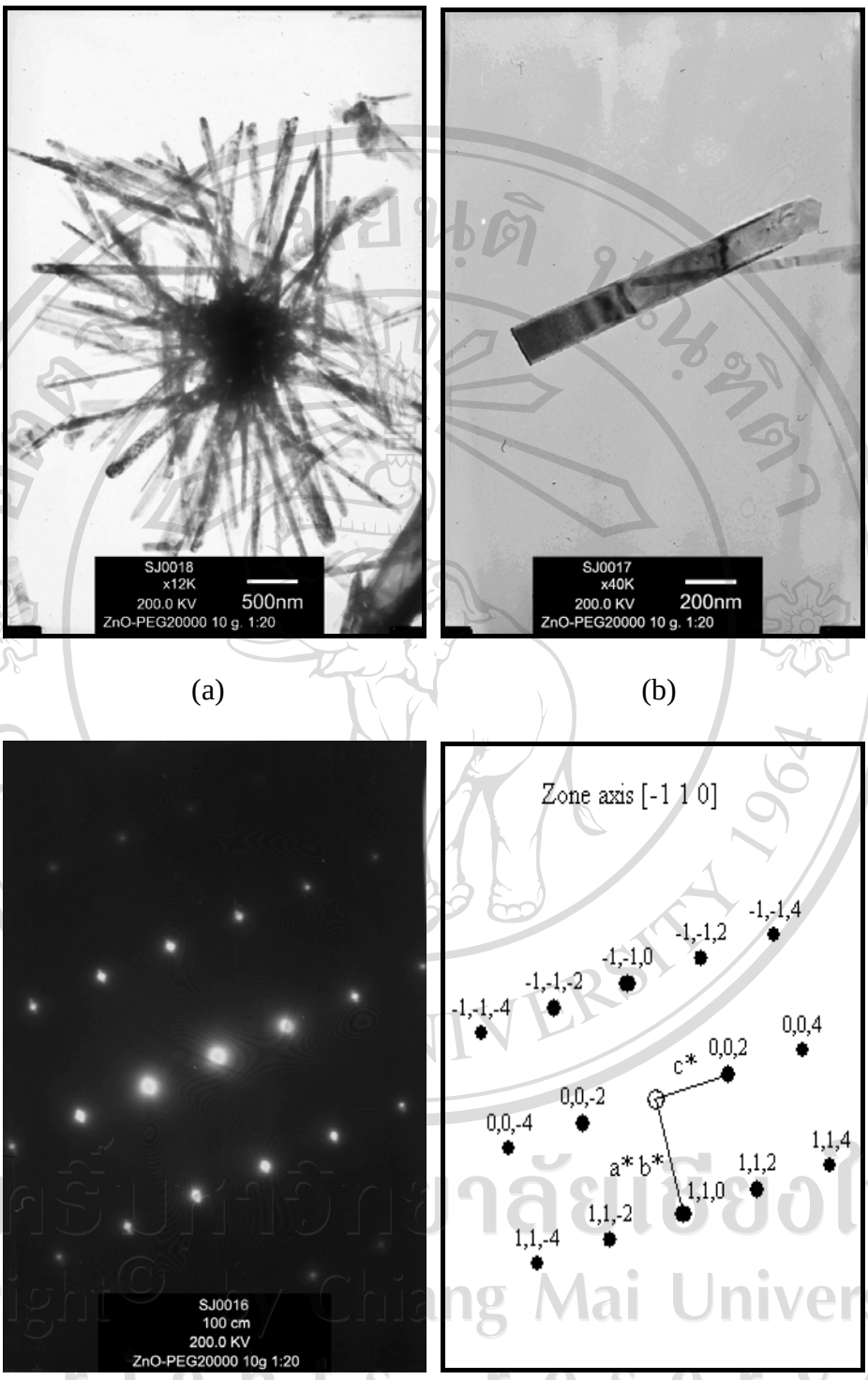


Figure 3.29 TEM images, SAED and simulated patterns of the product synthesized using $Zn(NO_3)_2$ to NaOH ratio.

(a) and (b) Bright field images (c) SAED pattern (d) simulated pattern

TEM image of the product is shown in the Figures 3.29. It was found that the rods of the flower are as long as 1.8 μm with 54 nm in diameter. SAED pattern of a single nanorod with electron beam in the [-1 1 0] direction confirmed that the nanorod was good crystalline. The diffraction pattern can be index as hexagonal structure ZnO.

3.2.2 Effect of reaction time

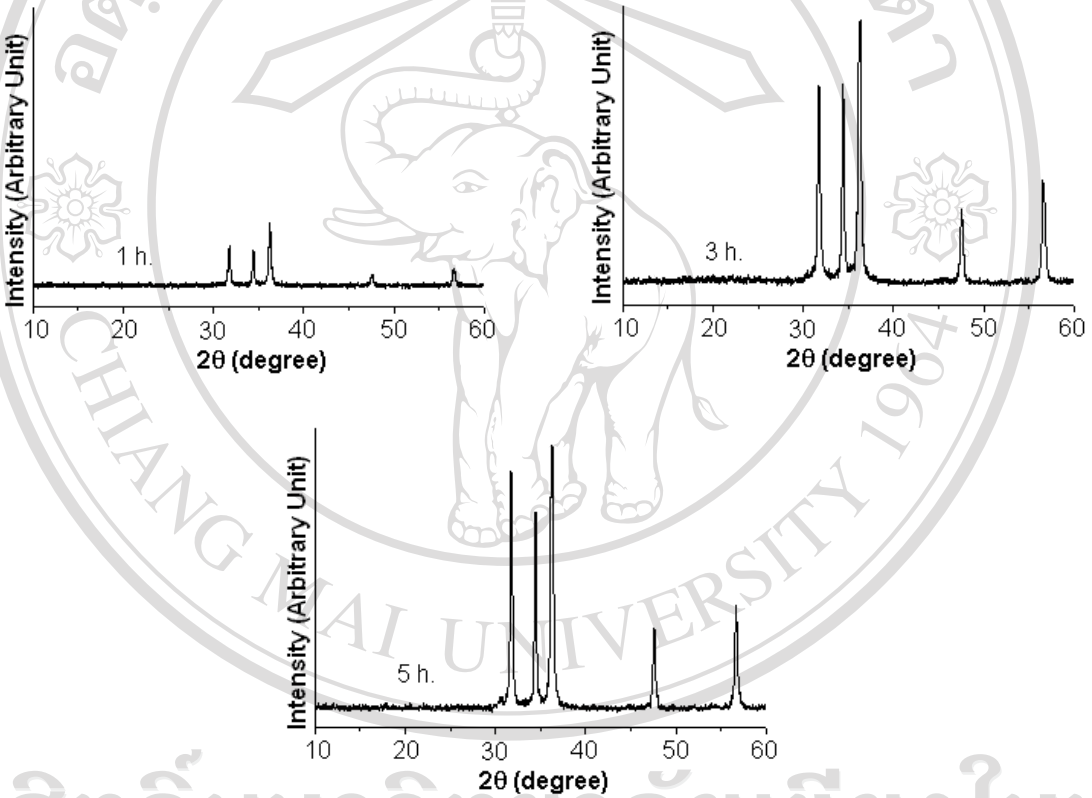


Figure 3.30 XRD patterns of the samples synthesized using different prolonged times.

In order to study the effect of prolonged time on their crystallinity, the samples were synthesized using 1, 3 and 5 h, respectively. For 1 h, the degree of crystallinity of the sample was very low. At longer time, the degree of crsytallinity was increased.

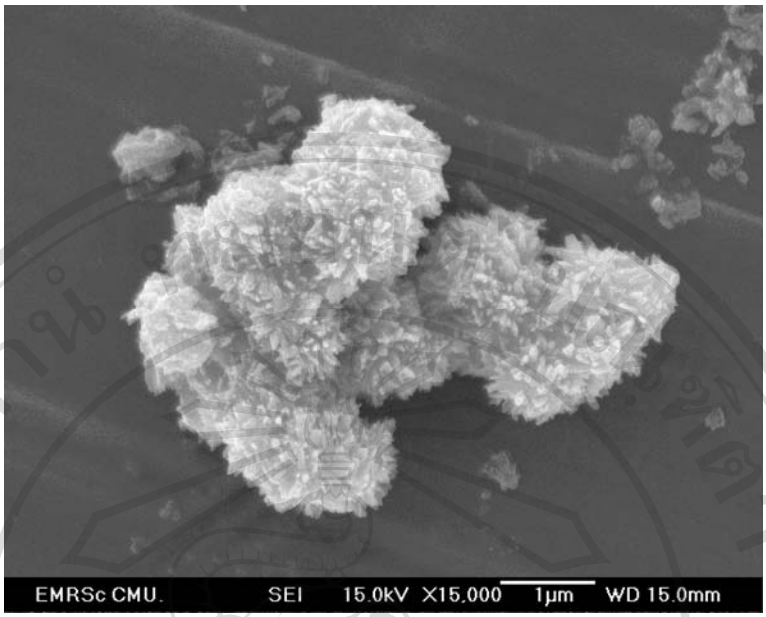


Figure 3.31 SEM image of the sample synthesized using 1:10 $Zn(NO_3)$ to NaOH ratio.

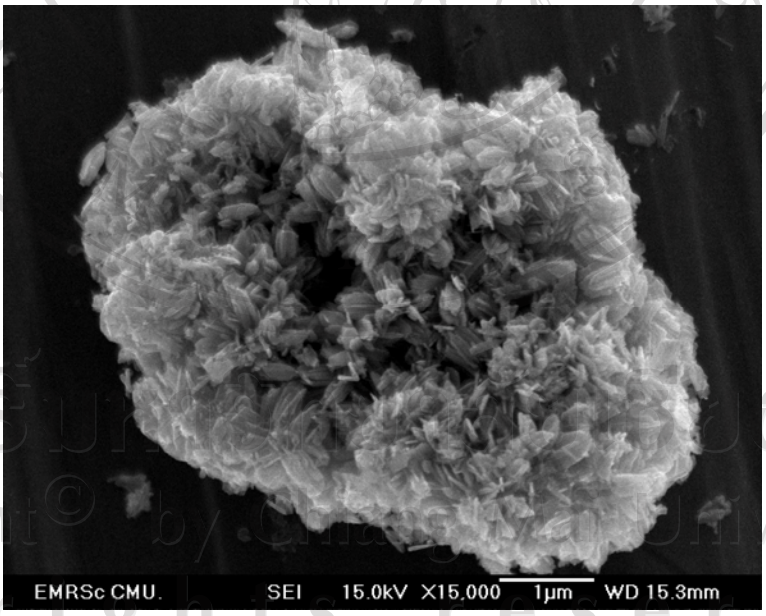


Figure 3.32 SEM image of the sample synthesized using 1:10 $Zn(NO_3)$ to NaOH ratio.

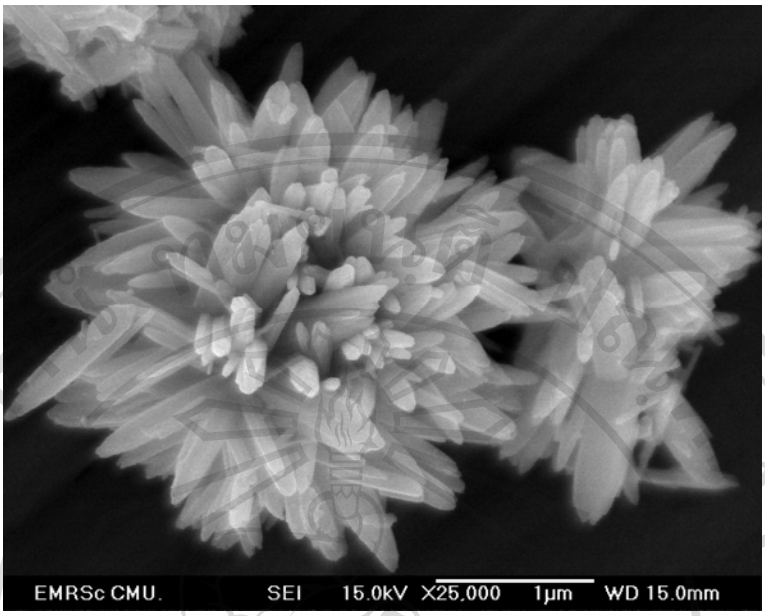


Figure 3.33 SEM image of the sample synthesized using 1:10 $Zn(NO_3)$ to NaOH ratio.

In order to study the effect of prolonged time on the final morphologies of ZnO, the products were synthesized using 1:10 of $Zn(NO_3)_2$ to NaOH ratio with different prolonged time. Figures 3.31-3.33 shows SEM images of the products synthesized using different prolonged time. For 1h, the products were composed of short nanorods in clusters. When the prolonged time was lengthen, the products became larger by Ostward ripening process [71]. For 5 h long, the flowers of nanorod were detected.

3.2.3 Effect of the amount of PEG20000

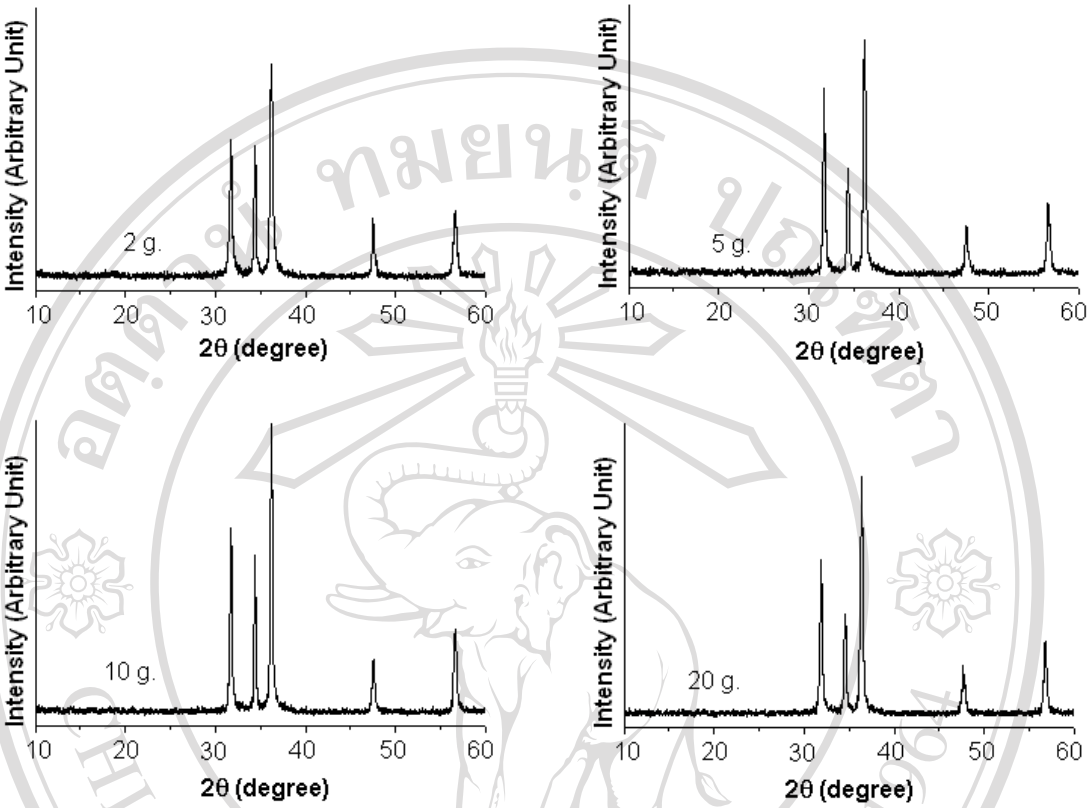


Figure 3.34 XRD patterns of the samples synthesized using different amount of PEG20000.

In order to study the effect of the amount of PEG20000 on their crystallinity, the samples were prepared using 6 g, 10 g and 20 g PEG20000, respectively. XRD patterns of these samples were shown in figure 3.24. It was found that the crystallinity of the samples was increased when the amount of PEG20000 increased.

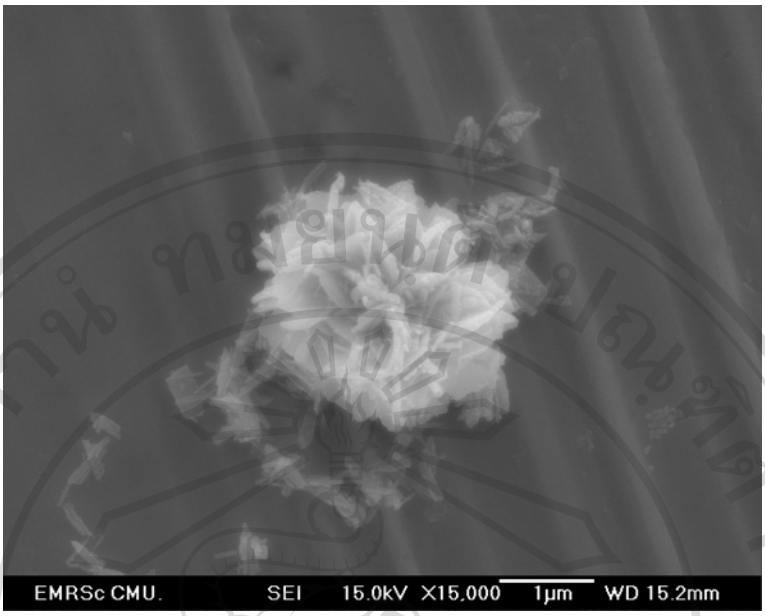


Figure 3.35 SEM image of the sample synthesized using PEG20000.

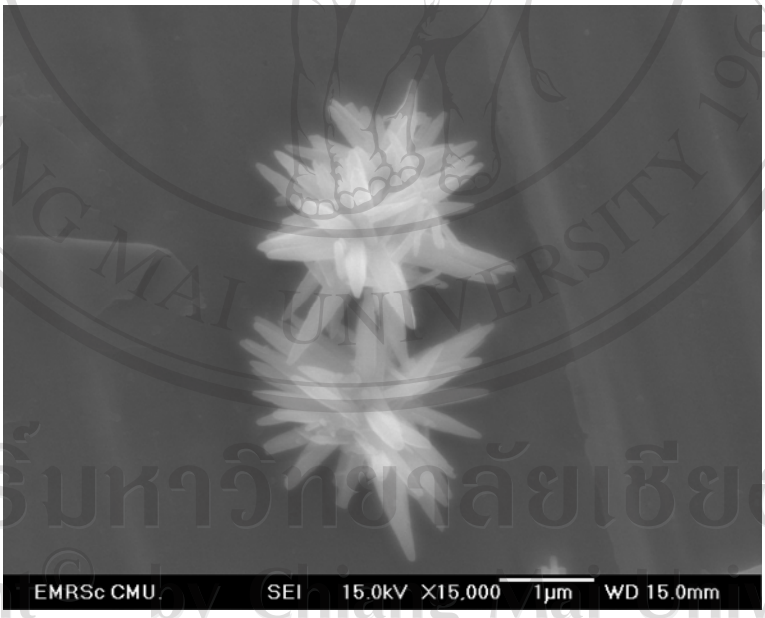


Figure 3.36 SEM image of the sample synthesized using PEG20000.

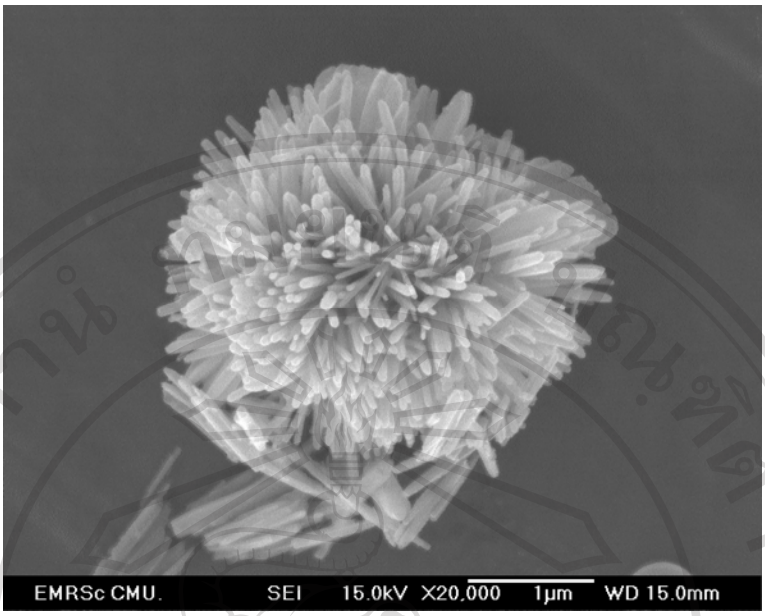


Figure 3.37 SEM image of the sample synthesized using PEG20000.

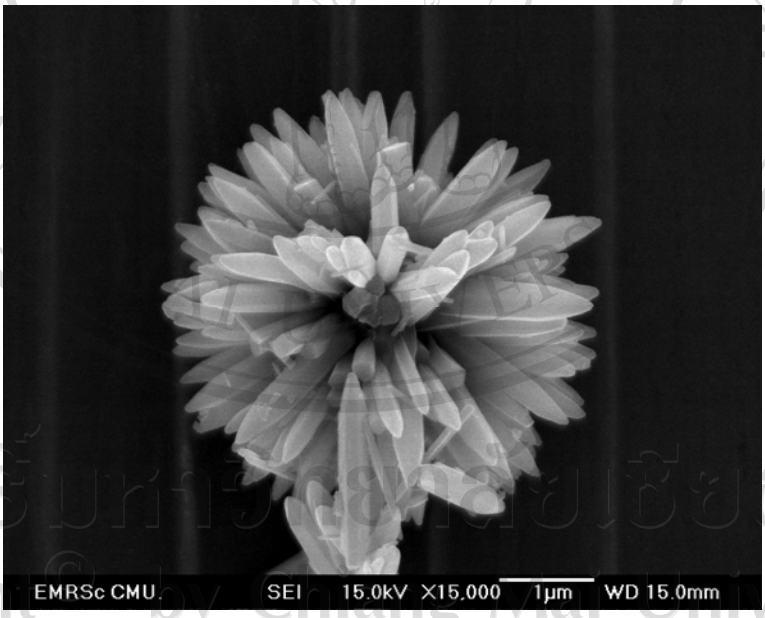


Figure 3.38 SEM image of the sample synthesized using PEG20000.

Figures 3.35-3.38 shows SEM images of the samples prepared using PEG20000 as a surfactant. When different amounts of PEG20000 with the same precursor ratio were used, different morphologies were synthesized. By using 2 g PEG20000, non-uniform plates which caused by the incomplete capping on the ZnO crystallographic faces were detected. For 5 g and 10 g PEG20000, plate-shaped particles were no longer detected but non-uniform flower-like shape was detected. They transformed into complete flower-like shape when using 20 g PEG20000 was used.