CHAPTER II

EXPERIMENTALS AND RESULTS

In order to facilitate the complexity of the experiments, a sequential order of preparations will be presented in this chapter. In each experiment, an easy-to-understand flow chart which illustrates the experimental procedure is included at the beginning of the section.

2.1) EQUIPMENT REQUIREMENT FOR THE EXPERIMENTAL WORK

T.K. Auto Homo Mixer Model M, Tokushu Kika Kogyo Co., Ltd., Japan, was used for preparing the emulsion of encapsulated material containing the first reactant dispersed in water as continuous phase before adding the aqueous solution of the second reactant to form high molecular weight condensation polymer film at the interface.

Heidon Laboratory Stirrer Type-600G, Shinto Scientific Co., Ltd., Japan, was used for mixing the emulsion of the encapsulated material containing first reactant and aqueous solution of the second reactant to form microcapsules.

Water bath having a cooling and heating unit was used for controlling temperatures during the preparation of microcapsules.

Optical microscope was used for examining microscopic properties and picture taking of the microcapsules.

Scanning electron microscope, JEM-35CF, was used for examining microscopic properties and picture taking of the microcapsules.

Spectrophotometer Model UV-101, Shimadzu Corporation, Japan, was used for the determination of the average particle size of emulsion by turbidity method.

Particle Size Analyzer Series SA-CP2, Shimadzu Corporation, Japan, was used for the determination of the average particle size and size distribution of the microcapsules by ultra-centrifuge method.

Gas chromatograph Series GC-14A, Shimadzu Corporation, Japan, was used for measuring the unencapsulated material or the determination of microencapsulation efficiency.

IBM personal computer with SizeCalc, Lotus 123, and Microsoft-chart as application software used for the calculation of average particle size and size distribution of the emulsion and the microcapsules.

Glassware and other equipment : 100 ml. cylinder, 500 ml. beaker, 250 ml. separatory funnel, thermometer, stop watch, analytical balance, etc.

2.2) CHEMICAL SELECTION FOR EXPERIMENTS

All chemicals used in this thesis were chemical-pure grade. They were used without prior purification but their concentrations calculated based on the purity provided by manufacturers. The chemicals mentioned are :-

Two kinds of polyamide were selected to synthesize a polymeric microcapsule shell. Poly(hexamethylene sebacamide) was synthesized by using sebacoyl chloride reacting with hexamethylene diamine while poly(para-phenylene terephthalamide) was synthesized by using terephthaloyl chloride reacting with para-phenylene diamine.

Sebacoyl chloride from Fluka Chemie, Switzerland, having a minimum purity of 97.0% and a molecular weight of 239.14 gm./mole; assigned name : SBC.

Hexamethylene diamine from Fluka Chemie, Switzerland, having a

minimum purity of 97.0% and a molecular weight of 116.20 gm./mole; assigned name : HMDA.

Terephthaloyl chloride from Fluka Chemie, Switzerland, having a minimum purity of 99.7% and a molecular weight of 203.03 gm./mole; assigned name : TPC.

Para-phenylene diamine from Fluka Chemie, Switzerland, having a minimum purity of 97.0% and a molecular weight of 108.14 gm./mole; assigned name : PNDA.

Two kinds of encapsulated materials which have different properties were butyl acetate and dibutyl phthalate. Butyl acetate has a low boiling point, high vapor pressure and is a water-insoluble encapsulated material whereas dibutyl phthalate possesses high boiling point, low vapor pressure and is a water-insoluble encapsulated material.

Butyl acetate from Alusuisse, Italy, having a minimum purity of 99.0%, a molecular weight of 116.0 gm./mole, a vapor pressure of 8.7 mm.Hg at 20.0°C, a specific gravity of 0.8826 (20/20°C) and a boiling point of 126.3°C; assigned name : BAT.

Dibutyl phthalate from Alusuisse, Italy, having a minimum purity of 99.0%, a molecular weight of 278.35 gm./mole, a vapor pressure of 1.1 mm.Hg at 150.0°C, a specific gravity of 1.0484 (20/20°C) and a boiling point of 340.0°C; assigned name : DBP.

Two types of emulsifiers, protective colloids and surface active agents, were used. Poly(vinyl alcohol) and styrene maleic anhydride copolymer in sodium salt forms as protective colloid and poly(oxyethylene lauryl ether) and sodium dodecyl benzene sulfonate as surface active agent.

Poly(vinyl alcohol) from Kuraray Poval (PVA 224E), Japan, having a minimum purity of 99.7%, a hydrolyzed percentage of 87-89% and a degree polymerization of 2,400 - 2,500; assigned name : PVA.

Sodium salt of styrene maleic anhydride copolymer from Arco Chemical (SMA-3000), U.S.A., having a minimum purity of 99.7%, a styrene/maleic anhydride ratio of 3/1 and a molecular weight of 1,900 gm./mole; assigned name : SMA.

Poly(oxyethylene lauaryl ether) from Kao Corporation (Emulgen-120), Japan, having a minimum purity of 99.9%, a ethylene oxide number of 14 and a hydrophilic lipophilic balance of 15.3; assigned name : POLE.

Sodium dodecyl benzene sulfonate Kao Corporation (Neopelex F-35), Japan, having a minimum purity of 35.0% and a molecular weight of 351.5 gm./mole; assigned name : SDBS.

An acid-receiver, sodium hydroxide, was used to neutralize hydrochloric acid which is generated by polycondensation of diacid chloride with diamine.

Sodium hydroxide from Aldrich Chemie, U.S.A., having a minimum purity of 99.7% and a molecular weight of 40.0 gm./mole; assigned name : NaOH.

Other chemicals for analyzing methods were of analytical grade having a minimum purity of 99.9%. Water using as an aqueous medium was deionized water; assigned name : DIW.

2.3) SOLUBILITY OF DIACID CHLORIDE IN ENCAPSULATED MATERIAL

2.3.1) Purpose

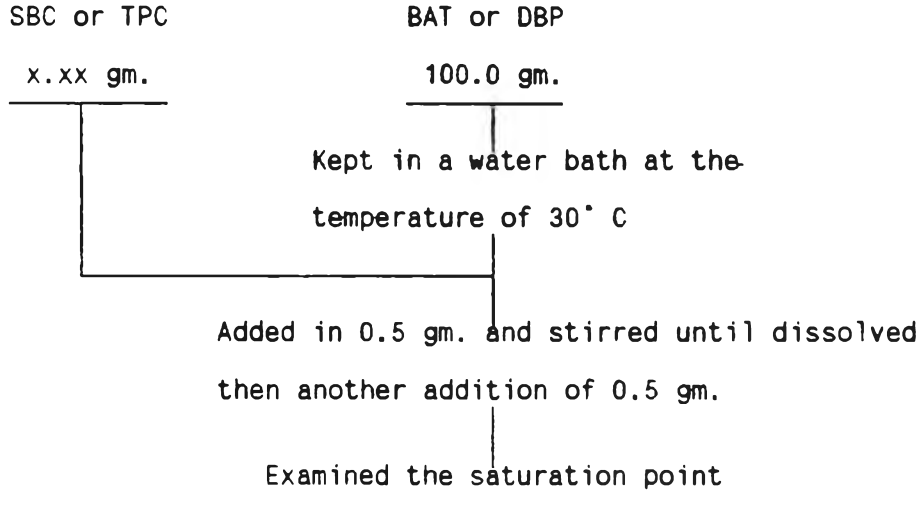
To determine the solubility of sebacoyl chloride and

terephthaloyl chloride in butyl acetate and dibutyl phthalate.

2.3.2) Procedure

The solution of diacid chloride was prepared as shown in Flow Chart 1 to determine the solubility of sebacoyl chloride in butyl acetate; sebacoyl chloride in dibutyl phthalate; terephthaloyl chloride in butyl acetate; and terephthaloyl chloride in dibutyl phthalate. 100.00 gm. of encapsulated oil was firstly weighted into a 250 ml. beaker and kept it at the temperature of 30°C a in water bath. Then 0.5 gm. of diacid chloride was added into the beaker and was stirred until the diacid chloride was completely dissolved. Another 0.5 gm. of diacid chloride was added to the encapsulated oil until a saturated point was obtained. By the other means, 15.0 gm. of diacid chloride was added and stirred until it was completely dissolved.

Flow Chart 1 Solubility Determination of Diacid Chlrides.



2.3.3) Results

The solubility of diacid chlorides : sebacoyl chloride and terephthaloyl chloride, in encapsulated materials of butyl acetate and dibutyl phthalate is shown in Tables 1, 2, 3 and 4 as follows :-

Table 1 Solubility of Sebacoyl Chloride in Butyl Acetate.

Sebacoyl Chloride (gm.) in 100.0 gm. of Butyl Acetate	Appearance
0.5 - 10.0	clear solution

Table 2 Solubility of Sebacoyl Chloride in Dibutyl Phthalate.

Sebacoyl Chloride (gm.) in 100.0 gm. of Dibutyl Phthalate	Appearance
0.5 - 10.0	clear solution

Table 3 Solubility of Terephthaloyl Chloride in Butyl Acetate.

Terephthaloyl Chloride (gm.) in 100.0 gm. of Butyl Acetate	Appearance
0.5 - 8.0	clear solution
8.5	slightly turbid
9.0	not dissolve

Table 4 Solubility of Terephthaloyl Chloride in Dibutyl Phthalate.

Terephthaloyl Chloride (gm.) in 100.0 gm. of Dibutyl Phthalate	Appearance
0.5 - 4.5	clear solution
5.0	slightly turbid
5.5	significantly turbid
6.0	not dissolve

2.3.4) Conclusions

Sebacoyl chloride can dissolve in butyl acetate or dibutyl phthalate in any portion but terephthaloyl chloride has a limited solubility as shown in Table 5. The optimum concentration of diacid chloride used for microencapsulation should be carefully considered.

Table 5 Solubility of Diacid Chloride in the Encapsulated Oil.

Items	Solubility in 100.0 gm.
sebacoyl chloride in butyl acetate	infinity
sebacoyl chloride in dibutyl phthalate	infinity
terephthaloyl chloride in butyl acetate	9.0 gm.
terephthaloyl chloride in dibutyl phthalate	6.0 gm.

2.4) SOLUBILITY OF DIAMINE IN WATER

2.4.1) Purpose

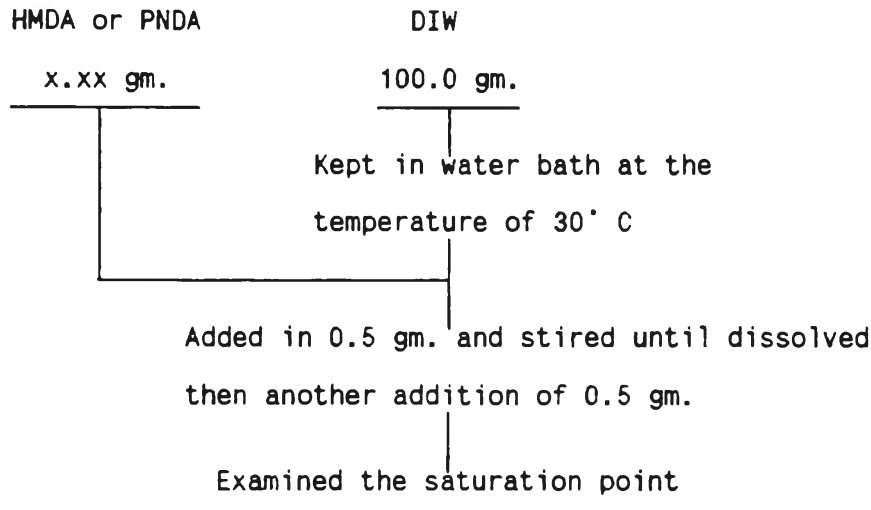
To determine the solubility of hexamethylene diamine and para-phenylene diamine in deionized water.

2.4.2) Procedure

The solubility of hexamethylene diamine and para-phenylene diamine in deionized water was examined as shown in the Flow Chart 2. 100.0 gm. of deionized water was firstly weighted into a 250 ml. beaker and kept it at the temperature of 30°C in a water bath. Then 0.5 gm. of diamine was added into the beaker and was stirred until it was completely dissolved. Another 0.5 gm. of diamine was added to the deionized water until the saturated point was obtained. By the other

means, 10.0 gm. of diamine was added and stirred until it was completely dissolved.

Flow Chart 2 Solubility Determination of Diamines.



2.4.3) Results

The solubility of hexamethylene diamine and para-phenylene diamine in water is shown in Tables 6 and 7.

Table 6 Solubility of Hexamethylene Diamine in Deionized Water.

Hexamethylene Diamine (gm.) in 100.0 gm. of Deionized Water	Appearance
0.5 - 10.0	clear solution

Table 7 Solubility of Para-phenylene Diamine in Deionized Water.

Para-phenylene Diamine (gm.) in 100.0 gm. of Deionized Water	Appearance
0.5 - 4.0	clear brown solution
4.5	slightly turbid
5.0	not dissolve

2.4.4) Conclusions

Hexamethylene diamine has an infinite solubility in water but the solubility of para-phenylene diamine is saturated at about 5.0 gm. in 100.0 gm. of water as shown in Table 8. The concentrations used are correlated to the concentration of diacid chloride in 1:1 mole ratio.

Table 8 Solubility of the Diamines in Deionized Water.

Items	Solubility in 100.0 gm.
Hexamethylene diamine in deionized water	infinity
Para-phenylene diamine in deionized water	5.0 gm.

2.5) OPTIMUM OIL-TO-WATER PHASE RATIO

2.5.1) Purpose

To find optimum phase ratio of dibutyl phthalate and butyl acetate to deionized water.

2.5.2) Procedure

The optimum oil-to-water phase ratio of butyl acetate and dibutyl phthalate was examined as shown in the Flow Chart 3 and the oil to water phase ratio was illustrated in Table 9. 240.0 gm. of deionized water and 60.0 gm. of encapsulated oil were weighted into a 500 ml. beaker. This mixture was homogenized with T.K. homogenizer using a speed of the propeller at 10,000 rpm. for 5.0 minutes to produce emulsification. This emulsion was immediately poured into a 500 ml. cylinder to measure the separation time, and general appearance was determined by visual evaluation.

Flow Chart 3 Optimum Oil to Water Phase Ratio Determination.

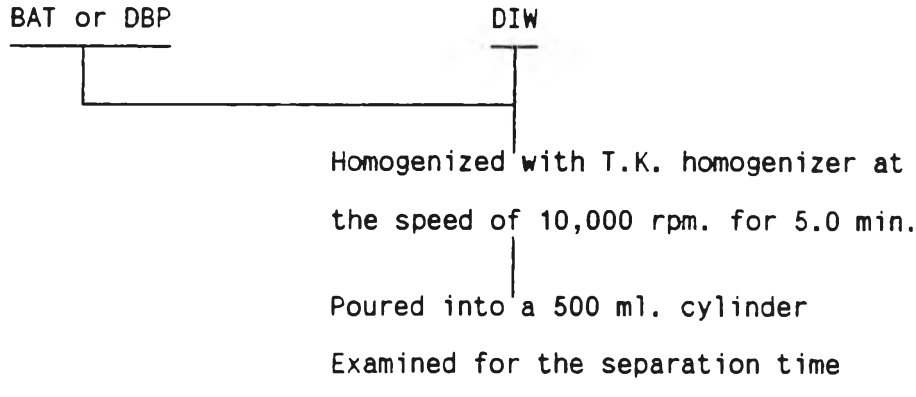


Table 9 Phase Ratio of Encapsulated Oil to Water.

Butyl Acetate (gm.) or Dibutyl Phthalate	Deionized Water (gm.)	Oil-to-Water Ratio (gm. : gm.)
60.0	240.0	20:80
90.0	210.0	30:70
120.0	180.0	40:60
150.0	150.0	50:50
180.0	120.0	60:40
210.0	90.0	70:30
240.0	60.0	80:20

2.5.3) Results

The variation of oil-to-water phase ratio of butyl acetate and dibutyl phthalate is shown in Tables 10 and 11 as follows :-

Table 10 Butyl Acetate to Deionized Water Phase Ratio.

Oil-to-Water Ratio	Rate of Separation and Appearance
20:80	suddenly separated, oil in water
30:70	separated after 12 minutes, oil in water

Table 10 Butyl Acetate to Deionized Water Phase Ratio.

Oil-to-Water Ratio	Rate of Separation and Appearance
40:60	separated after 5 minutes, oil in water
50:50	separated after 2 minutes, oil in water
60:40	suddenly separated, water in oil
70:30	suddenly separated, water in oil
80:20	suddenly separated, water in oil

Table 11 Dibutyl Phthalate to Deionized Water Phase Ratio.

Oil-to-Water Ratio	Rate of Separation and Appearance
20:80	suddenly separated, oil in water
30:70	separated after 9 minutes, oil in water
40:60	separated after 4 minutes, oil in water
50:50	separated after 1 minutes, oil in water
60:40	suddenly separated, oil in water
70:30	suddenly separated, water in oil
80:20	suddenly separated, water in oil

2.5.4) Conclusions

The optimum phase ratio of butyl acetate and dibutyl phthalate to deionized water is 30:70. This ratio will be used for next experiments.

2.6) PROPELLER SPEED AND HOMOGENIZING TIME RANGE

2.6.1) Purpose

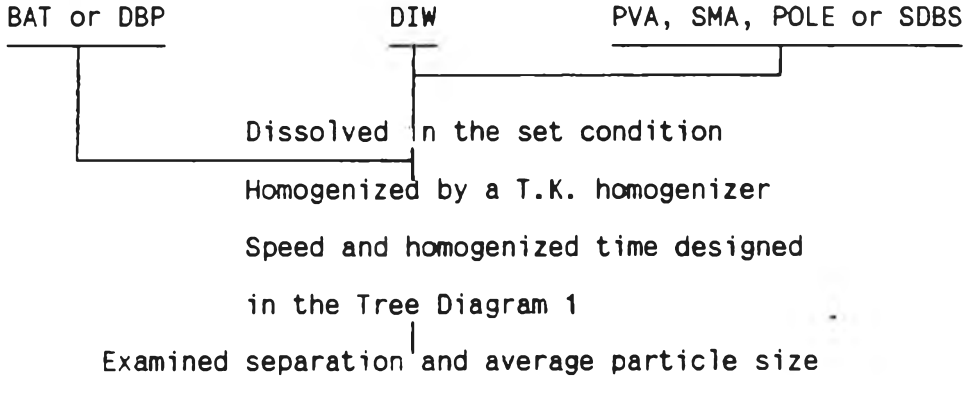
To find the minimum and maximum propeller speed and homogenizing time that can disperse the encapsulated oil into the

smaller droplets which have a diameter of around 1.0-100.0 micrometers.

2.6.2) Procedure

Emulsifier solutions were prepared by using the weights listed in Table 12. PVA or SMA was boiled in deionized water at 80°C for one hour to make a completely soluble solution and then the solution of PVA or SMA was cooled to 30°C. POLE and SDBS were dissolved in deionized water at 30°C. To a 500 ml. beaker, 210.0 gm. of emulsifier solution and 90.0 gm. of encapsulated oil were added. This mixture was homogenized with a T.K. homogenizer at the propeller speeds and homogenized times which are shown in the Tree Diagram 1.

Flow Chart 4 Procedure of Propeller Speed and Homogenizing Time Range.



The total amount of emulsifier was 7.5% of encapsulated oil, the oil-to-water phase ratio was 30:70 w/w, the propeller speeds were chosen at 2,000, 6,000 and 10,000 rpm. and the homogenized times were selected at 30, 90 and 150 seconds.

Table 12 Formulation of Encapsulated Oils in Various Emulsifiers.

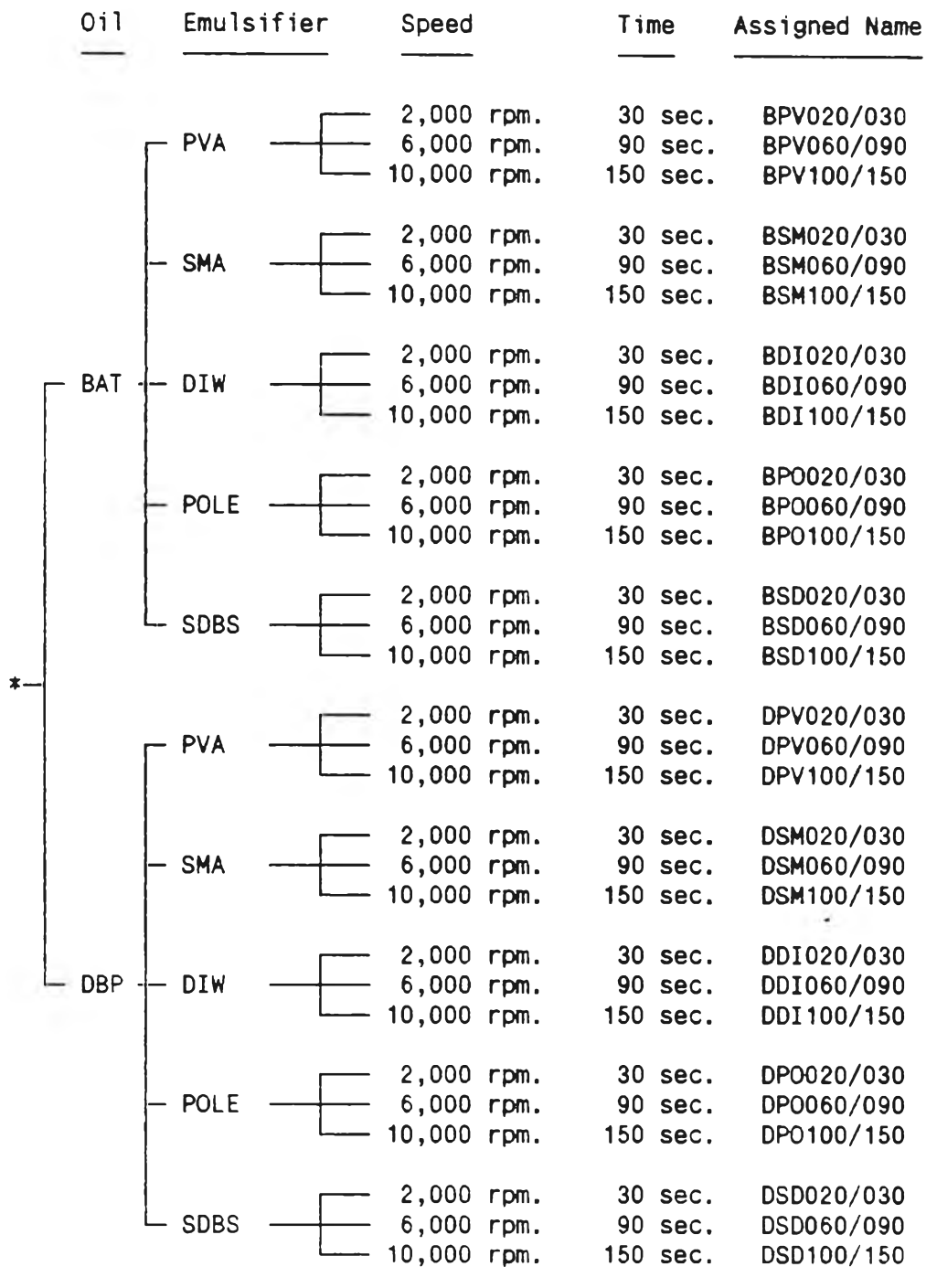
Table 12-1 Formulations of Butyl Acetate in Various Emulsifiers.

Assigned Name Chemicals	BPV (gm.)	BSM (gm.)	BPO (gm.)	BSD (gm.)	BDI (gm.)
BAT	90.00	90.00	90.00	90.00	90.00
PVA	6.75				
SMA		6.75			
POLE			6.75		
SDBS				19.29	
DIW	203.25	203.25	203.25	190.71	210.00
TOTAL	300.00	300.00	300.00	300.00	300.00

Table 12-2 Formulations of Dibutyl Phthalate in Various Emulsifiers.

Assigned Name Chemicals	DPV (gm.)	DSM (gm.)	DPO (gm.)	DSD (gm.)	DDI (gm.)
DBP	90.00	90.00	90.00	90.00	90.00
PVA	6.75				
SMA		6.75			
POLE			6.75		
SDBS				19.29	
DIW	203.25	203.25	203.25	190.71	210.00
TOTAL	300.00	300.00	300.00	300.00	300.00

Tree Diagram 1 Propeller Speed and Homogenizing Time Variations.



Oil	Emulsifier	Speed	Time	Assigned Name
BAT	PVA	2,000 rpm.	30 sec.	BPV020/030
		6,000 rpm.	90 sec.	BPV060/090
		10,000 rpm.	150 sec.	BPV100/150
	SMA	2,000 rpm.	30 sec.	BSM020/030
		6,000 rpm.	90 sec.	BSM060/090
		10,000 rpm.	150 sec.	BSM100/150
	DIW	2,000 rpm.	30 sec.	BDI020/030
		6,000 rpm.	90 sec.	BDI060/090
		10,000 rpm.	150 sec.	BDI100/150
	POLE	2,000 rpm.	30 sec.	BPO020/030
		6,000 rpm.	90 sec.	BPO060/090
		10,000 rpm.	150 sec.	BPO100/150
	SDBS	2,000 rpm.	30 sec.	BSD020/030
		6,000 rpm.	90 sec.	BSD060/090
		10,000 rpm.	150 sec.	BSD100/150
DBP	PVA	2,000 rpm.	30 sec.	DPV020/030
		6,000 rpm.	90 sec.	DPV060/090
		10,000 rpm.	150 sec.	DPV100/150
	SMA	2,000 rpm.	30 sec.	DSM020/030
		6,000 rpm.	90 sec.	DSM060/090
		10,000 rpm.	150 sec.	DSM100/150
	DIW	2,000 rpm.	30 sec.	DDI020/030
		6,000 rpm.	90 sec.	DDI060/090
		10,000 rpm.	150 sec.	DDI100/150
	POLE	2,000 rpm.	30 sec.	DPO020/030
		6,000 rpm.	90 sec.	DPO060/090
		10,000 rpm.	150 sec.	DPO100/150
	SDBS	2,000 rpm.	30 sec.	DSD020/030
		6,000 rpm.	90 sec.	DSD060/090
		10,000 rpm.	150 sec.	DSD100/150

2.6.3) Analysis Methods

2.6.3.1) Emulsion Stability

100.0 ml. of the emulsion was poured into a 100 ml. cylinder and a stop watch was used to measure the rate of phase separation. The volume of the separated emulsion was measured after one hour.

2.6.3.2) Average Particle Size

Dispersing liquid was prepared by dissolving 0.01 gm. of acrylamide-acrylic acid copolymer in 1000.0 gm. of deionized water. This is a water clear and high viscosity solution. Dispersion liquid was firstly poured into a spectrophotometric glass cell and the transmittance was adjusted to 100.0% at the wave-length of 400 nanometer. Subsequently the transmittances of dispersing liquid were carried out at 450, 500, 550, 600 nanometer which were the blank values of the solution. The emulsion of encapsulated oil was diluted with this dispersing liquid until the transmittance at 400 nanometer was 65.0% then were measured the transmittances at 450, 500, 550 and 600 nanometer which were considered as the sample values. Calculation was performed by using an IBM personal computer and a software of SizeCalc program (Appendix I) to obtain the average particle diameter of the encapsulated oil droplets.

2.6.4) Results

The variation of propeller speeds and agitation times of homogenizer to produce oil-in-water emulsion in which oil droplets with a diameter between 1.0-100.0 micrometers are showed on Tables 13, 14, 15, 16, 17 and 18 as follows :-

Table 13 Appearance of Butyl Acetate Droplets after 2,000 rpm. of Shear and 30 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
PVA -BPV020/030	no separation	20% separation	95.0
SMA -BSM020/030	60%separation	100%separation	110.0
POLE-BPO020/030	no separation	no separation	9.0
SDBS-BSD020/030	no separation	5%separation	2.0
DIW -BDI020/030	100%separation	100%separation	cannot be measured

Table 14 Appearance of Butyl Acetate Droplets after 6,000 rpm. of Shear and 90 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
PVA -BPV060/090	no separation	10%separation	45.0
SMA -BSM060/090	50%separation	100%separation	80.0
POLE-BPO060/090	no separation	no separation	3.0
SDBS-BSD060/090	no separation	no separation	0.6
DIW -BDI060/090	100%separation	100%separation	cannot be measured

Table 15 Appearance of Butyl Acetate Droplets after 10,000 rpm. of Shear and 150 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
PVA -BPV100/150	not separation	5%separation	20.0
SMA -BSM100/150	30%separation	100%separation	65.0

Table 15 Appearance of Butyl Acetate Droplets after 10,000 rpm. of Shear and 150 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
POLE-BPO100/150	no separation	no separation	0.9
SDBS-BSD100/150	no separation	no separation	0.4
DIW -BDI100/150	100%separation	100%separation	cannot be measured

Table 16 Appearance of Dibutyl Phthalate Droplets after 2,000 rpm. of Shear and 30 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
PVA -DPV020/030	no separation	15%separation	70.0
SMA -DSM020/030	45%separation	100%separation	97.0
POLE-DPO020/030	no separation	no separation	12.0
SDBS-DSD020/030	no separation	10%separation	6.0
DIW -DDI020/030	100%separation	100%separation	cannot be measured

Table 17 Appearance of Dibutyl Phthalate Droplets after 6,000 rpm. of Shear and 90 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
PVA -DPV060/090	no separation	5%separation	36.0
SMA -DSM060/090	30%separation	90%separation	82.0
POLE-DPO060/090	no separation	no separation	7.0
SDBS-DSD060/090	no separation	no separation	1.2

Table 17 Appearance of Dibutyl Phthalate Droplets after 6,000 rpm. of Shear and 90 sec. of Homogenizing Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
DIW -DDI060/090	100%separation	100%separation	cannot be measured

Table 18 Appearance of Dibutyl Phthalate Droplets after 10,000 rpm. of Shear and 150 sec. of Homogenized Time in Various Emulsifiers.

Emulsifiers & Assigned Name	Appearance after 1 hour	Appearance after 3 hours	Average Diameter (micrometers)
PVA -DPV100/150	no separation	no separation	18.0
SMA -DSM100/150	20%separation	70%separation	69.0
POLE-DPO100/150	no separation	no separation	3.5
SDBS-DSD100/150	no separation	no separation	0.8
DIW -DDI100/150	100%separation	100%separation	cannot be measured

2.6.5) Conclusions

1) The order of emulsion stability when using various emulsifiers is in the following trend : SDBS > POLE >> PVA >>> SMA. Where deionized water was used instead, the stability of emulsion could not be evaluated due to its immediate phase separation after homogenizing.

2) The average particle sizes of oil droplets were in the range of 1.0 to 100.0 micrometers which could only be produced when the propeller speeds between 2,000 and 10,000 rpm. and homogenizing times from 30 to 150 sec. were employed.

3) The higher the propeller speed, the smaller the average diameter of the particles based on the same type of chemicals.

4) The higher the propeller speed, the higher the stability of emulsion.

2.7) MICROENCAPSULATION PROCESSES

2.7.1) Purpose

To study the effect of non-emulsifier microencapsulation system in comparison between addition emulsion to diamine solution process and addition diamine solution to emulsion process.

2.7.2) Synthesis Method

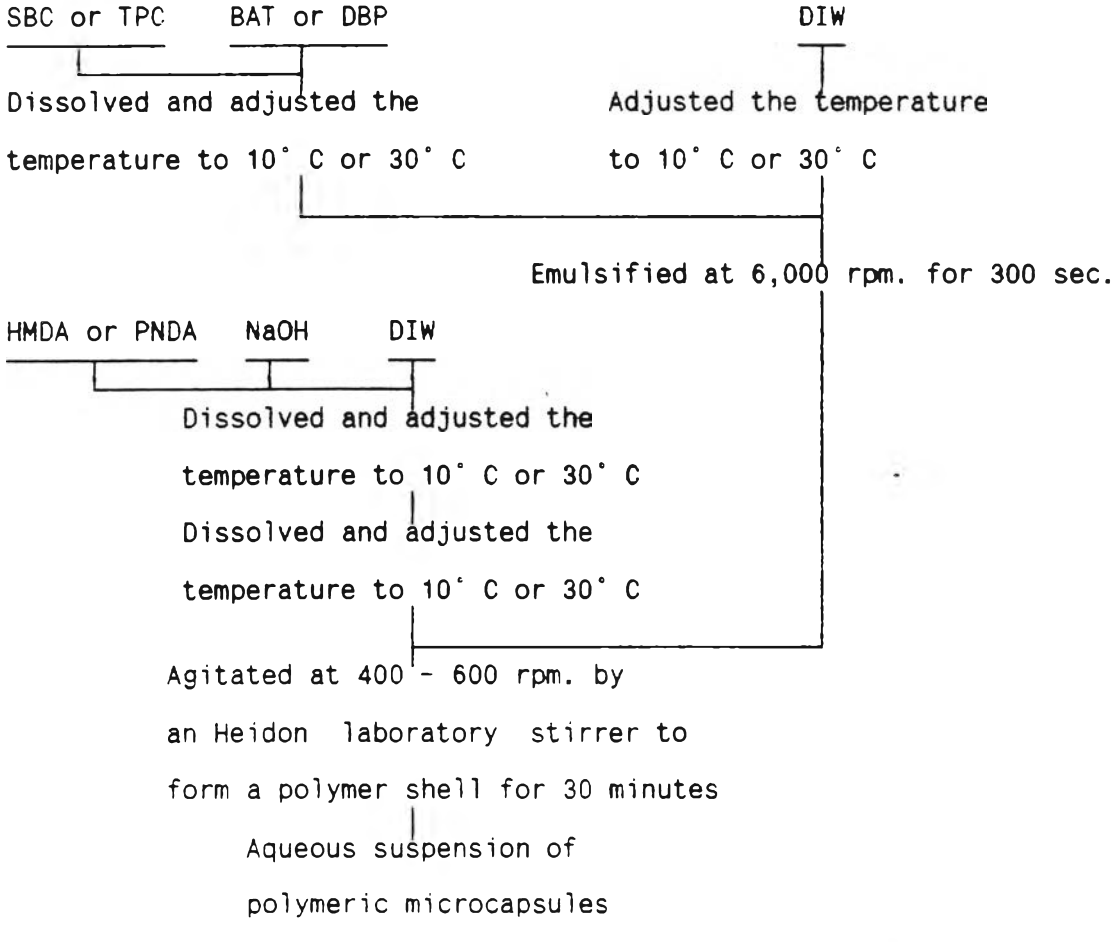
The encapsulated microcapsules of butyl acetate and dibutyl phthalate were synthesized by following the steps in the Flow Charts 5 and 6. The solution of diacid chloride and diamine was prepared by using formulations which were shown in Tables 19 and 20. Tree Diagram 2 was designed for this experiment to ease the experimental works. Poly(hexamethylene sebacamide) and poly(para-phenylene terephthalamide) microcapsules were synthesized by interfacial polycondensation reaction of sebacoyl chloride with hexamethylene diamine at 10°C and terephthaloyl chloride with para-phenylene diamine at 30°C, respectively.

2.7.2.1) Addition of Emulsion to Diamine Solution

Tables 19 and 20 showed the weights of chemicals for the preparation of the stock solutions of diacid chloride and diamine. The stock solutions were kept in a water bath to maintain the solution temperature at 10°C for sebacoyl chloride solution and 30°C for terephthaloyl chloride solution. 210.0 gm. of deionized water and 90.0 gm. of diacid chloride solution were transferred to a T.K.

Homogenizer vessel to be dispersed at the propeller speed of 6,000 rpm. for 300 sec. Concurrently, 200 gm. of diamine solution in 500 ml. beaker was agitated separately with an Heidon laboratory stirrer. The emulsion of diacid chloride solution was then added into the diamine solution and agitated with the propeller speed of 400-600 rpm. for 30 min. to form the polyamide shell at the interface and the polymer shell encapsulated oil droplets dispersed and diffused from the emulsion layer.

Flow Chart 5 Synthesis Method for Addition of Emulsion to Diamine Solution.

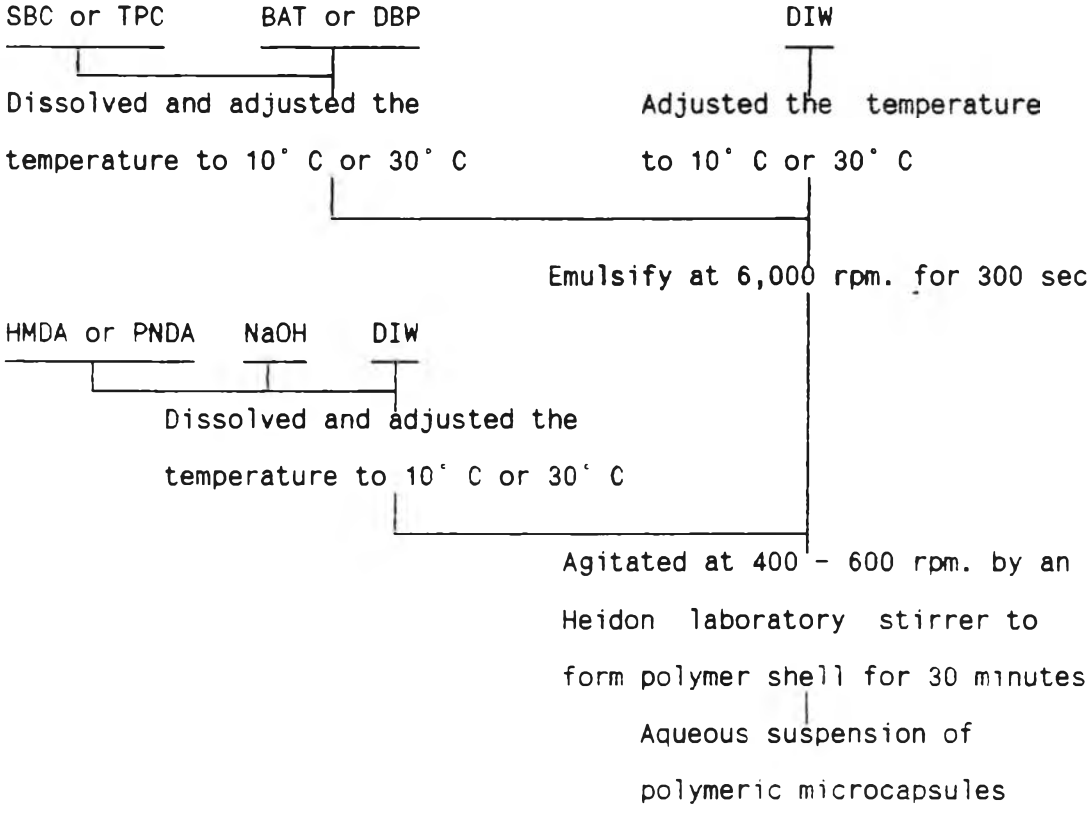


2.7.2.2) Addition of Diamine Solution to Emulsion

Tables 19 and 20 showed the weights of chemicals for the preparation of the stock solutions of diacid chloride

and diamine. The stock solutions were kept in a water bath to maintain the solution temperature at 10°C for sebacoyl chloride solution and 30°C for terephthaloyl chloride solution. 210.0 gm. of deionized water and 90.0 gm. of diacid chloride solution were transferred to a T.K. Homogenizer vessel to be dispersed at the propeller speed of 6,000 rpm. for 300 sec. Immediately, the emulsion was poured into 500 ml. beaker and agitated with an Heidon laboratory stirrer at the propeller speeds of 400-600 rpm., then 200 gm. of the diamine solution was continuously added into the emulsion and further agitated for 30 min. to form the polyamide shell at the interface and the polymer shell encapsulated the oil droplets dispersed and diffused from the emulsion layer.

Flow Chart 6 Synthesis Method for Addition of Diamine Solution to Emulsion.



Tree Diagram 2 Nomenclature of Microencapsulation Process without Emulsifiers.

Monomer	Oil	Process	Speed rpm.	Time sec.	Assigned Name
SBC + HMDA	BAT	Emulsion/diamine	6,000	300	SB-E/D
	BAT	Diamine/emulsion	6,000	300	SB-D/E
	DBP	Emulsion/diamine	6,000	300	SD-E/D
	DBP	Diamine/emulsion	6,000	300	SD-D/E
TPC + PNDA	BAT	Emulsion/diamine	6,000	300	TB-E/D
	BAT	Diamine/emulsion	6,000	300	TB-D/E
	DBP	Emulsion/diamine	6,000	300	TD-E/D
	DBP	Diamine/emulsion	6,000	300	TD-D/E

Table 19 Poly(hexamethylene sebacamide) Microcapsules Formulation.

Assigned Name Chemicals	SB-E/D (gm.)	SB-D/E (gm.)	SD-E/D (gm.)	SD-D/E (gm.)
SBC	9.28	9.28	9.28	9.28
BAT	80.72	80.72		
DBP			80.72	80.72
DIW	210.00	210.00	210.00	210.00
HMDA	4.50	4.50	4.50	4.50
NaOH	3.01	3.01	3.01	3.01
DIW	192.49	192.49	192.49	192.49

Table 20 Poly(para-phenylene terephthalamide) Microcapsules Formulation.

Assigned Name / Chemicals	TB-E/D (gm.)	TB-D/E (gm.)	TD-E/D (gm.)	TD-D/E (gm.)
TPC	6.06	6.06	6.06	6.06
BAT	83.94	83.94		
DBP			83.94	83.94
DIW	210.00	210.00	210.00	210.00
PNDA	3.29	3.29	3.29	3.29
NaOH	2.37	2.37	2.37	2.37
DIW	194.34	194.34	194.34	194.34

2.7.3) Analysis Method

The phenomena of each steps were visual evaluated and compared the final products in term of uniformity and general appearance of the microcapsules in aqueous suspension.

2.7.4) Results

In these synthesis processes, the effect of addition routes on microencapsulation in the absence of emulsifier was compared, i.e. the addition of the emulsion to the diamine solution and vice versa are given in Tables 21 and 22 as follows :-

Table 21 Poly(hexamethylene sebacamide) Microcapsules Containing Butyl Acetate and Dibutyl Phthalate in Different Addition Routes.

Assigned Name	Appearance after Addition
SB-E/D	disperse to uniform suspension
SB-D/E	agglomerate suddenly to become big lumps
SD-E/D	disperse to uniform suspension
SD-D/E	agglomerate suddenly to become big lumps

Table 22 Poly(para-phenylene terephthalamide) Microcapsules Containing Butyl Acetate and Dibutyl Phthalate in Different Addition Routes.

Assigned Name	Appearance after Addition
TB-E/D	disperse to uniform suspension
TB-D/E	agglomerate suddenly to become big lumps
TD-E/D	disperse to uniform suspension
TD-D/E	agglomerate suddenly to become big lumps

2.7.5) Conclusions

The addition of the emulsion to the diamine solution process gives better uniformity and encapsulation efficiency of the aqueous suspension microcapsules than that of the vice versa addition.

2.8) EFFECTS OF MONOMERS, ENCAPSULATED MATERIALS AND EMULSIFIERS ON THE PROPERTIES OF MICROCAPSULES

2.8.1) Purpose

1) To compare the properties of polymer shells synthesized by different monomer-pairs. Poly(hexamethylene sebacamide) was synthesized by sebacoyl chloride reacting with hexamethylene diamine; and poly(para-phenylene terephthalamide) using terephthaloyl chloride reacts with para-phenylene diamine. Encapsulated oils and emulsifiers were also varied to observe the properties of the polymer shell.

2) To compare the encapsulation efficiency of volatile encapsulated oil with non-volatile encapsulated oil in various polymeric shells and types of the emulsifier.

3) To find the suitable emulsifier for different polymer shells and encapsulated oils.

2.8.2) Synthesis Method

Microencapsulation was performed at two temperatures depending on the stability and solubility of sebacoyl chloride and terephthaloyl chloride. Sebacoyl chloride having high solubility in encapsulated oil and being hydrolyzed easily in water was kept at low temperature as shown in Flow Chart 7. Terephthaloyl chloride having less solubility in encapsulated oil and slight hydrolysis in water was used at room temperature as shown in Flow Chart 8. The combination of factors of this experiment was arranged as follows in Tree Diagram 3.

2.8.2.1) Sebacoyl Chloride Process

Emulsifier, diacid chloride and diamine solutions were prepared based on weights giving in Tables 23 and 24. The

solutions were kept in water bath to control the temperature at 10°C. 90.0 gm. of diacid chloride solution was added into a T.K. homogenizer vessel containing 210.0 gm. of the emulsifier solution, this mixture was then homogenized at 6,000 rpm. of propeller speed and 90 sec. of homogenized time to form the oil-in-water emulsion. The emulsion was added into a 500 ml. beaker containing 200.0 gm. of diamine solution and was agitated for 30 minutes with an Heidon laboratory stirrer at 400 - 600 rpm. of propeller speed.

Flow Chart 7 Synthesis Method of SBC for Studying Effect on Microcapsule Properties.

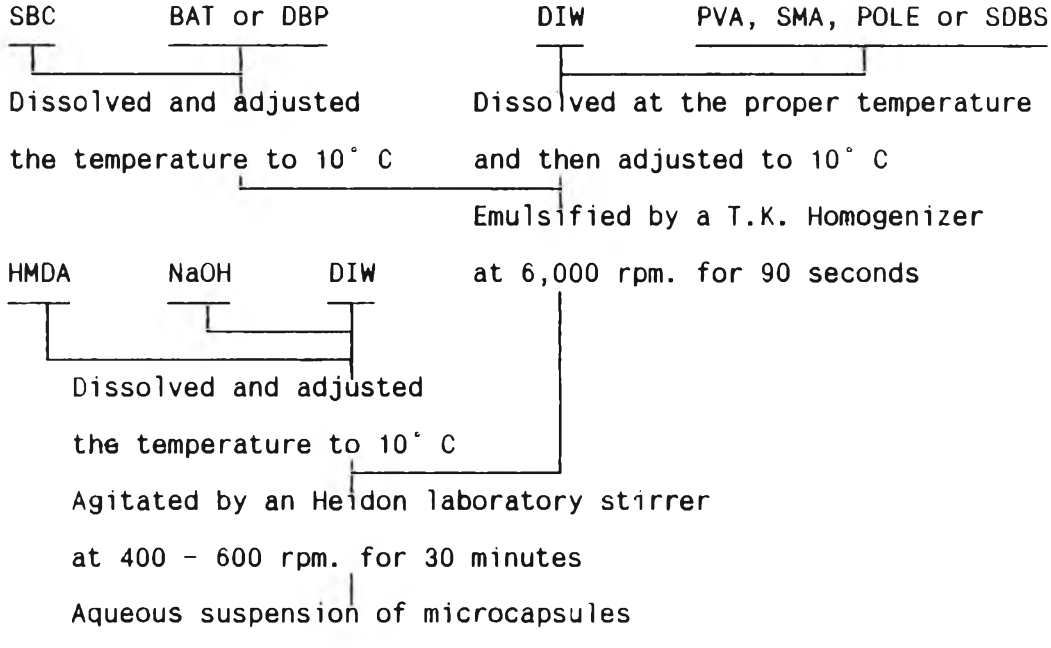


Table 23 Butyl Acetate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Assigned Name / Chemicals	SBPV (gm.)	SBSM (gm.)	SBPO (gm.)	SBSD (gm.)
SBC	9.28	9.28	9.28	9.28
BAT	80.72	80.72	80.72	80.72

Table 23 Butyl Acetate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Assigned Name / Chemicals	SBPV (gm.)	SBSM (gm.)	SBPO (gm.)	SBSD (gm.)
PVA	6.75			
SMA		6.75		
POLE			6.75	
SDBS				19.29
DIW	203.25	203.25	203.25	109.71
HMDA	4.50	4.50	4.50	4.50
NaOH	3.01	3.01	3.01	3.01
DIW	192.49	192.49	192.49	192.49

Table 24 Dibutyl Phthalate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Assigned Name / Chemicals	SDPV (gm.)	SDSM (gm.)	SDPO (gm.)	SDSD (gm.)
SBC	9.28	9.28	9.28	9.28
DBP	80.72	80.72	80.72	80.72
PVA	6.75			
SMA		6.75		
POLE			6.75	
SDBS				19.29
DIW	203.25	203.25	203.25	109.71

Table 24 Dibutyl Phthalate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Assigned Name Chemicals	SDPV (gm.)	SDSM (gm.)	SDPO (gm.)	SDSD (gm.)
HMDA	4.50	4.50	4.50	4.50
NaOH	3.01	3.01	3.01	3.01
DIW	192.49	192.49	192.49	192.49

2.8.2.2) Terephthaloyl Chloride Process

Emulsifier, diacid chloride and diamine solutions were prepared by following weights giving in Tables 25 and 26. The solutions were kept in a water bath to control the temperature at 30°C. 90.0 gm. of diacid chloride solution was added into a T.K. homogenizer vessel containing 210.0 gm. of emulsifier solution. This mixture was then homogenized at 6,000 rpm. of propeller speed and 90 sec. of homogenized time to form oil-in-water emulsion. The emulsion was added into a 500 ml. beaker containing 200.0 gm. of diamine solution and agitated for 30 minutes with an Heidon laboratory stirrer at 400 - 600 rpm. of propeller speed.

Flow Chart 8 Synthesis Method of TPC for Studying Effect on Microcapsule Properties.

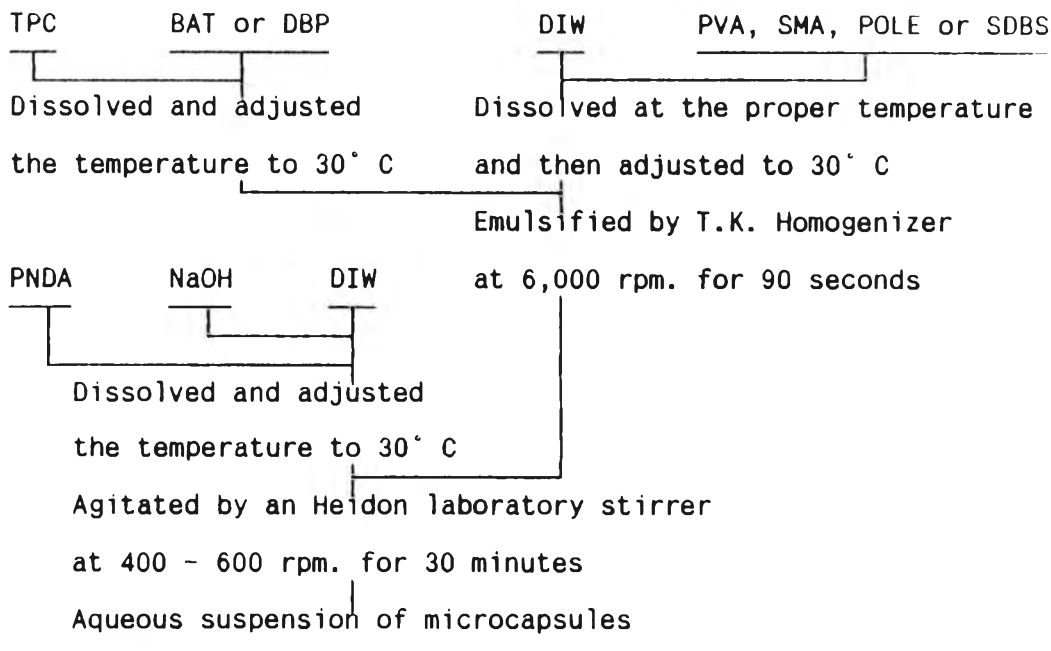


Table 25 Butyl Acetate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Assigned Name / Chemicals	TBPV (gm.)	TBSM (gm.)	TBPO (gm.)	TBSD (gm.)
TPC	6.06	6.06	6.06	6.06
BAT	83.94	83.94	83.94	83.94
PVA	6.75			
SMA		6.75		
POLE			6.75	
SDBS				19.29
DIW	203.25	203.25	203.25	109.71
PNDA	3.29	3.29	3.29	3.29
NaOH	2.37	2.37	2.37	2.37

Table 25 Butyl Acetate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Assigned Name Chemicals	TBPV (gm.)	TBSM (gm.)	TBPO (gm.)	TBSD (gm.)
DIW	194.34	194.34	194.34	194.34

Table 26 Dibutyl Phthalate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Assigned Name Chemicals	TDPV (gm.)	TDSM (gm.)	TDPO (gm.)	TDSD (gm.)
TPC	6.06	6.06	6.06	6.06
DBP	83.94	83.94	83.94	83.94
PVA	6.75			
SMA		6.75		
POLE			6.75	
SDBS				19.29
DIW	203.25	203.25	203.25	109.71
PNDA	3.29	3.29	3.29	3.29
NaOH	2.37	2.37	2.37	2.37
DIW	194.34	194.34	194.34	194.34

Tree Diagram 3 Different Polymers, Oils, Monomers and Emulsifiers Combination.

Monomer	Oil	Emulsifier	Speed rpm.	Time sec.	Assigned Name
SBC + HMDA	BAT	PVA	6,000	90	SBPV
		SMA	6,000	90	SBSM
		POLE	6,000	90	SBPO
		SDBS	6,000	90	SBSD
	DBP	PVA	6,000	90	SDPV
		SMA	6,000	90	SDSM
		POLE	6,000	90	SDPO
		SDBS	6,000	90	SDSD
TPC + PNDA	BAT	PVA	6,000	90	TBPV
		SMA	6,000	90	TBSM
		POLE	6,000	90	TBPO
		SDBS	6,000	90	TBSD
	DBP	PVA	6,000	90	TDPV
		SMA	6,000	90	TDSM
		POLE	6,000	90	TDPO
		SDBS	6,000	90	TDSD

2.8.3) Analysis Method

2.8.3.1) Optical Microscopy

One drop of aqueous microcapsules was placed on a glass slide then one drop of water was added to dilute the microcapsules and gently spread into a thin layer. The proper magnification was selected to observe the physical properties of microcapsules such as diameter and distribution of the polymeric microcapsules etc. and then optical micrographs were taken with a Zeiss optical microscope before and after the water was evaporated.

2.8.3.2) Scanning Electron Microscopy

The aqueous microcapsules were diluted about ten times with deionized water. One drop of dilute aqueous microcapsules

was then placed on a glass slide and gently spread into a thin layer. The aqueous microcapsules layer was dried at room temperature for one day then the dried layer was coated with gold. The microcapsule layer was examined and the electron micrographs were taken with a Joel scanning electron microscope at proper magnifications.

2.8.3.3) Gas Chromatography

50.0 gm. of chloroform was added into a 250 ml. separatory funnel containing 100.0 gm. of aqueous microcapsules. The mixture was subsequently shaken and kept on a stand to render the separation of the emulsion. The lower layer, aqueous microcapsules, was drained out and the upper layer, containing extracted chloroform, was filtered by a filter paper. 1.0 microliter of the extracted chloroform was injected in to a gas chromatograph which was installed with a PEG 20M coated capillary column and the temperature was set at 300°C for split injector, column oven of 250°C, 300°C for the FID detector. The concentration of unencapsulated oil was calculated by the external standard method via the standard dibutyl phthalate solution.

2.8.3.4) Particle Size Analyzer

The instrument was set at centrifuge mode and 1,500 rpm. of rotational speed was also selected. Deionized water was poured into the first glass cell until the water front reached the upper mark of the cell. The transmittance of this blank solution was then adjusted to 0.0%T. The transmittance of the second glass cell containing the aqueous microcapsules was adjusted to 100.0%T by diluting with deionized water. Before starting, the parameters for calculation : 1.05 for particle density, 1.00 for liquid density, 1.00 for liquid viscosity and 0.00 for the distance path were entered. The analytical result was printed out in percentage cumulative size distribution given in forms of tables and histograms. Furthermore, all results were recalculated by an

IBM personal computer with the Lotus 123 release 2.01 and the Microsoft Chart version 3.0 software.

2.8.3.5) Stability of the Suspension or Emulsion

100.0 ml. of an aqueous suspension or emulsion of the microcapsules was added into a 100 ml. cylinder and was kept for 24 hours to measure the volume of microcapsules sedimented to the bottom of the cylinder.

2.8.3.6) General Properties

Uniformity, color, separation, sedimentation and etc. were observed by eye evaluation.

2.8.4) Results

2.8.4.1) General Appearance

The general appearances of poly(hexamethylene sebacamide) and poly(para-phenylene terephthalamide) microcapsules are reported in Tables 27, 28, 29 and 30 as follows :-

Table 27 Butyl Acetate being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	Appearance
SBPV	PVA	large oily layer on the surface
SBSM	SMA	coagulum during emulsification
SBPO	POLE	coagulum during polymerization
SBSD	SDBS	large oily layer on tne surface

Table 28 Dibutyl Phthalate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	Appearance
SDPV	PVA	uniform suspension
SDSM	SMA	coagulum during emulsification
SDPO	POLE	coagulum during polymerization
SDSD	SDBS	little oily layer on the surface

Table 29 Butyl Acetate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	Appearance
TBPV	PVA	large oily layer on the surface
TBSM	SMA	coagulum during emulsification
TBPO	POLE	coagulum during polymerization
TBSD	SDBS	large oily layer on the surface

Table 30 Dibutyl Phthalate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	Appearance
TDPV	PVA	uniform suspension
TDSM	SMA	coagulum during emulsification
TDPO	POLE	coagulum during polymerization
TDSD	SDBS	little oily layer on the surface

2.8.4.2) Microscopic Properties

Photomicrograph series 1 showed that microcapsules could not be synthesized in any case, whereas these of series 2 showed that microcapsules could not be synthesized when using SMA, POLE and SDBS as emulsifier but only PVA as emulsifier could. The result was confirmed by % unencapsulated oil analyzed by gas chromatograph as shown in Tables 35 and 36. The same trends were observed by photomicrograph series 3 and 4 and Tables 37 and 38.

2.8.4.3) Particle Size Distribution

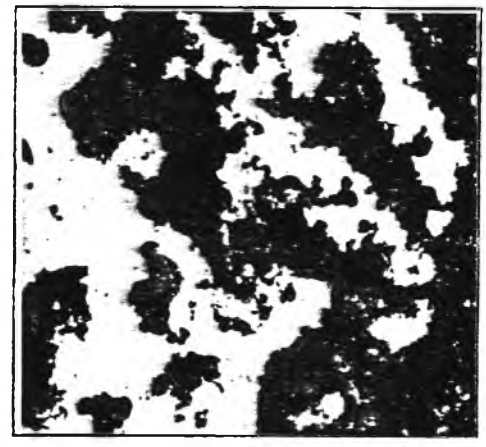
All average particle sizes and particle size distributions. of the sample synthesized by using butyl acetate as encapsulated oil and styrene maleic anhydride copolymer, poly(oxyethylene lauryl ether) and sodium dodecyl benzene sulfonate as emulsifier cannot be measured. Only the samples synthesized by using dibutyl phthalate as encapsulated oil and poly(vinyl alcohol) as emulsifier can form microcapsules. The particle size and size distribution for SDPV and TDPV, dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) and poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier, are showed in Tables 31, 32, 33, and 34. Graph series 1 and 2 depict the particle size and particle size distribution of the microcapsules presented in Tables 31 - 32.

2.8.4.4) Microencapsulation Efficiency

Tables 35, 36, 37, and 38 show the percentage of unencapsulated oil of all the samples synthesized by using butyl acetate as encapsulated oil and styrene maleic anhydride copolymer, poly(oxyethylene luaryl ether), and sodium dodecyl benzene sulfonate as emulsifier, and the percentage of unencapsulated oil was greater than

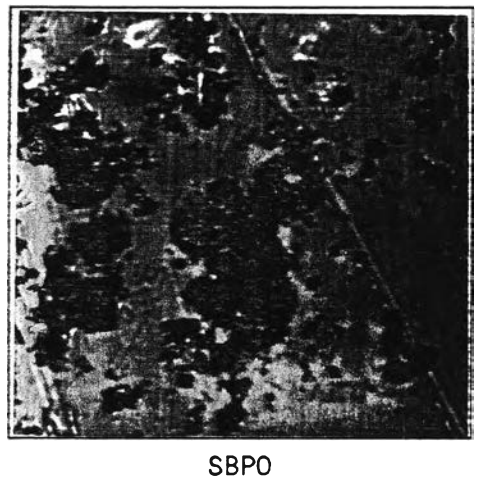
SBPV

Poly(vinyl alcohol)



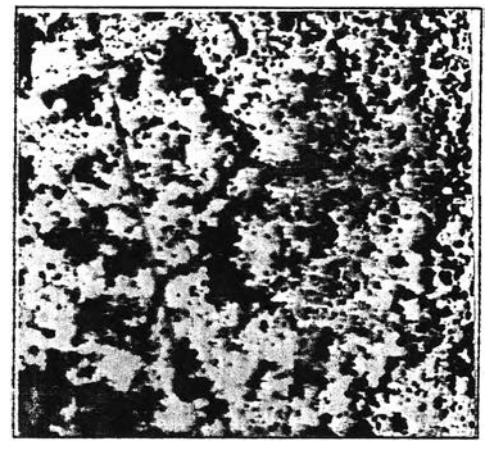
SBSM

Styrene maleic anhydride (Na)



SBPO

Poly(oxyethylene luaryl ether)

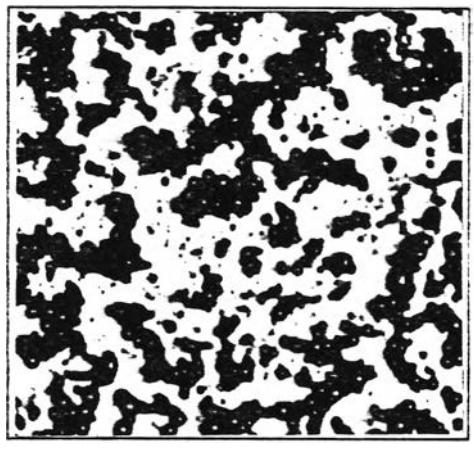


SBSD

Sodium dodecyl benzene sulfonate

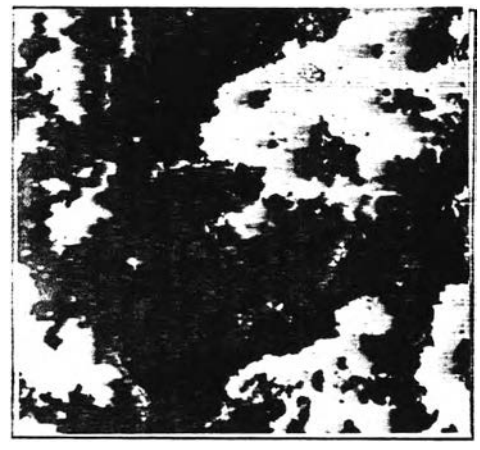
Photomicrograph series 1

Butyl acetate being encapsulated by poly(hexamethylene sebacamide) microcapsules in various emulsifiers. Zeiss optical microscope, 100 times magnification and 2.5 times print enlargement.



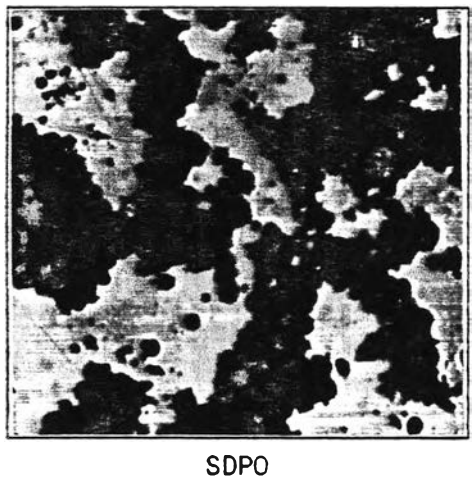
SDPV

Poly(vinyl alcohol)



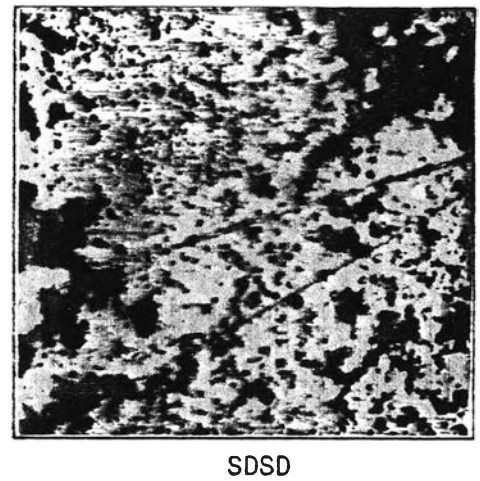
SDSM

Styrene maleic anhydride (Na)



SDPO

Poly(oxyethylene luaryl ether)

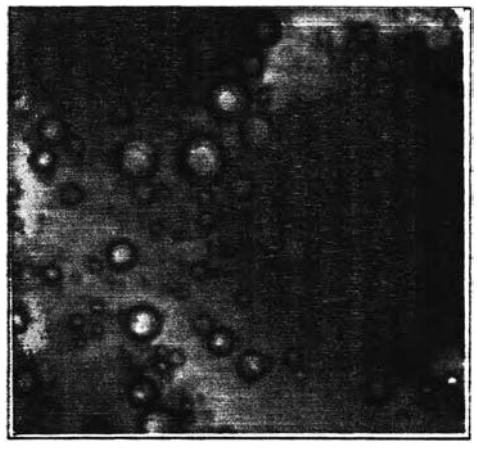


SDSD

Sodium dodecyl benzene sulfonate

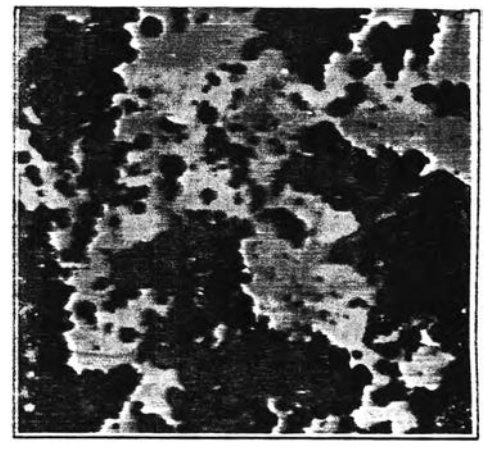
Photomicrograph series 2

Dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules in various emulsifiers. Zeiss optical microscope, 100 times magnification and 2.5 times print enlargement.



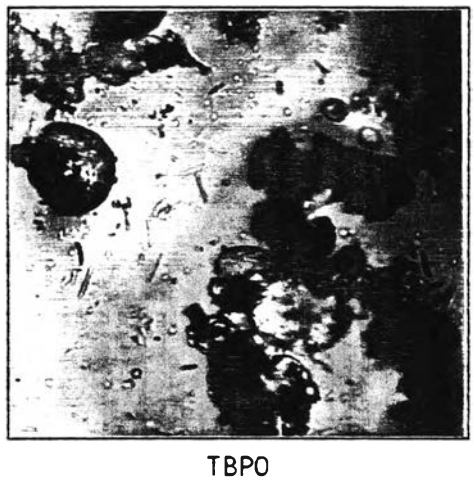
TBPV

Poly(vinyl alcohol)



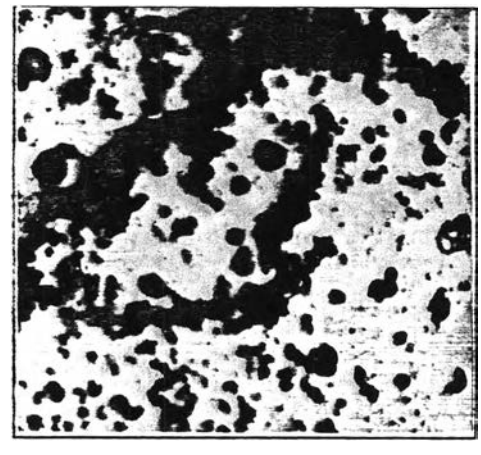
TBSM

Styrene maleic anhydride (Na)



TBPO

Poly(oxyethylene luaryl ether)

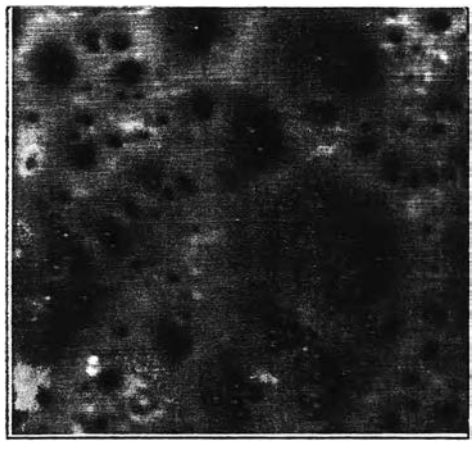


TBSD

Sodium dodecyl benzene sulfonate

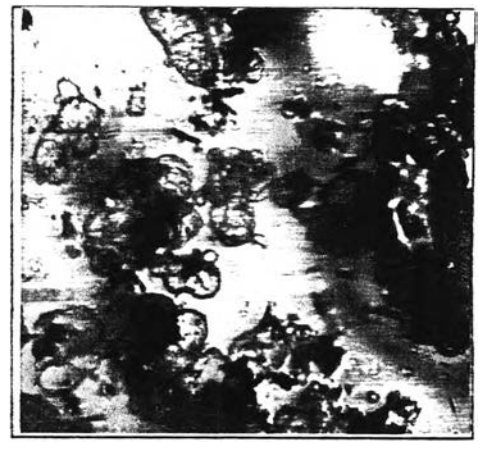
Photomicrograph series 3

Butyl acetate being encapsulated by poly(para-phenylene terephthalamide) microcapsules in various emulsifiers. Zeiss optical microscope, 100 times magnification and 2.5 times print enlargement.



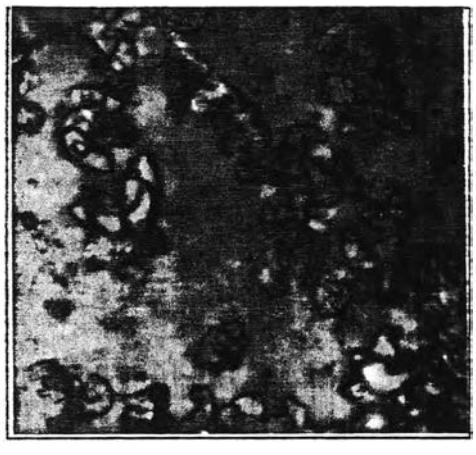
TDPV

Poly(vinyl alcohol)



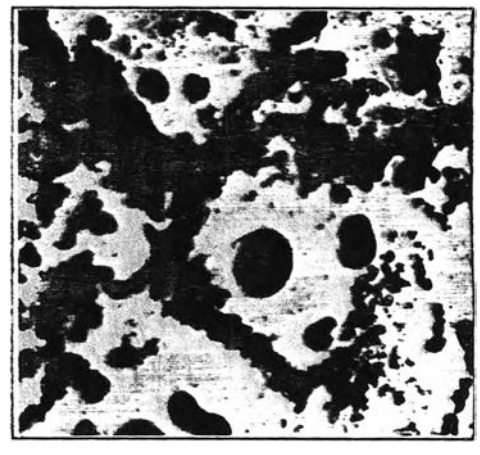
TDSM

Styrene maleic anhydride (Na)



TDPO

Poly(oxyethylene luaryl ether)



TDSD

Sodium dodecyl benzene sulfonate

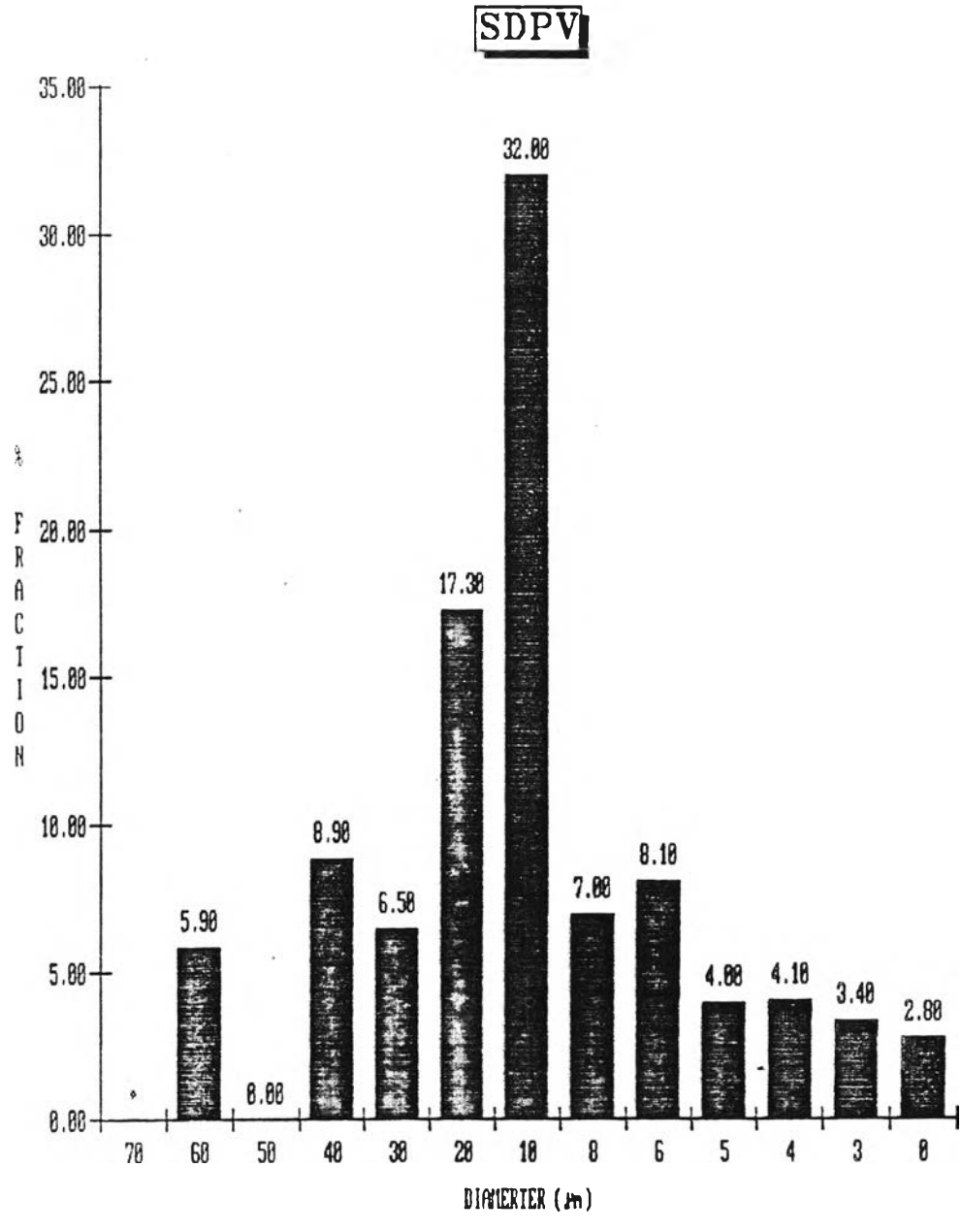
Photomicrograph series 4

Dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules in various emulsifiers. Zeiss optical microscope, 100 times magnification and 2.5 times print enlargement.

Table 31 Particle Size Distribution of SDPV.

Dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier, 6,000 rpm. of propeller speed and 90 sec. of homogenized time; assigned name : SDPV

Diameter (μm) (Micrometer)	Average Diameter	Percentage Cumulative	Percentage Difference	Diameter Coefficient
70.00	*.**	0.0	0.00	0.00
60.00	65.00	5.9	5.90	383.50
50.00	55.00	5.9	0.00	0.00
40.00	45.00	14.8	8.90	400.50
30.00	35.00	21.3	6.50	227.50
20.00	25.00	38.6	17.30	432.50
10.00	15.00	70.6	32.00	480.00
8.00	9.00	77.6	7.00	63.00
6.00	7.00	85.7	8.10	56.70
5.00	5.50	89.7	4.00	22.00
4.00	4.50	93.8	4.10	18.45
3.00	3.50	97.2	3.40	11.90
0.00	1.50	100.0	2.80	4.20
			Average Particle Size ((μm)	21.00

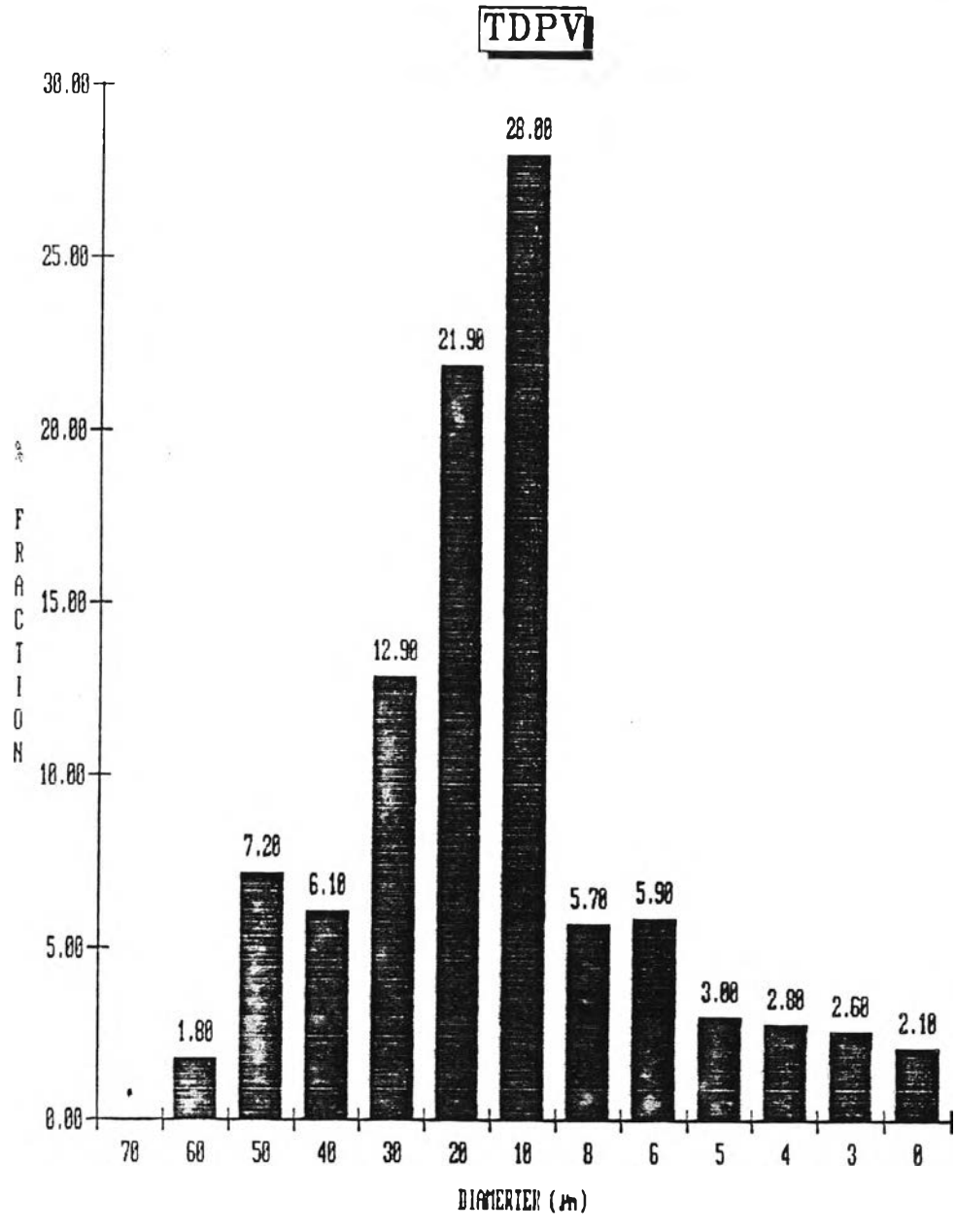


Graph series 1 Histogram of Particle Size Distribution of SDPV.
(The graphs were made from the data from Table 31)
Particle size distribution of SDPV of which dibutyl phthalate is encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.

Table 32 Particle Size Distribution of TDPV.

Dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier, 6,000 rpm. of propeller speed and 90 sec. of homogenized time; assigned name : TDPV

Diameter (μm) (Micrometer)	Average Diameter	Percentage Cumulative	Percentage Difference	Diameter Coefficient
70.00	*.**	0.0	0.00	0.00
60.00	65.00	1.8	1.80	117.00
50.00	55.00	9.0	7.20	396.00
40.00	45.00	15.1	6.10	274.50
30.00	35.00	28.0	12.90	451.50
20.00	25.00	49.9	21.90	547.50
10.00	15.00	77.9	28.00	420.00
8.00	9.00	83.6	5.70	51.30
6.00	7.00	89.5	5.90	41.30
5.00	5.50	92.5	3.00	16.50
4.00	4.50	95.3	2.80	12.60
3.00	3.50	97.9	2.60	9.10
0.00	1.50	100.0	2.10	3.15
			Average Particle Size ((μm)	23.40



Graph series 2 Histogram of Particle Size Distribution of TDPV.

(The graphs were made from the data from Table 32)

Particle size distribution of TDPV of which dibutyl phthalate is encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.

Table 33 Summarized Particle Size Distribution of SDPV.

Summarized particle size distribution from Table 31

Diameter Range (μm)	% Fraction
< 60	5.9
60 - 50	0.0
50 - 40	8.9
40 - 30	6.5
30 - 20	17.3
20 - 10	32.0
10 >	29.4

Table 34 Summarized Particle Size Distribution of TDPV.

Summarized particle size distribution from Table 32

Diameter Range (μm)	% Fraction
< 60	1.8
60 - 50	7.2
50 - 40	6.1
40 - 30	12.9
30 - 20	21.9
20 - 10	28.0
10 >	22.1

80%. Only the samples, SDPV and TDPV, which were synthesized by using dibutyl phthalate as encapsulated oil and poly(vinyl alcohol) as emulsifier had lesser percentage of unencapsulated oil.

Table 35 Butyl Acetate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	% Unencapsulated Butyl Acetate
SBPV	PVA	80.05
SBSM	SMA	97.49
SBPO	POLE	95.26
SBSD	SDBS	86.87

Table 36 Dibutyl Phthalate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	% Unencapsulated Dibutyl Phthalate
SDPV	PVA	1.97
SDSM	SMA	98.56
SDPO	POLE	92.47
SDSD	SDBS	87.65

Table 37 Butyl Acetate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	% Unencapsulated Butyl Acetate
TBPV	PVA	86.45

Table 37 Butyl Acetate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	% Unencapsulated Butyl Acetate
TBSM	SMA	94.74
TBPO	POLE	91.34
TBSD	SDBS	89.76

Table 38 Dibutyl Phthalate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules in Various Emulsifiers.

Name	Emulsifier	% Unencapsulated Dibutyl Phthalate
TDPV	PVA	2.03
TDSM	SMA	97.89
TDPO	POLE	91.35
TDSD	SDBS	88.43

2.8.5) Conclusions

1) Butyl acetate cannot be used as encapsulated oil in any cases because its vapor pressure is too high.

2) Styrene maleic anhydride copolymer cannot be used as emulsifier because its emulsifying efficiency during emulsification is too low.

3) Poly(oxyethylene luaryl ether) cannot be used as emulsifier because its emulsifying efficiency during polymerization is not enough.

4) Sodium dodecyl benzene sulfonate cannot be used as emulsifier because it interferes with the shell formation during interfacial polycondensation.

5) Microcapsules can be synthesized by using dibutyl phthalate as encapsulated oil and poly(vinyl alcohol) as emulsifier. Sebacoyl chloride and hexamethylene diamine or terephthaloyl chloride and para-phenylene diamine can also be used as monomer pairs to synthesize poly(hexamethylene sebacamide) and poly(para-phenylene terephthalamide) microcapsule shells.

2.9) EFFECT OF PROPELLER SPEED AND HOMOGENIZING TIME

2.9.1) Purpose

To find the effect of propeller speed and homogenizing time during emulsification on the properties of microcapsules under the following conditions :-

1) The microcapsules were synthesized by using sebacoyl chloride and hexamethylene diamine, and terephthaloyl chloride and para-phenylene diamine, as monomer pair; with dibutyl phthalate as encapsulated oil and poly(vinyl alcohol) as emulsifier.

2) The concentration of diacid chlorides in dibutyl phthalate was 3.0 gm./27.0 gm. for sebacoyl chloride and 2.0 gm./28.0 gm. for terephthaloyl chloride and poly(vinyl alcohol) was 7.5% of the total oil phase.

3) The oil to water phase ratio in emulsification was 30:70 and emulsion to diamine solution in interfacial polycondensation was 60:40 weight by weight.

4) Microencapsulation was carried out with the same

procedure in the previous experiment. The temperature was controlled at 10°C for sebacoyl chloride system and 30°C of terephthaloyl chloride system.

5) The propeller speed was varied from 2,000 to 10,000 rpm. and homogenizing time from 30 to 150 seconds.

2.9.2) Synthesis Method

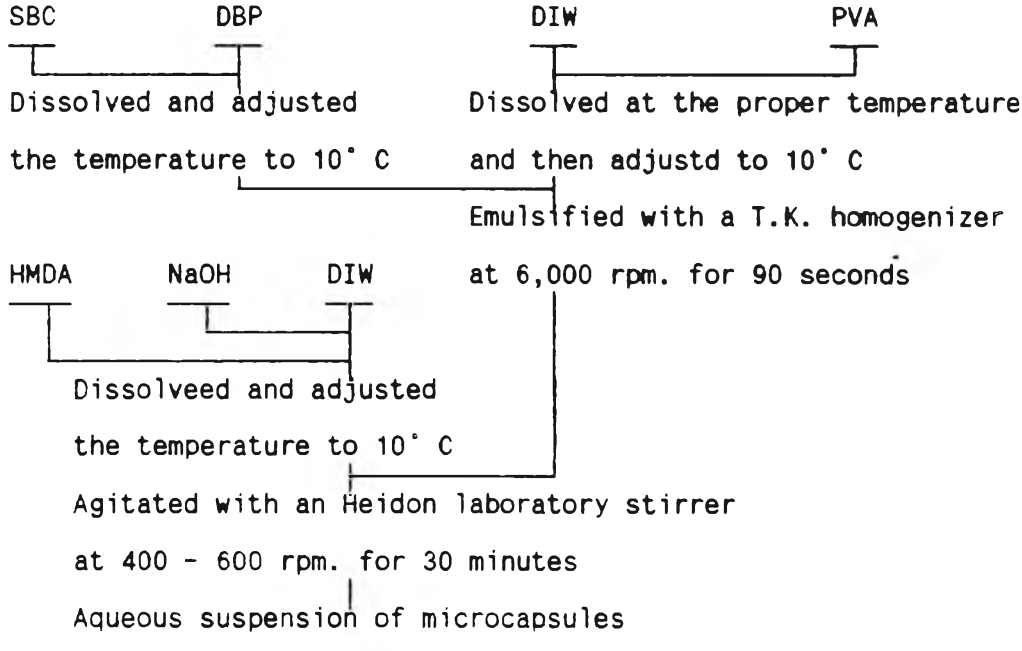
The stock solutions of diacid chloride, emulsifier and diamine were prepared and kept in a water bath to control temperature at 10°C for sebacoyl chloride and 30°C for terephthaloyl chloride. 210.0 gm. of the emulsifier solution and 90.0 gm. of the diacid chloride solution were poured into a T.K. homogenizer vessel. The mixture was then homogenized at the propeller speeds and homogenized times which were arranged as shown in the Tree Diagram 4 to form an oil-in-water emulsion. The emulsion was poured into a 500 ml. beaker containing 200.0 gm. of diamine solution while being stirred with an Heidon laboratory stirrer at the propeller speed 400-600 rpm. Microencapsulation occurred though the interfacial polycondensation at the interface of the diacid chloride solution with droplets of oil and the diamine solution which have emulsifier solution as stabilizer.

2.9.2.1) Sebacoyl Chloride System

6.75 gm. of poly(vinyl alcohol) was dissolved in 203.25 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 10°C and kept in the water bath to control the temperature. The diacid chloride solution which contained 9.28 gm. of sebacoyl chloride dissolved in 80.72 gm. of dibutyl phthalate, was prepared at room temperature and kept in the water bath to control the temperature at 10°C. The diamine solution consisting of 4.50 gm. of hexamethylene diamine and 3.01 of

sodium hydroxide which were added into a 500 ml. beaker containing 192.49 gm. of deionized water, was prepared at room temperature and then adjusted the temperature to 10°C. The diamine solution was then stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of propeller speed to be mixed with the emulsion portion. This emulsion was prepared by homogenizing the mixture of the diacid chloride and emulsifier solutions at the propeller speeds and homogenized time which were indicated in Tree Diagram 4. This emulsion portion was subsequently poured into the diamine solution and was continuously agitated for 30 minutes to form poly(hexamethylene sebacamide) microcapsules containing dibutyl phthalate as encapsulated material.

Flow Chart 9 Synthesis Method of SBC for Studying Effect of Propeller Speeds and Homogenizing Times.



2.9.2.2) Terephthaloyl Chloride System

6.75 gm. of poly(vinyl alcohol) was dissolved in 203.25 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 30°C and kept

in a water bath to control the temperature. To prepare the diacid chloride solution, 6.06 gm. of terephthaloyl chloride was dissolved in 83.94 gm. of dibutyl phthalate, this was prepared at room temperature and kept in a water bath to control the temperature at 30°C. The diamine solution containing 3.29 gm. of para-phenylene diamine and 2.37 of sodium hydroxide were added into a 500 ml. beaker containing 194.34 gm. of deionized water. The solutions were prepared at room temperature and were then adjusted to 30°C. The diamine solution was stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of the propeller speed. The emulsion was prepared by homogenizing the mixture of the diacid chloride and the emulsifier solutions at the propeller speed and homogenized time which were shown in Tree Diagram 4. This emulsion portion was poured into the diamine solution and was continuously agitated for 30 minutes to form poly(para-phenylene terephthalamide) microcapsules containing dibutyl phthalate as encapsulated material.

Flow Chart 10 Synthesis Method of TPC for Studying Effect of Propeller Speeds and Homogenizing Times.

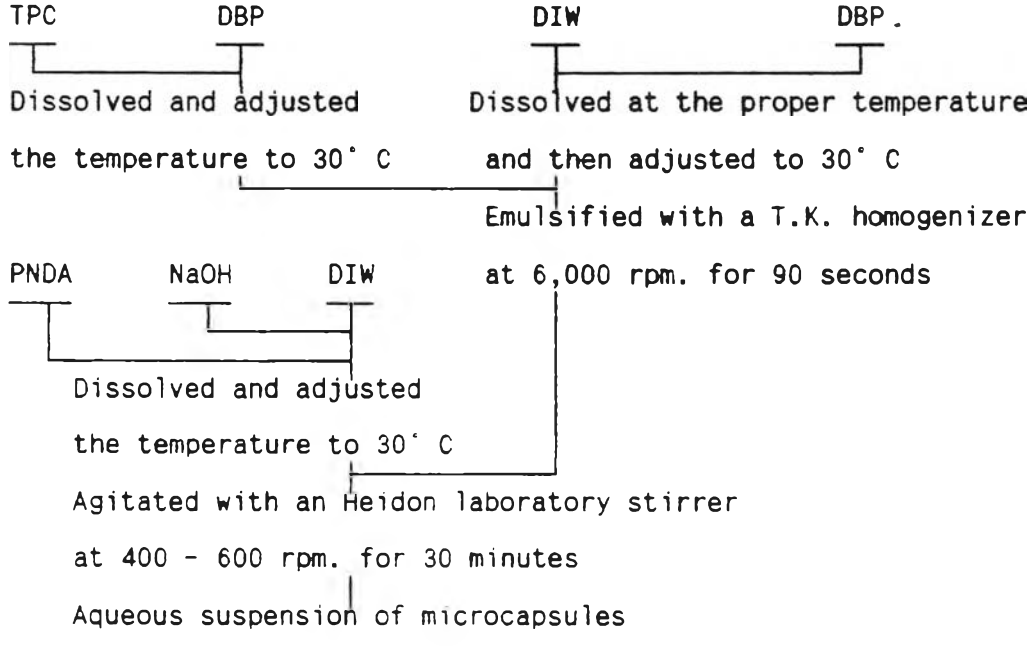


Table 39 Formulation of SDP and TDP Series.

Dibutyl phthalate was encapsulated by polyamide shell based on the following formulations in which the effects of propeller speed and homogenizing time were studied.

Assigned Name Chemicals	SDP Series (gm.)	TDP Series (gm.)
SBC	9.28	
TPC		6.06
DBP	80.72	83.94
PVA	6.75	6.75
DIW	203.25	203.25
HMDA	4.50	
PNDA		3.29
NaOH	3.01	2.37
DIW	192.49	194.34

Tree Diagram 4 Combination of the Propeller Speed and Homogenizing Time on Microcapsule Formation for SDP and TDP Series.

Tree Diagram 4-1 Propeller Speed and Homogenization Time Combination for Poly(hexamethylene sebacamide) Microcapsule Formation.

Tree Diagram 4-1 Propeller Speed and Homogenization Time Combination for Poly(hexamethylene sebacamide) Microcapsule Formation.

Monomer	Oil	Emulsifier	Speed (rpm.)	Time (sec.)	Assigned Name
SBC + HMDA	DBP	PVA	2,000	30	SDP020/030
				60	SDP020/060
				90	SDP020/090
				120	SDP020/120
				150	SDP020/150
	DBP	PVA	4,000	30	SDP040/030
				60	SDP040/060
				90	SDP040/090
				120	SDP040/120
				150	SDP040/150
	DBP	PVA	6,000	30	SDP060/030
				60	SDP060/060
				90	SDP060/090
				120	SDP060/120
				150	SDP060/150
	DBP	PVA	8,000	30	SDP080/030
				60	SDP080/060
				90	SDP080/090
				120	SDP080/120
				150	SDP080/150
	DBP	PVA	10,000	30	SDP100/030
				60	SDP100/060
				90	SDP100/090
				120	SDP100/120
				150	SDP100/150

Tree Diagram 4-2 Propeller Speed and Homogenization Time Combination for Poly(para-phenylene terephthalamide) Microcapsule Formation.

Monomer	Oil	Emulsifier	Speed	Time	Assigned Name
			rpm.	sec.	
TPC + PNDA	DBP	PVA	2,000	30	TDP020/030
				60	TDP020/060
				90	TDP020/090
				120	TDP020/120
				150	TDP020/150
	DBP	PVA	4,000	30	TDP040/030
				60	TDP040/060
				90	TDP040/090
				120	TDP040/120
				150	TDP040/150
	DBP	PVA	6,000	30	TDP060/030
				60	TDP060/060
				90	TDP060/090
				120	TDP060/120
				150	TDP060/150
	DBP	PVA	8,000	30	TDP080/030
				60	TDP080/060
				90	TDP080/090
				120	TDP080/120
				150	TDP080/150
	DBP	PVA	10,000	30	TDP100/030
				60	TDP100/060
				90	TDP100/090
				120	TDP100/120
				150	TDP100/150

2.9.3) Analysis Method

General appearance was observed by visual evaluation; volume of separation after sedimentation for 24 hours was measured in a 100 ml. cylinder; microscopic properties were examined by Zeiss optical microscope and Joel scanning electron microscope; particle size and particle size distribution were measured by Shimadzu particle size

analyzer; and microencapsulation efficiency was analyzed by Shimadzu gas chromatograph. The detail of each method was explained in the previous experiment.

2.9.4) Results

2.9.4.1) General Properties

The appearance and amount of microcapsule sedimentation after keep for 24 hours were shown in Tables 40 and 41. Increasing propeller speed and homogenizing time decrease the amount of sediments but increasing propeller speed have more effective than homogenized time.

Table 40 Sedimentation and Appearance of SDP020/030-SDP100/150. Dibutyl Phthalate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules Using Poly(vinyl alcohol), Emulsifier, 7.5% of the Total Oil Phase.

Name	Sedimentation after 24 hours	Appearance by Visual Evaluation
SDP020/030	19 ml.	milky white suspension, not uniform
SDP020/060	15 ml.	milky white suspension, not uniform
SDP020/090	14 ml.	milky white suspension, not uniform
SDP020/120	12 ml.	milky white suspension, not uniform
SDP020/150	11 ml.	milky white suspension, not uniform
SDP040/030	13 ml.	milky white suspension, not uniform
SDP040/060	12 ml.	milky white suspension, not uniform
SDP040/090	10 ml.	milky white suspension, not uniform
SDP040/120	8 ml.	milky white suspension, not uniform
SDP040/150	7 ml.	milky white suspension, not uniform

Table 40 Sedimentation and Appearance of SDP020/030-SDP100/150. Dibutyl Phthalate Being Encapsulated by Poly(hexamethylene sebacamide) Microcapsules Using Poly(vinyl alcohol), Emulsifier, 7.5% of the Total Oil Phase.

Name	Sedimentation after 24 hours	Appearance by Visual Evaluation
SDP060/030	9 ml.	milky white suspension and uniform
SDP060/060	7 ml.	milky white suspension and uniform
SDP060/090	7 ml.	milky white suspension and uniform
SDP060/120	6 ml.	milky white suspension and uniform
SDP060/150	5 ml.	milky white suspension and uniform
SDP080/030	4 ml.	milky white emulsion and uniform
SDP080/060	2 ml.	milky white emulsion and uniform
SDP080/090	1 ml.	milky white emulsion and uniform
SDP080/120	1 ml.	milky white emulsion and uniform
SDP080/150	0 ml.	milky white emulsion and uniform
SDP100/030	0 ml.	milky white emulsion and uniform
SDP100/060	0 ml.	milky white emulsion and uniform
SDP100/090	0 ml.	milky white emulsion and uniform
SDP100/120	0 ml.	milky white emulsion and uniform
SDP100/150	0 ml.	milky white emulsion and uniform

Table 41 Sedimentation and Appearance of TDP020/030-TDP100/150. Dibutyl Phthalate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules Using Poly(vinyl alcohol), Emulsifier, 7.5% of the Total Oil Phase.

Name	Sedimentation after 24 hours	Appearance by Visual Evaluation
TDP020/030	22 ml.	dark brown suspension, not uniform
TDP020/060	19 ml.	dark brown suspension, not uniform
TDP020/090	18 ml.	dark brown suspension, not uniform
TDP020/120	15 ml.	dark brown suspension, not uniform
TDP020/150	14 ml.	dark brown suspension, not uniform
TDP040/030	15 ml.	dark brown suspension, not uniform
TDP040/060	13 ml.	dark brown suspension, not uniform
TDP040/090	11 ml.	dark brown suspension, not uniform
TDP040/120	8 ml.	dark brown suspension, not uniform
TDP040/150	7 ml.	dark brown suspension, not uniform
TDP060/030	7 ml.	dark brown suspension and uniform
TDP060/060	6 ml.	dark brown suspension and uniform
TDP060/090	5 ml.	dark brown emulsion and uniform
TDP060/120	5 ml.	dark brown emulsion and uniform
TDP060/150	4 ml.	dark brown emulsion and uniform
TDP080/030	5 ml.	milky brown emulsion and uniform
TDP080/060	4 ml.	milky brown emulsion and uniform
TDP080/090	4 ml.	milky brown emulsion and uniform
TDP080/120	3 ml.	milky brown emulsion and uniform
TDP080/150	2 ml.	milky brown emulsion and uniform

Table 41 Sedimentation and Appearance of TDP020/030-TDP100/150. Dibutyl Phthalate Being Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules Using Poly(vinyl alcohol), Emulsifier, 7.5% of the Total Oil Phase.

Name	Sedimentation after 24 hours	Appearance by Visual Evaluation
TDP100/030	2 ml.	milky brown emulsion and uniform
TDP100/060	1 ml.	milky brown emulsion and uniform
TDP100/090	0 ml.	milky brown emulsion and uniform
TDP100/120	0 ml.	milky brown emulsion and uniform
TDP100/150	0 ml.	milky brown emulsion and uniform

2.9.4.2) Microscopic Properties

1) Photomicrograph series 5 - 9 show that poly(hexamethylene sebacamide) microcapsules which contain dibutyl phthalate as encapsulated material can be synthesized by using poly(vinyl alcohol) as emulsifier. When the speed of propeller is increased the average particle size decreases and when the homogenizing time is increased the particle size distribution is much more even.

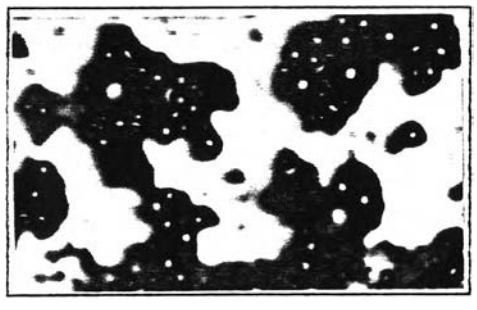
2) Photomicrograph series 10 - 14 show that poly(para-phenylene terephthalamide) microcapsules which contain dibutyl phthalate as encapsulated material can be synthesized by using poly(vinyl alcohol) as emulsifier. When the speed of propeller is increased the average particle size decreases and when the homogenizing time is increased the particle size distribution is much more even.

SDP020/030

2,000 rpm., 30 sec.

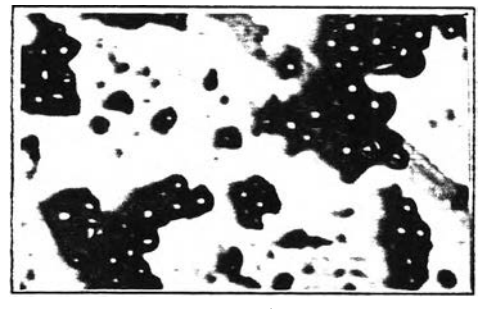
SDP020/120

2,000 rpm., 120 sec.



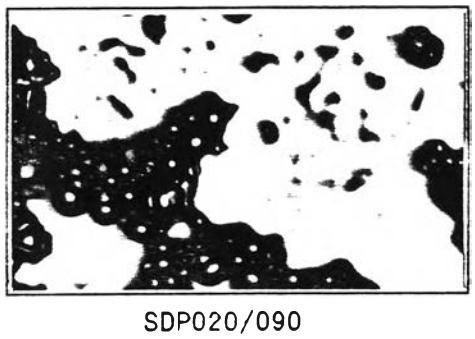
SDP020/060

2,000 rpm., 60 sec.



SDP020/150

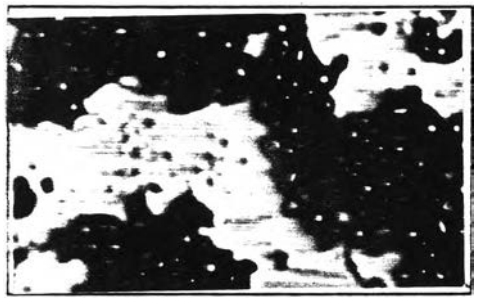
2,000 rpm., 150 sec.



SDP020/090

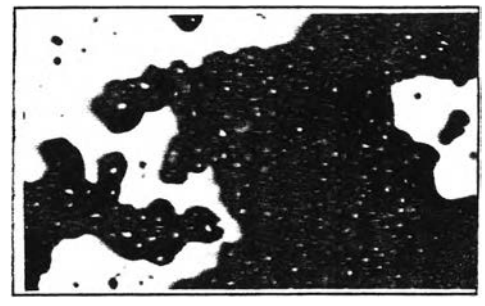
2,000 rpm., 90 sec.

Photomicrograph series 5 Photomicrographs of SDP020/030-SDP020/150. Poly(hexamethylene sebacamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 2,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.



SDP040/030

4,000 rpm., 30 sec.

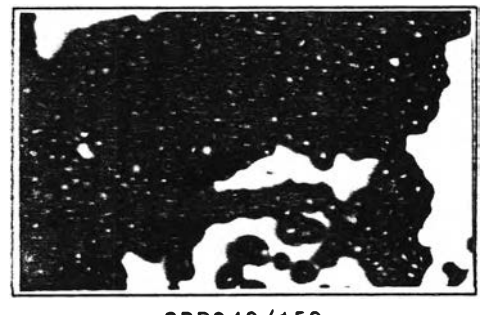


SDP040/120

4,000 rpm., 120 sec.

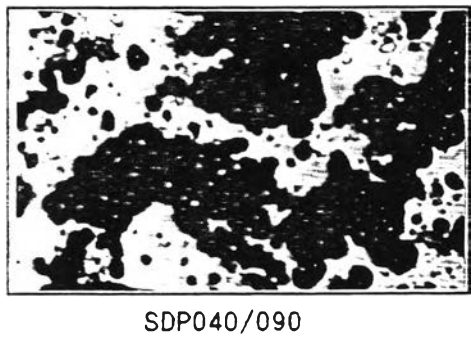
SDP040/060

4,000 rpm., 60 sec.



SDP040/150

4,000 rpm., 150 sec.



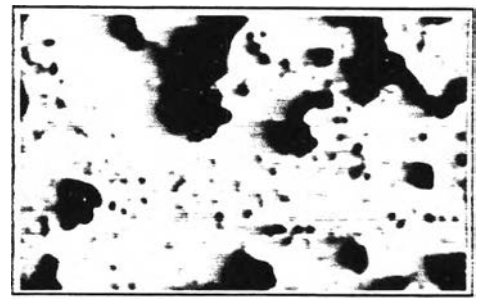
SDP040/090

4,000 rpm., 90 sec.

Photomicrograph series 6 Photomicrographs of SDP040/030-SDP040/150. Poly(hexamethylene sebacamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 4,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.

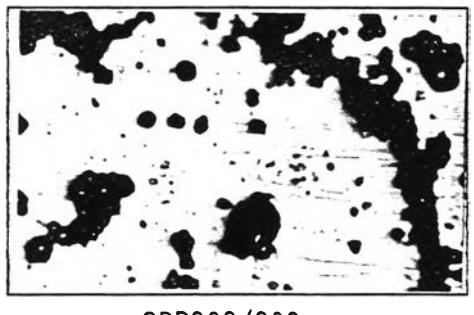
SDP060/030

6,000 rpm., 30 sec.



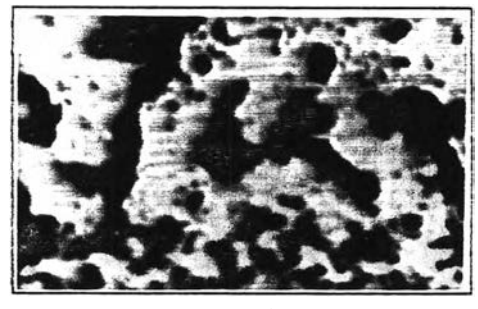
SDP060/120

6,000 rpm., 120 sec.



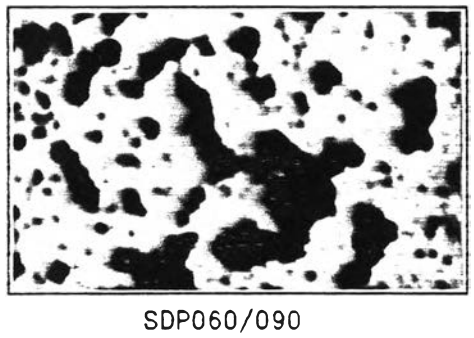
SDP060/060

6,000 rpm., 60 sec.



SDP060/150

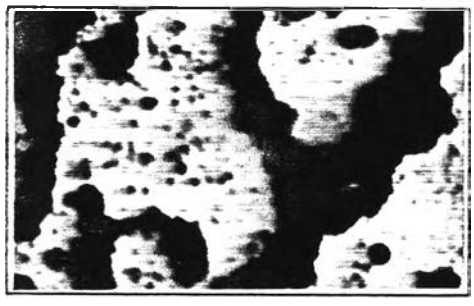
6,000 rpm., 150 sec.



SDP060/090

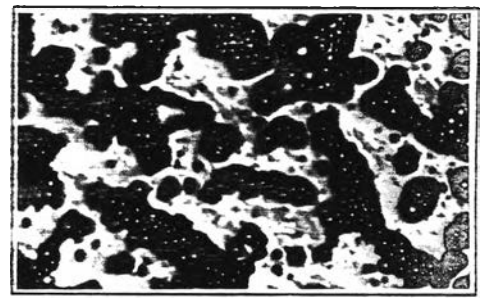
6,000 rpm., 90 sec.

Photomicrograph series 7 Photomicrographs of SDP060/030-SDP060/150. Poly(hexamethylene sebacamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 6,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.



SDP080/030

8,000 rpm., 30 sec.

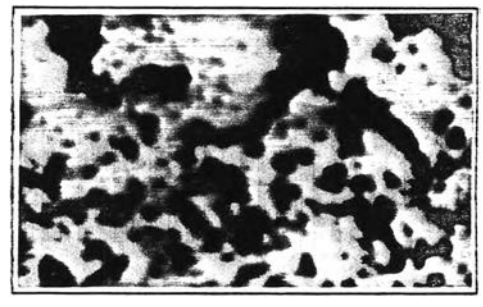


SDP080/120

8,000 rpm., 120 sec.

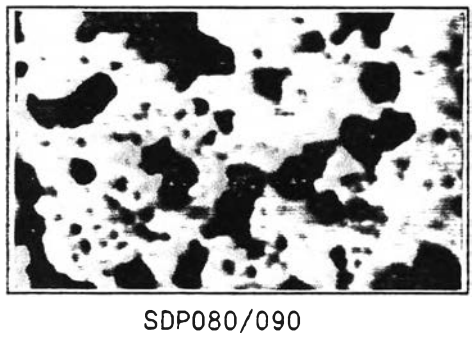
SDP080/060

8,000 rpm., 60 sec.



SDP080/150

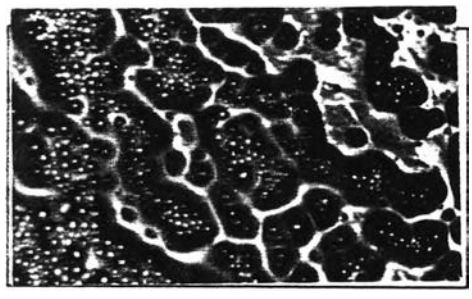
8,000 rpm., 150 sec.



SDP080/090

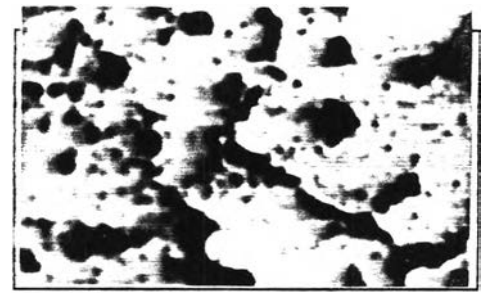
8,000 rpm., 90 sec.

Photomicrograph series 8 Photomicrographs of SDP080/030-SDP080/150. Poly(hexamethylene sebacamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 8,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.



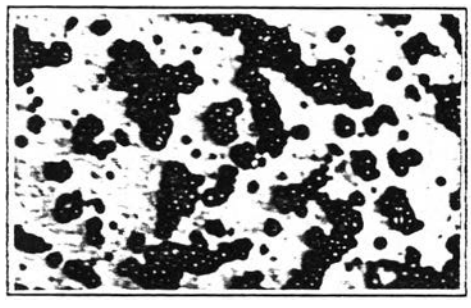
SDP100/030

10,000 rpm., 30 sec.



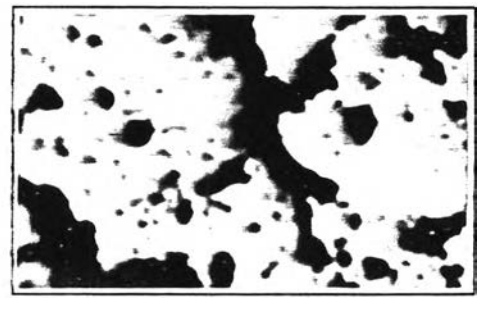
SDP100/120

10,000 rpm., 120 sec.



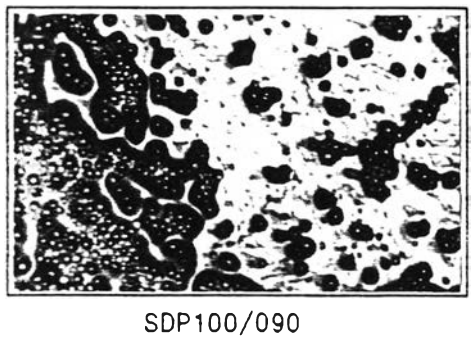
SDP100/060

10,000 rpm., 60 sec.



SDP100/150

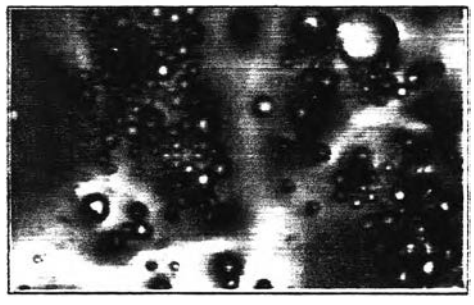
10,000 rpm., 150 sec.



SDP100/090

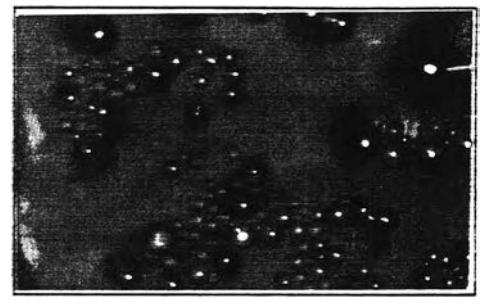
10,000 rpm., 90 sec.

Photomicrograph series 9 Photomicrographs of SDP100/030-SDP100/150. Poly(hexamethylene sebacamide) as polymeric microcapsule shell; dibutyl phtnalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 10,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.



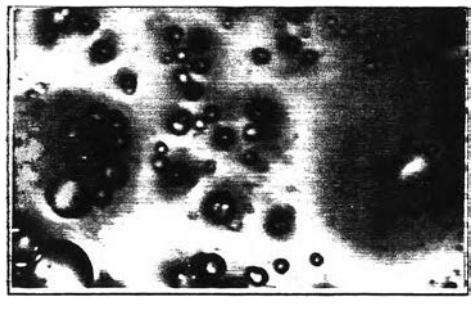
TDP020/030

2,000 rpm., 30 sec.



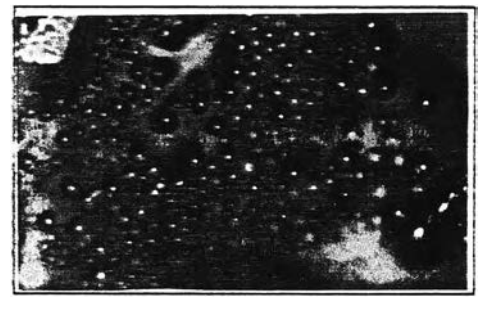
TDP020/120

2,000 rpm., 120 sec.



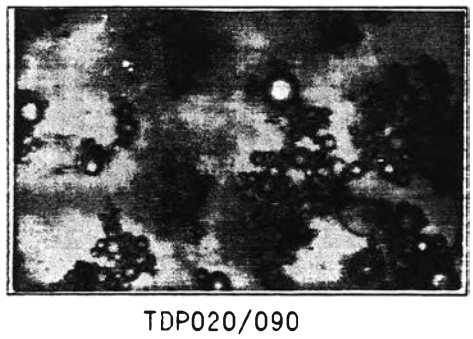
TDP020/060

2,000 rpm., 60 sec.



TDP020/150

2,000 rpm., 150 sec.



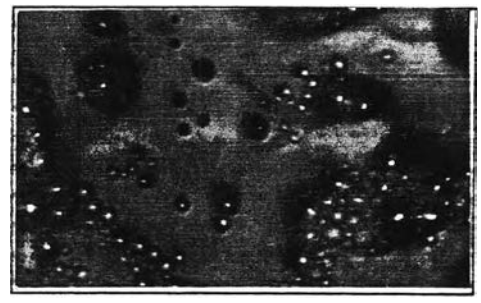
TDP020/090

2,000 rpm., 90 sec.

Photomicrograph series 10 Photomicrographs of TDP020/030-TDP020/150. Poly(para-phenylene terephthalamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 2,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.

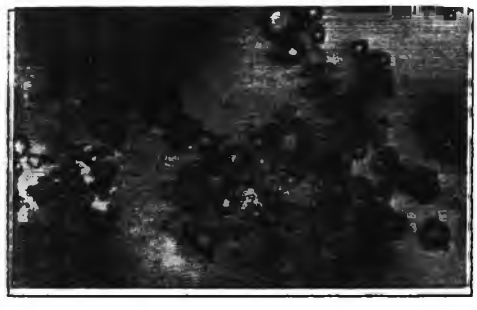
TDP040/030

4,000 rpm., 30 sec.



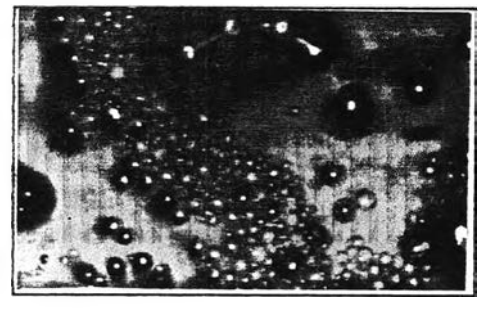
TDP040/120

4,000 rpm., 120 sec.



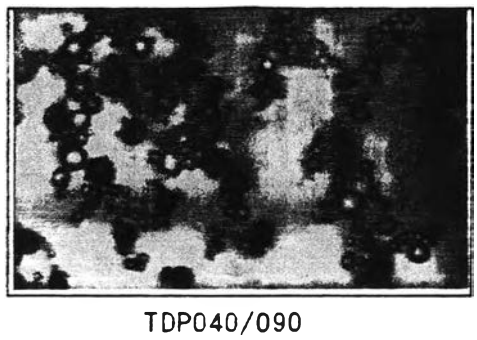
TDP040/060

4,000 rpm., 60 sec.



TDP040/150

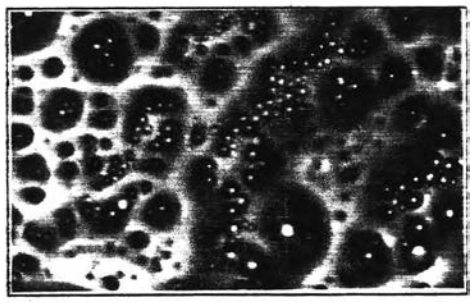
4,000 rpm., 150 sec.



TDP040/090

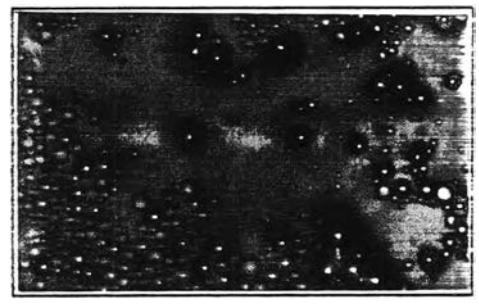
4,000 rpm., 90 sec.

Photomicrograph series 11 Photomicrographs of TDP040/030-TDP040/150. Poly(para-phenylene terephthalamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 4,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.



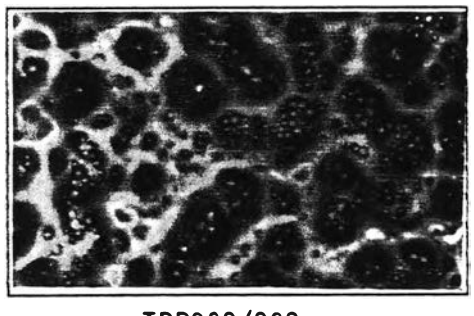
TDP060/030

6,000 rpm., 30 sec.



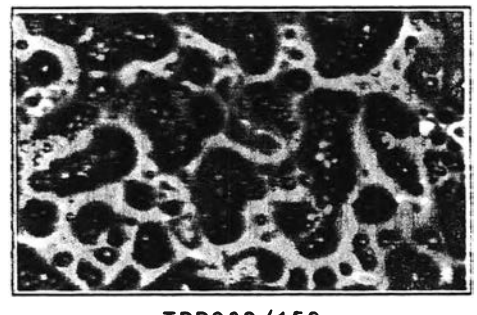
TDP060/120

6,000 rpm., 120 sec.



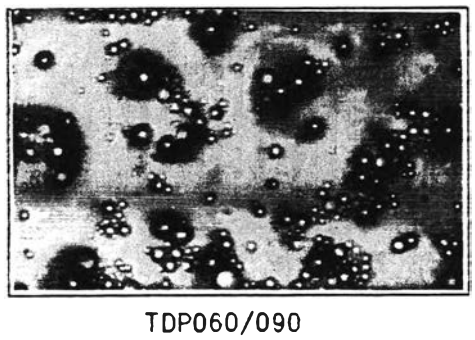
TDP060/060

6,000 rpm., 60 sec.



TDP060/150

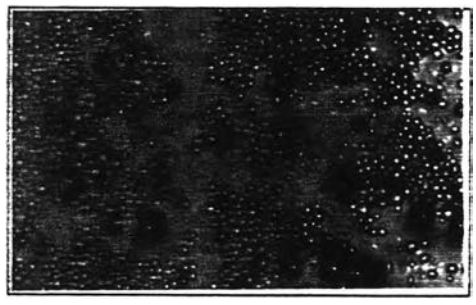
6,000 rpm., 150 sec.



TDP060/090

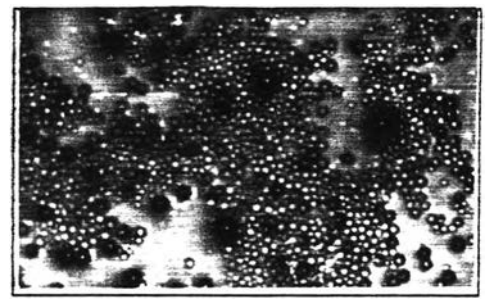
6,000 rpm., 90 sec.

Photomicrograph series 12 Photomicrographs of TDP060/030-TDP060/150. Poly(para-phenylene terephthalamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 6,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.



TDP080/030

8,000 rpm., 30 sec.

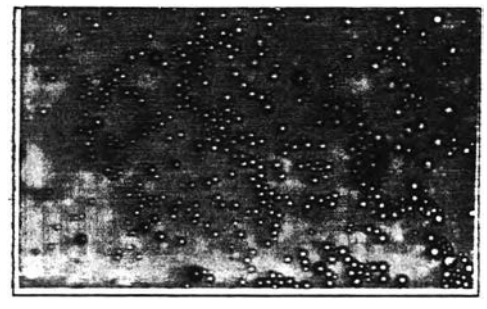


TDP080/120

8,000 rpm., 120 sec.

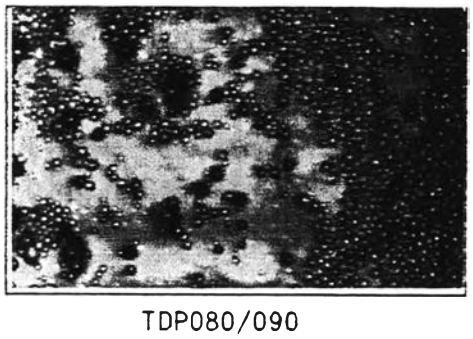
TDP080/060

8,000 rpm., 60 sec.



TDP080/150

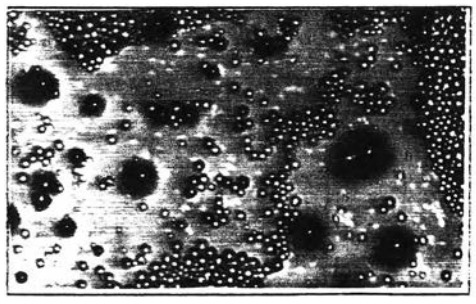
8,000 rpm., 150 sec.



TDP080/090

8,000 rpm., 90 sec.

Photomicrograph series 13 Photomicrographs of TDP080/030-TDP080/150. Poly(para-phenylene terephthalamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 8,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.

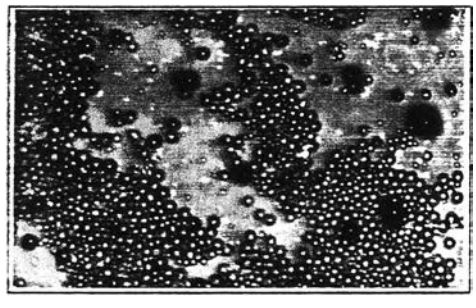


TDP100/030

10,000 rpm., 30 sec.

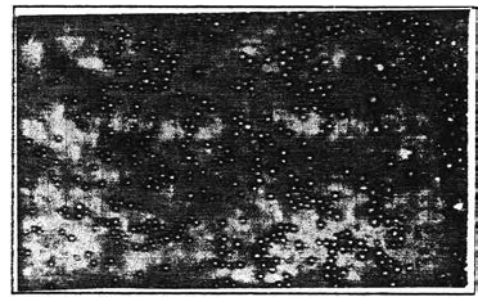
TDP100/120

10,000 rpm., 120 sec.



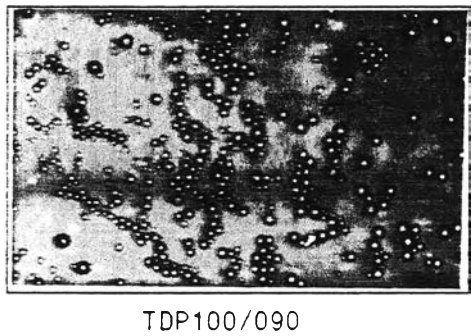
TDP100/060

10,000 rpm., 60 sec.



TDP100/150

10,000 rpm., 150 sec.



TDP100/090

10,000 rpm., 90 sec.

Photomicrograph series 14 Photomicrographs of TDP100/030-TDP100/150. Poly(para-phenylene terephthalamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; poly(vinyl alcohol) as emulsifier; the propeller speed fixed at 10,000 rpm. and vary the homogenizing times from 30 to 150 sec. Photomicrographs taken with Zeiss optical microscope, magnification 100 times and the print was magnified by 2.5 times.

2.9.4.3) Particle Size Distribution

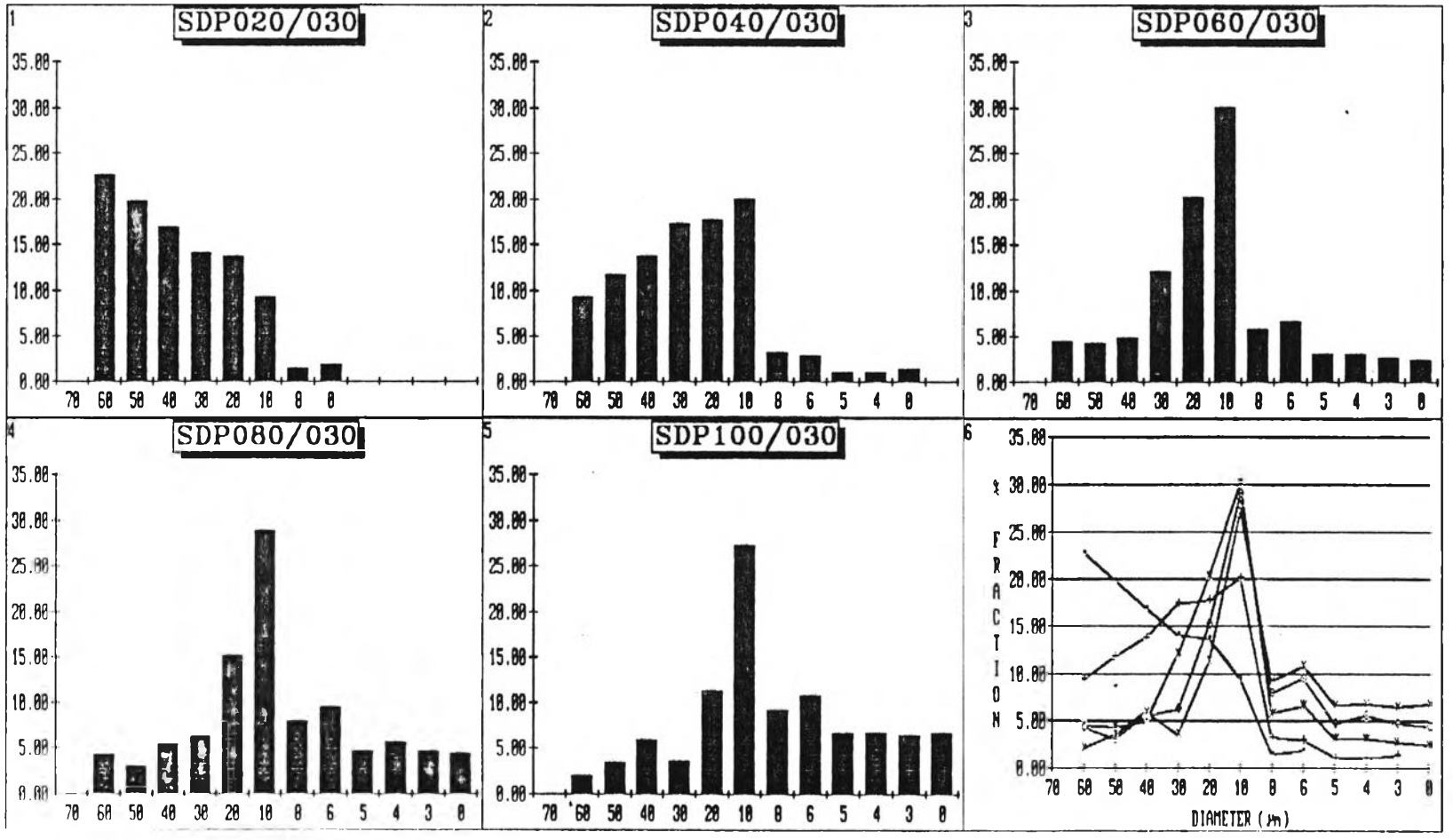
All of the particle size distribution data are presented in the same style of Tables 31 - 34 which are illustrated in the previous section. For additional data, all of the tables of this section are shown in Appendix III.

1) Particle size distribution and average particle size of poly(hexamethylene sebacamide) microcapsules are shown in Appendix III, Tables 69 - 73, and the summary and comparison of these tables are shown in Tables 74 - 78. The data of each table are presented by graph. The graph which depicts the effect of propeller speeds is presented in graph series 3 - 8 and the effect of homogenizing times is presented by graph series 9 - 14.

2) Particle size distribution and average particle size of poly(para-phenylene terephthalamide) microcapsules are shown in Appendix III, Tables 79 - 83, and the summary and comparison these tables are in Tables 84 - 88. The data from each table are presented by graph. The graph which depicts the effect of propeller speeds are shown in graph series 15 - 20 and the effect of homogenized times are presented in graph series 21 - 26.

2.9.4.4) Average Particle Size and Encapsulation Efficiency

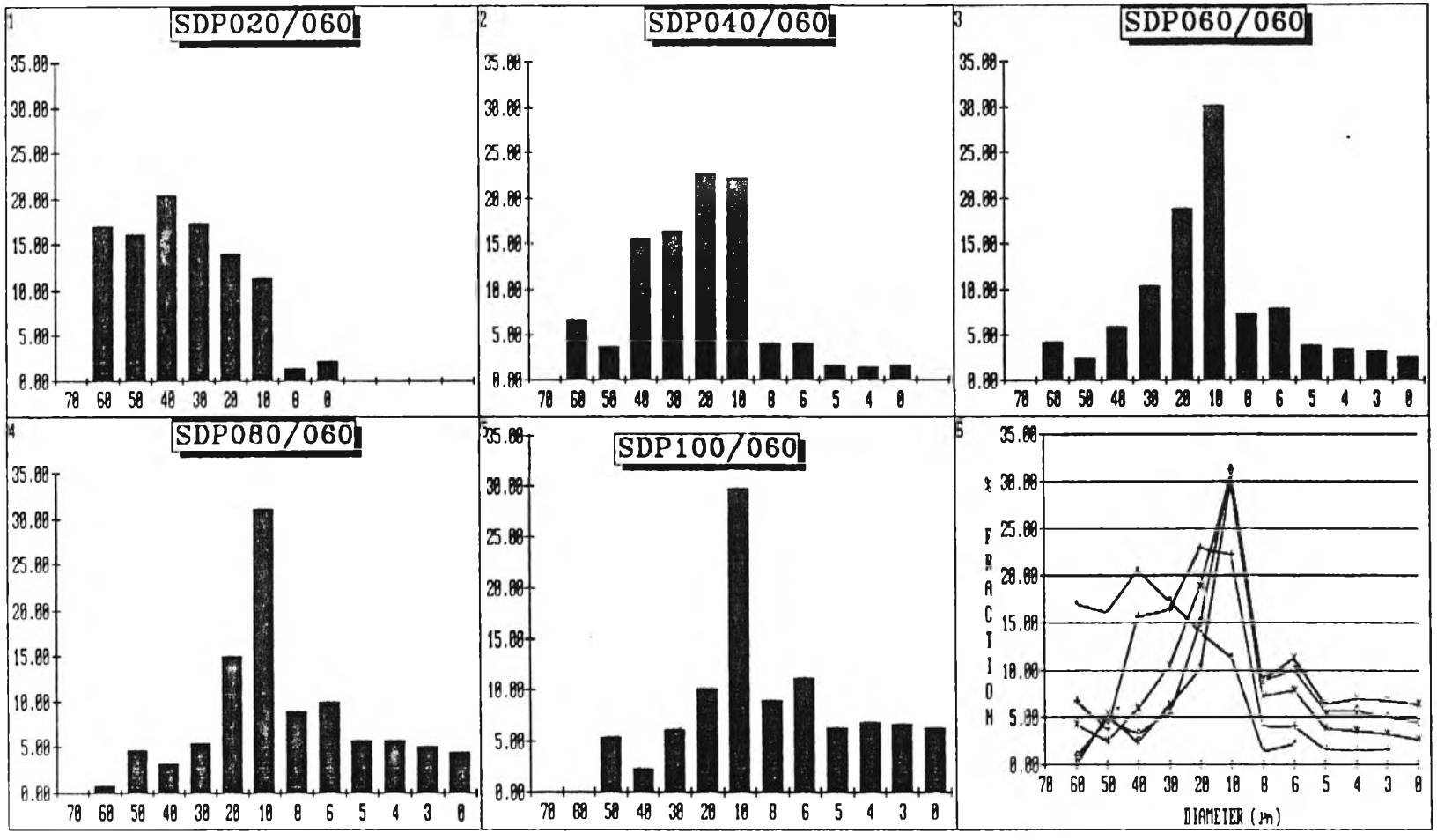
The results of all average particle size and encapsulation efficiency are shown in Tables 42 and 43 as follows :-



Graph series 3 Histogram of Particle Size Distribution of SDP020/030-SDP100/030.

(The graphs were made from the data from Tables 69-1 - 69-5)

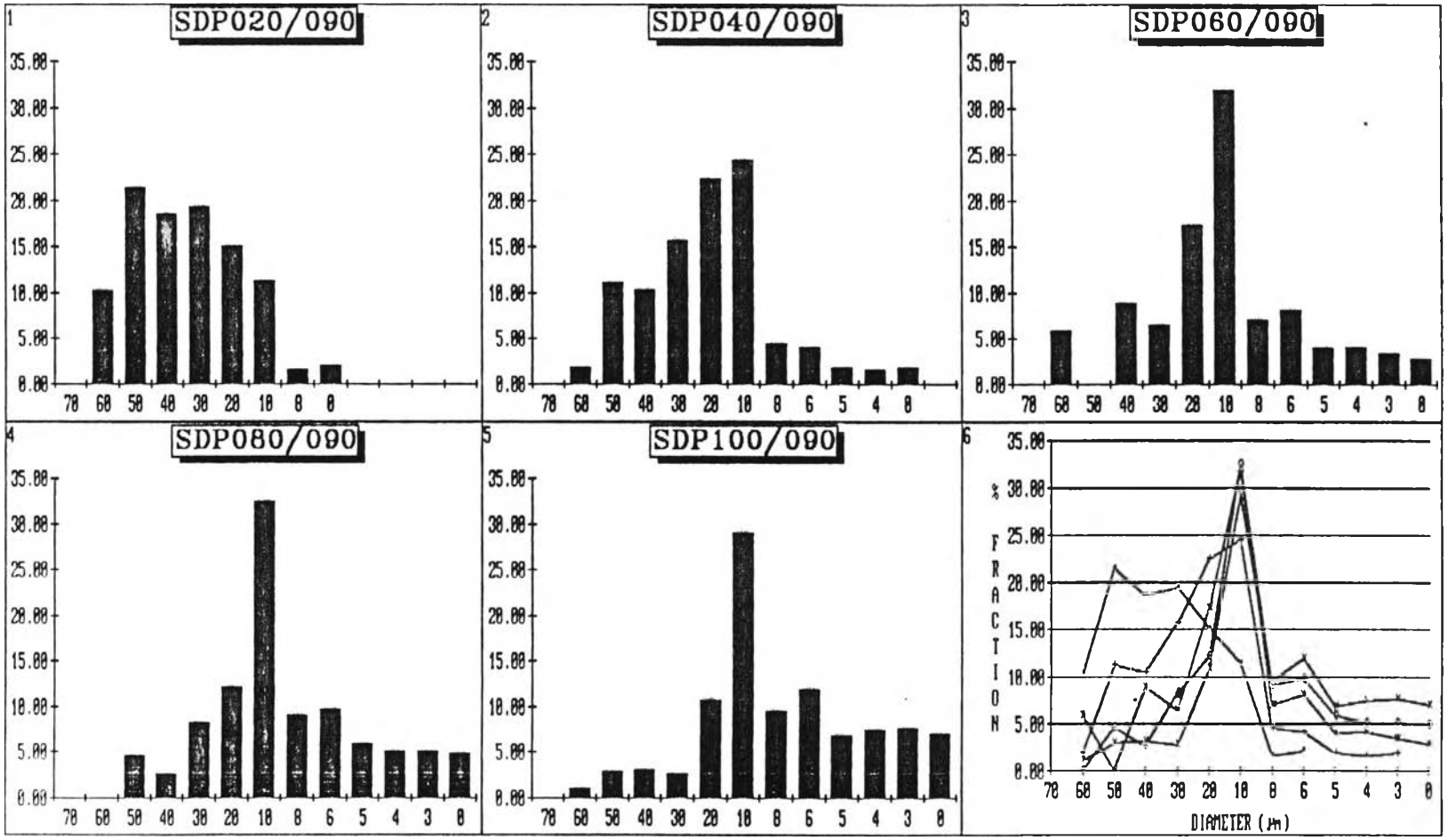
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 30 sec. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 4 Histogram of Particle Size Distribution of SDP020/060-SDP100/060.

(The graphs were made from the data from Tables 70-1 - 70-5)

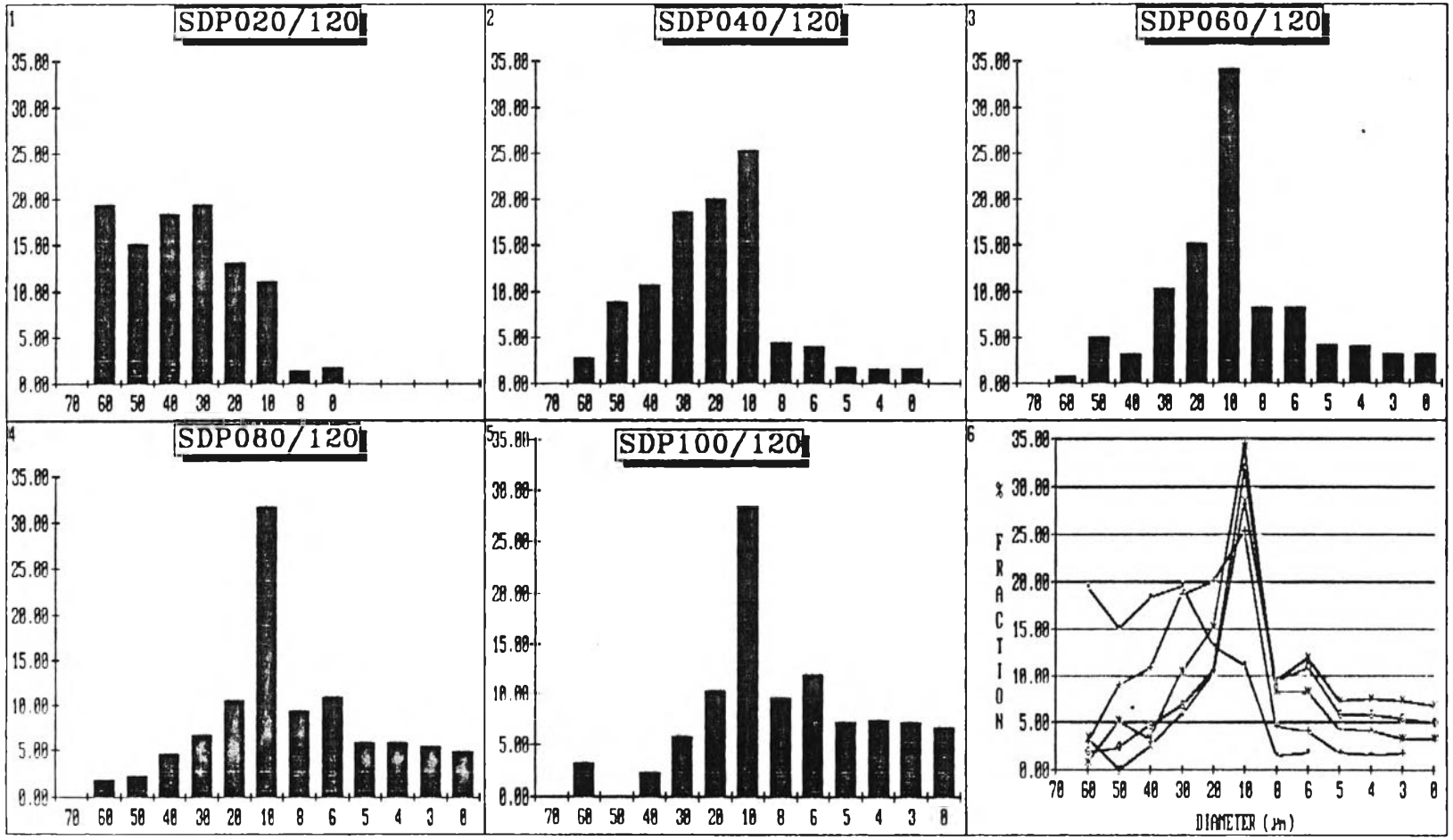
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 60 sec. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 5 Histogram of Particle Size Distribution of SDP020/090-SDP100/090.

(The graphs were made from the data from Tables 71-1 - 71-5)

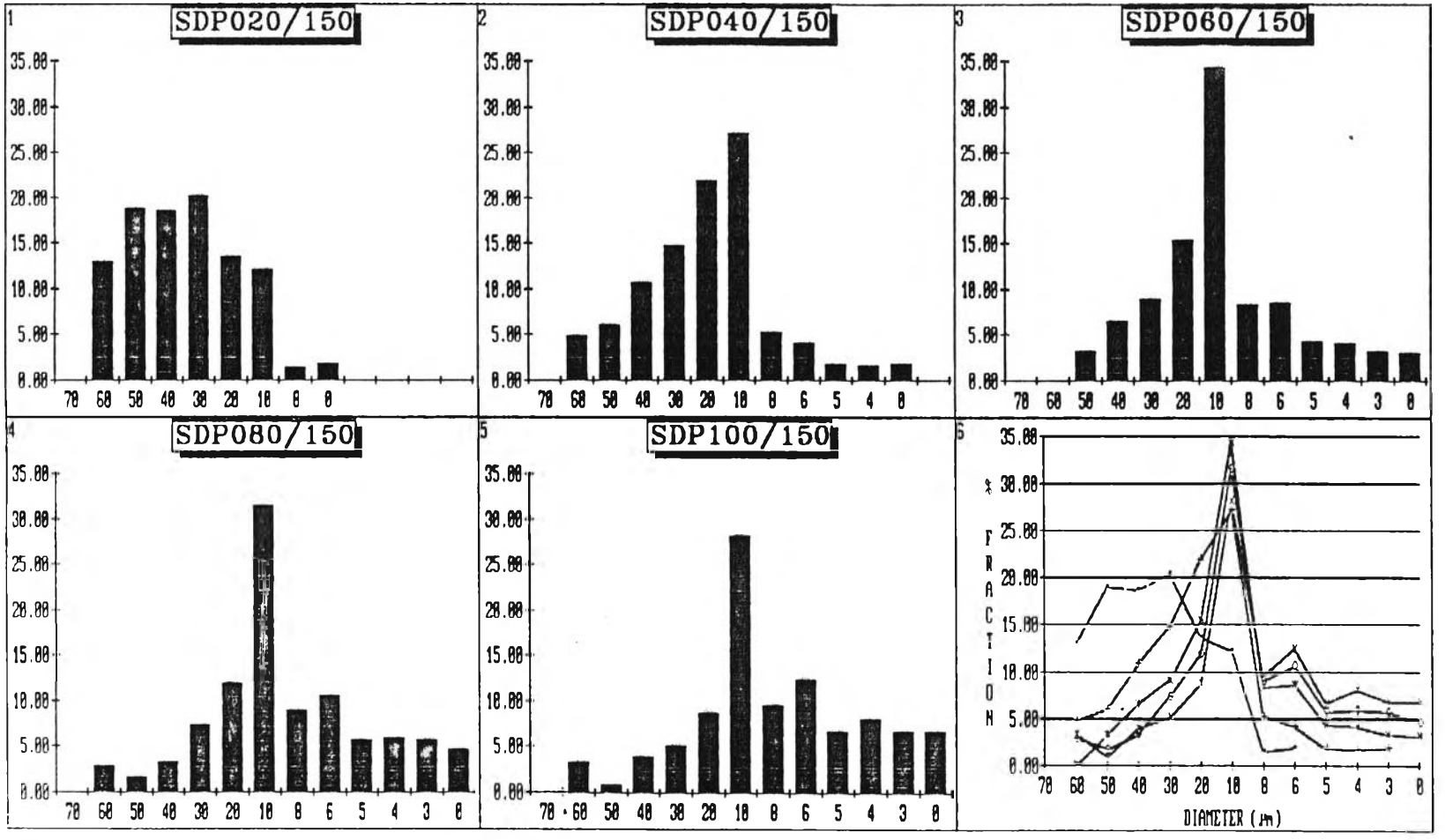
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 90 sec. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 6 Histogram of Particle Size Distribution of SDP020/120-SDP100/120.

(The graphs were made from the data from Tables 72-1 - 72-5)

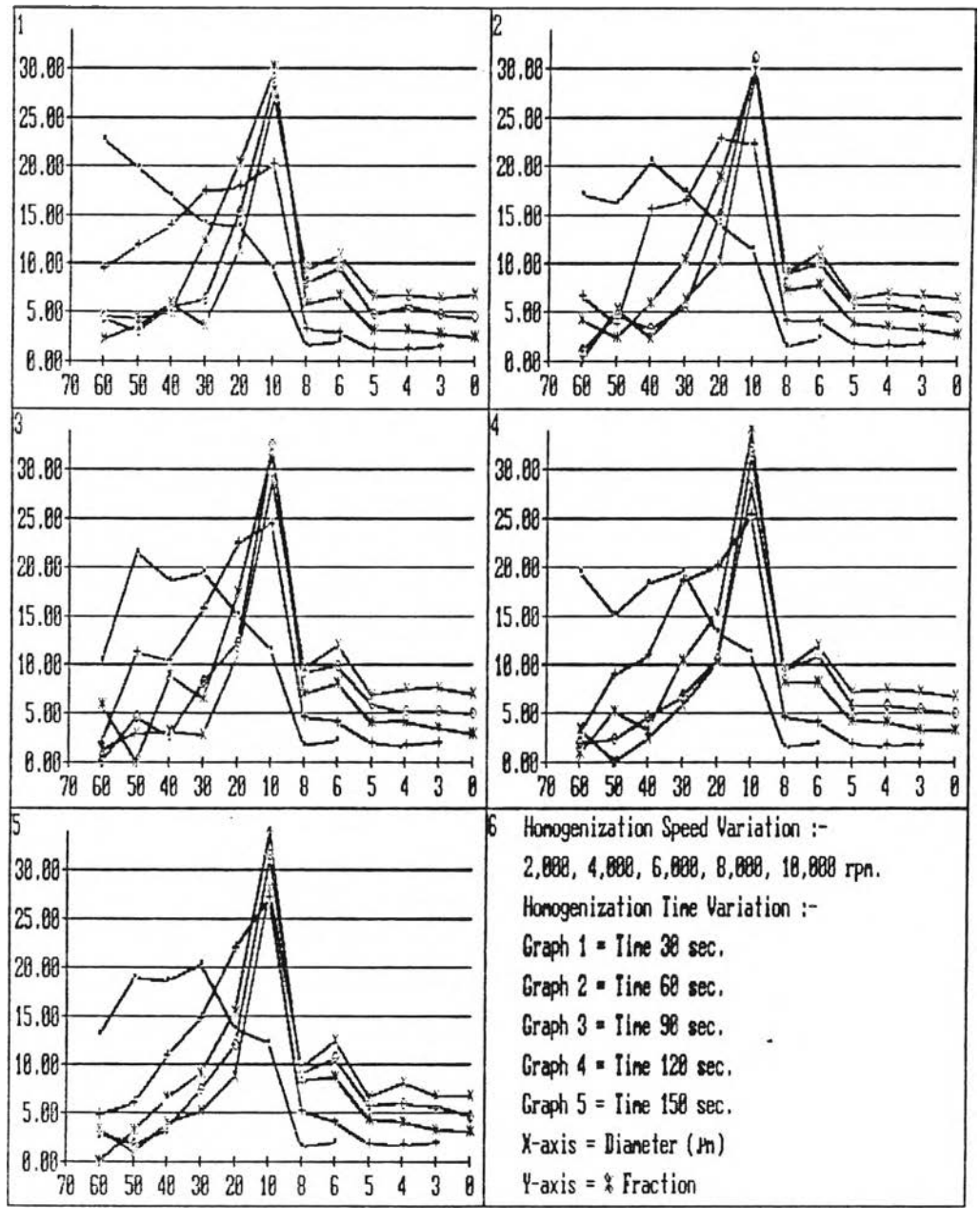
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 120 sec. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 7 Histogram of Particle Size Distribution of SDP020/150-SDP100/150.

(The graphs were made from the data from Tables 73-1 - 73-5)

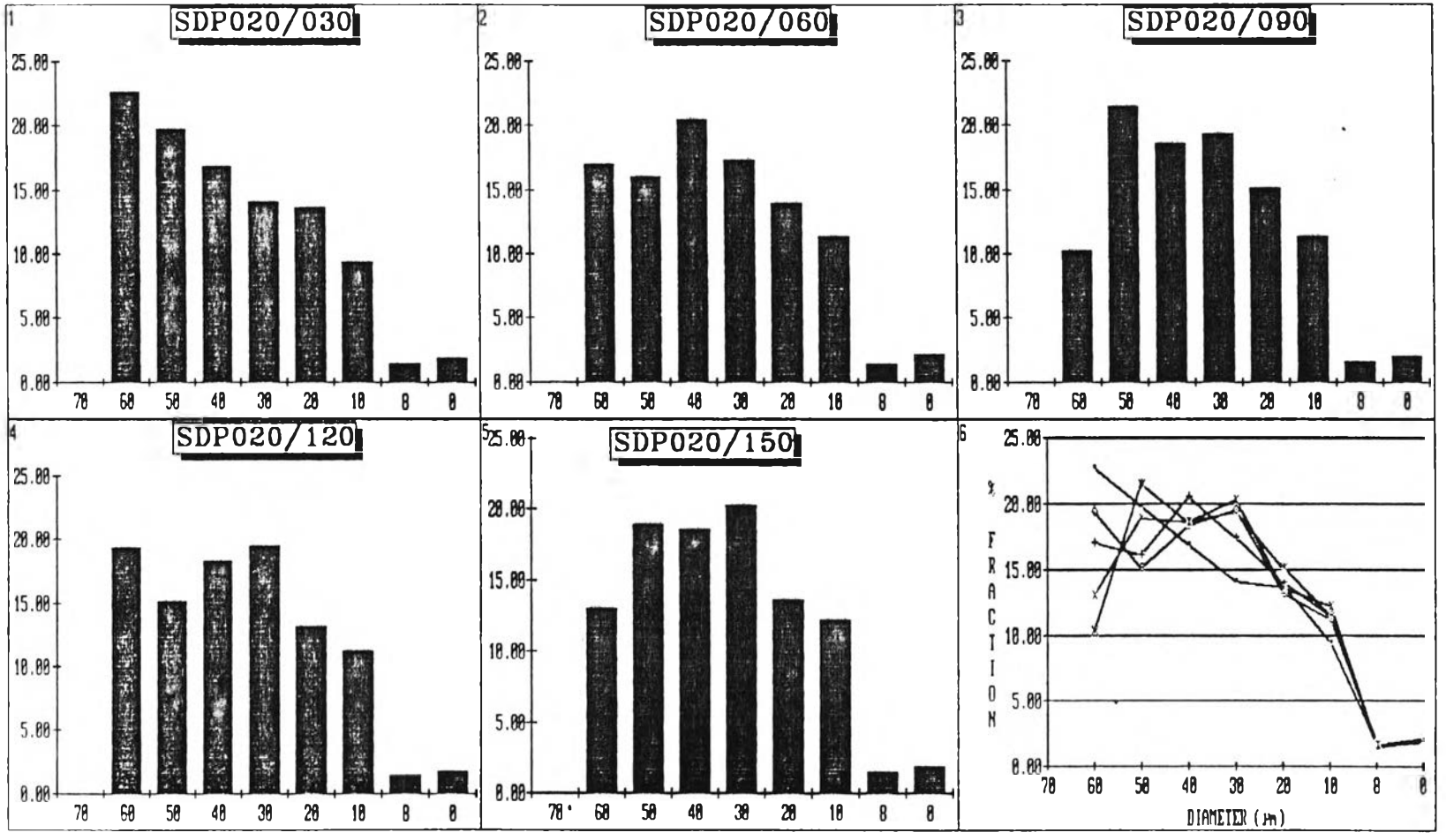
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 150 sec. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 8 Summary of the Graph series 3 - 7 on Effect of Propeller Speed.

(The graphs were made from the data from Tables 69 - 73)

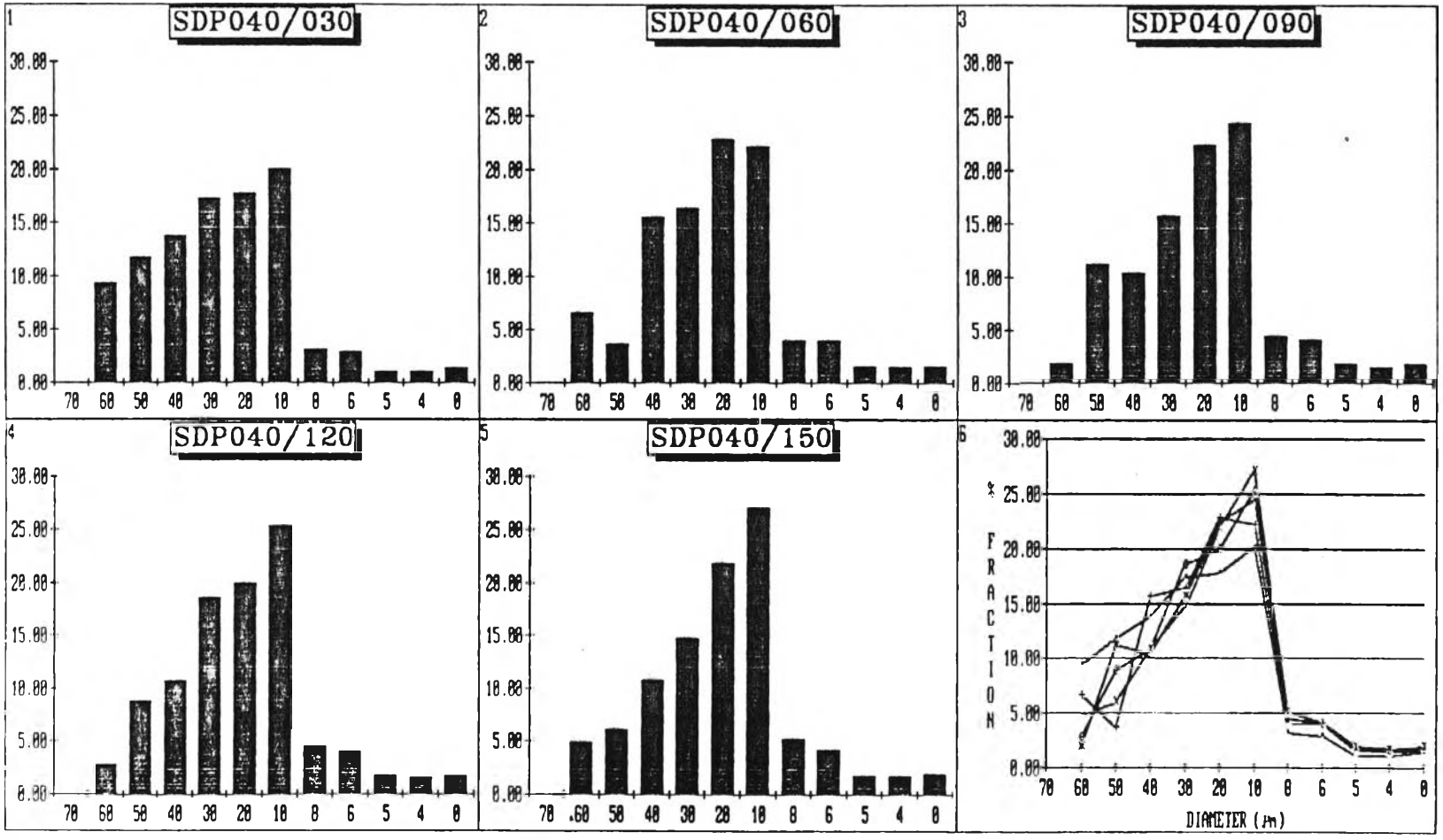
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing times from 30 to 150 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 9 Histogram of Particle Size Distribution of SDP020/030-SDP020/150.

(The graphs were made from the data from Tables 69-1 - 73-1)

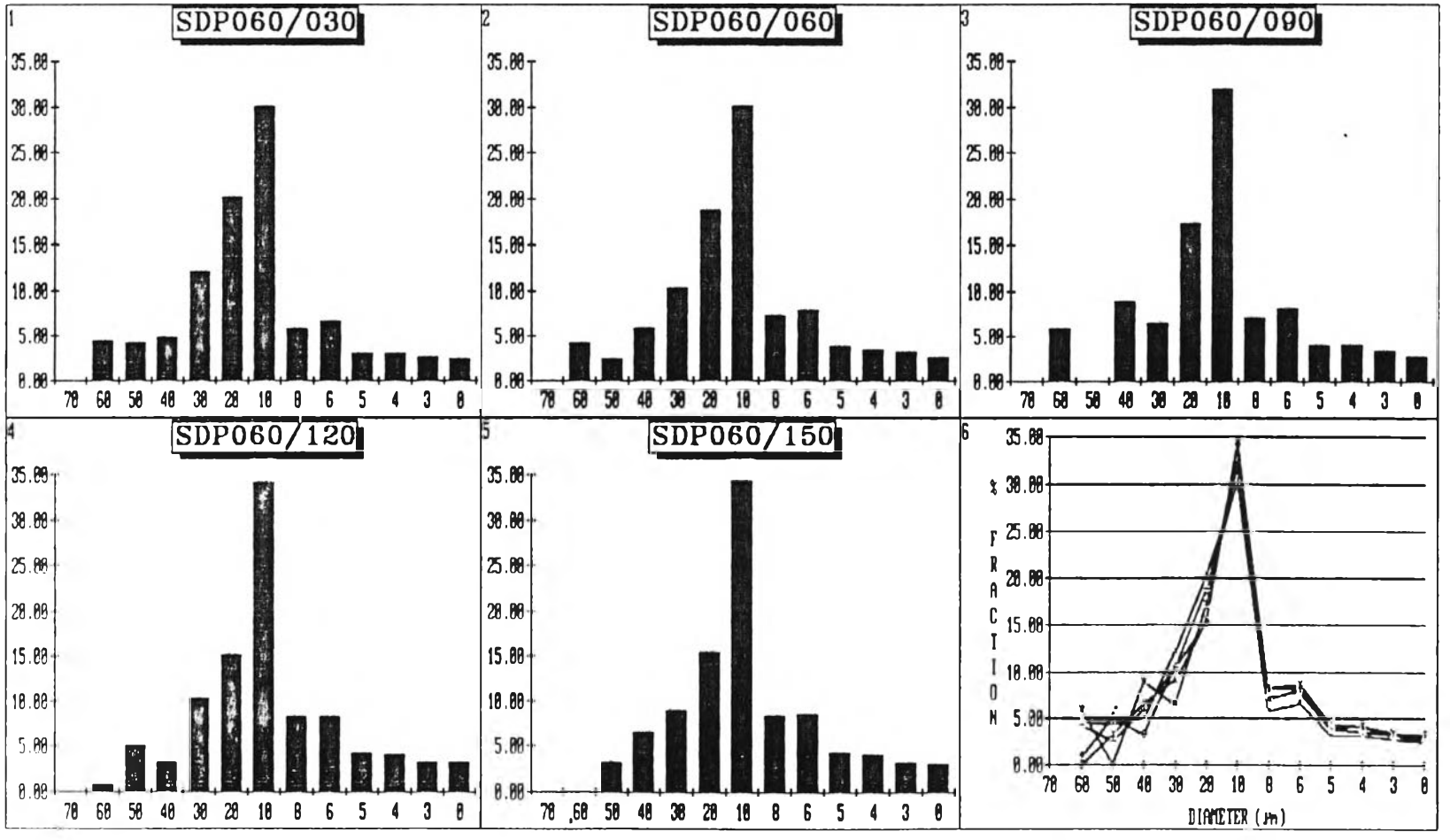
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 2,000 rpm. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 10 Histogram of Particle Size Distribution of SDP040/030-SDP040/150.

(The graphs were made from the data from Tables 69-2 - 73-2)

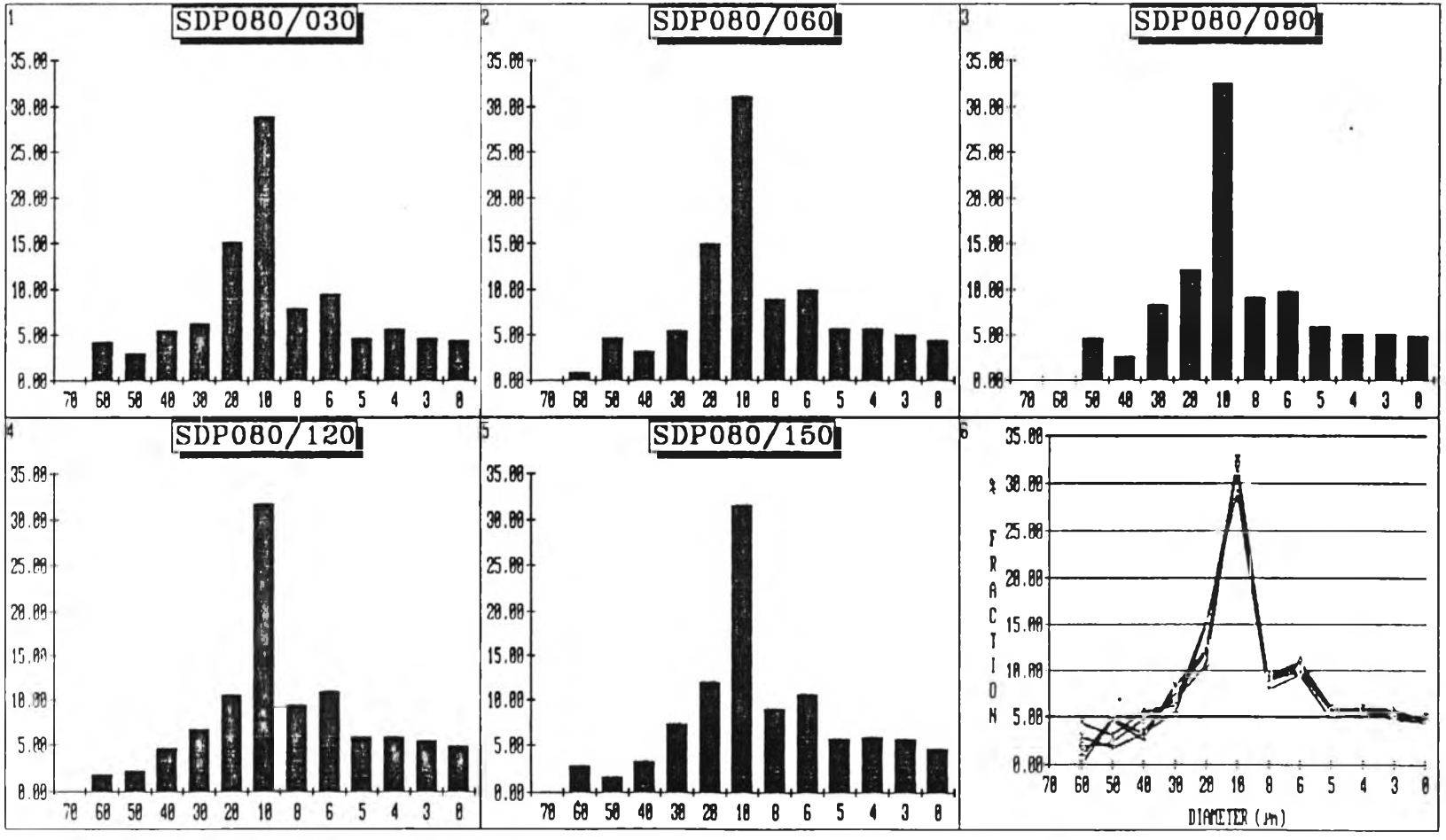
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 4,000 rpm. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 11 Histogram of Particle Size Distribution of SDP060/030-SDP060/150.

(The graphs were made from the data from Tables 69-3 - 73-3)

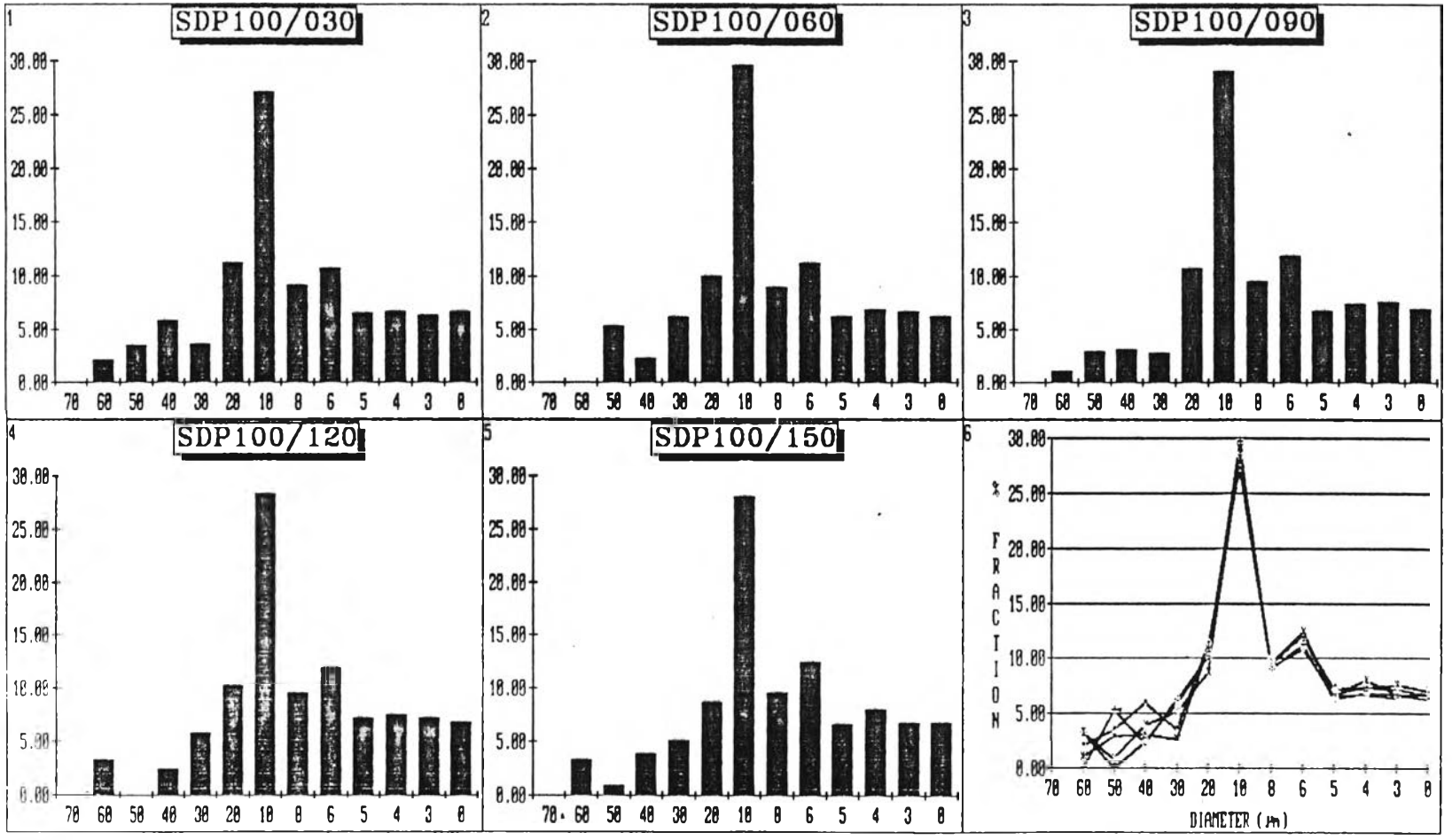
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 6,000 rpm. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 12 Histogram of Particle Size Distribution of SDP080/030-SDP080/150.

(The graphs were made from the data from Tables 69-4 - 73-4)

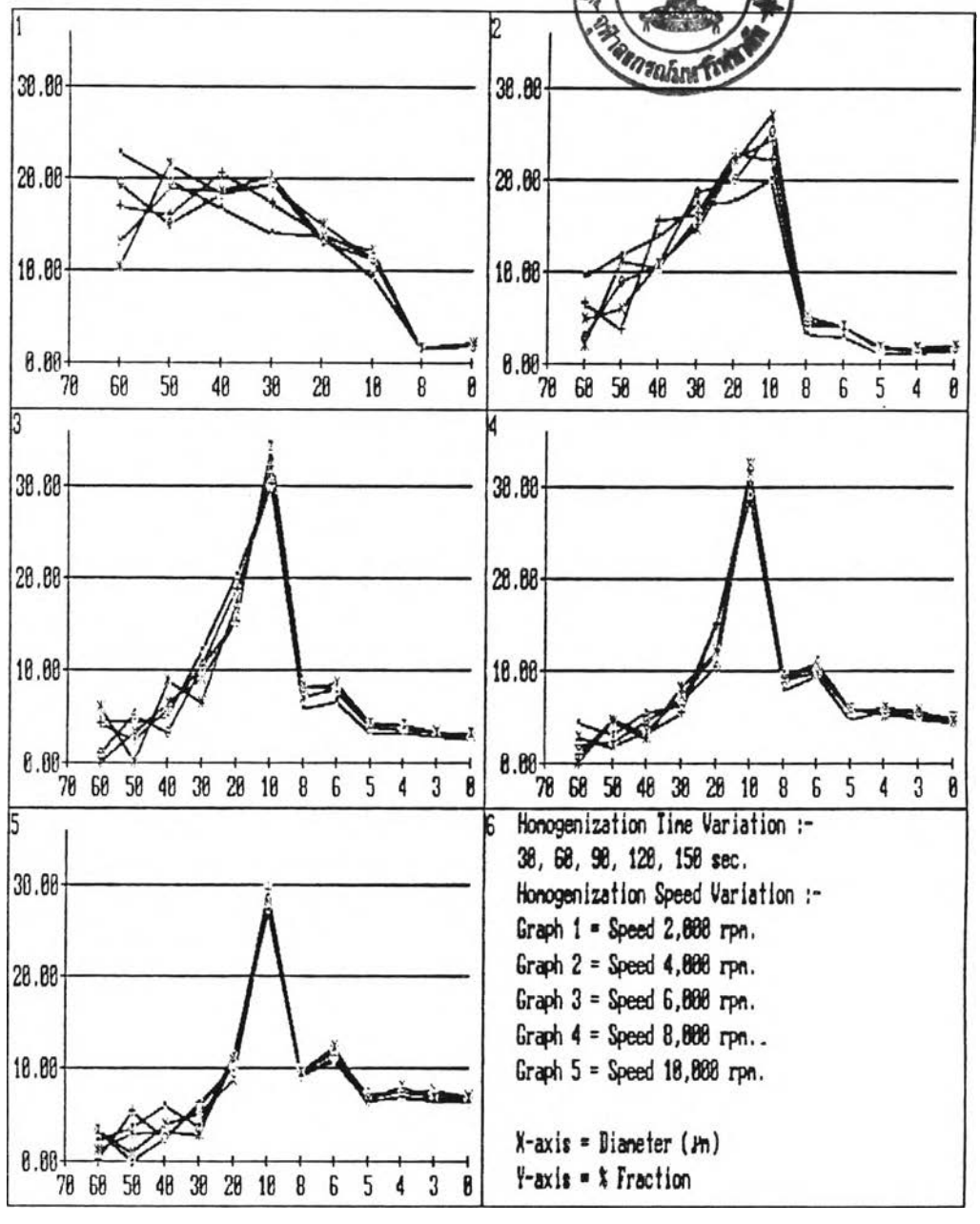
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 8,000 rpm. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 13 Histogram of Particle Size Distribution of SDP100/030-SDP100/150.

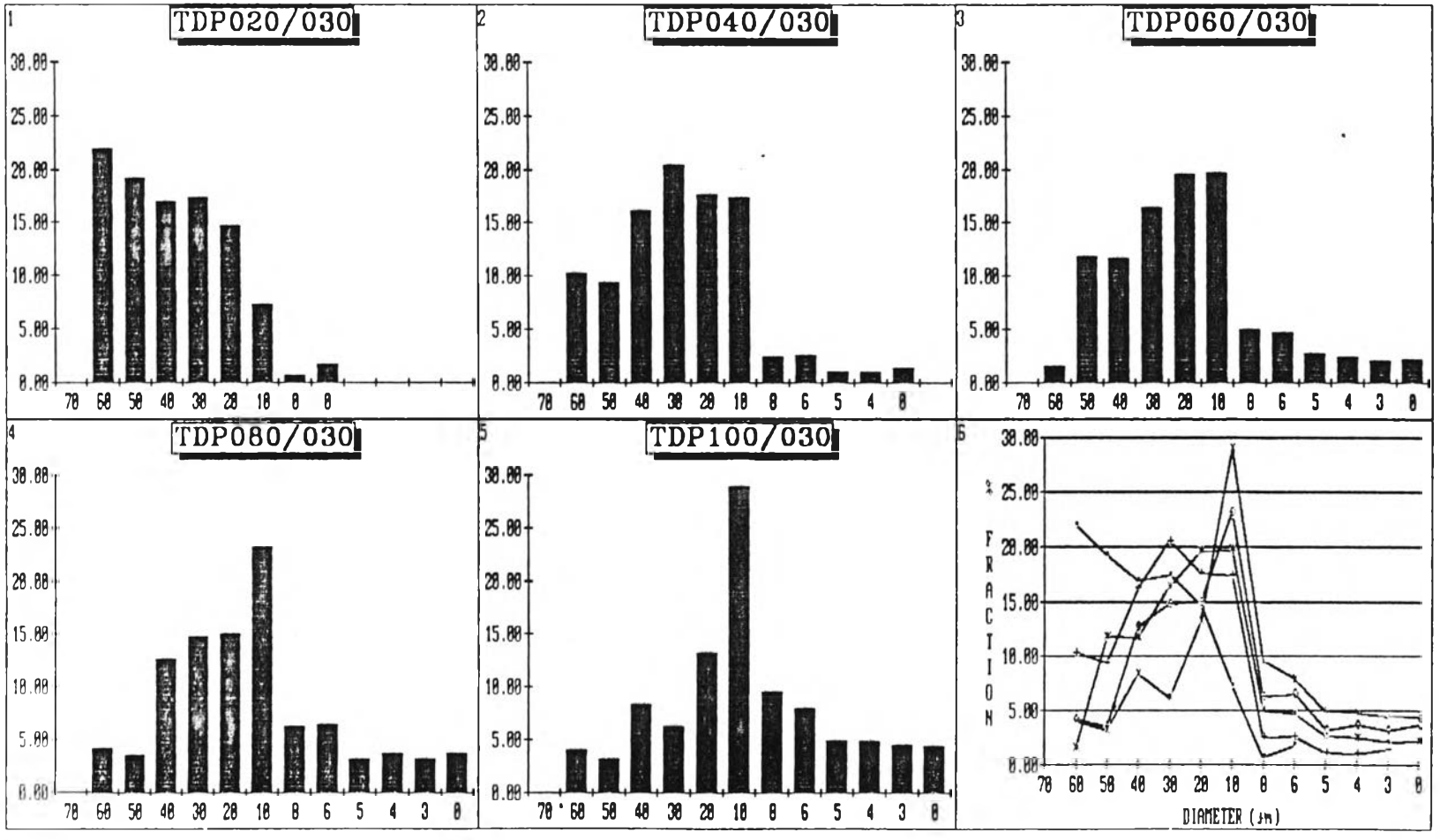
(The graphs were made from the data from Tables 69-5 - 73-5)

Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 10,000 rpm. on particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 14 Summary of the Graph series 9 - 13 on Effect of Homogenizing Time. (The graphs were made from the data from Tables 69 - 73)

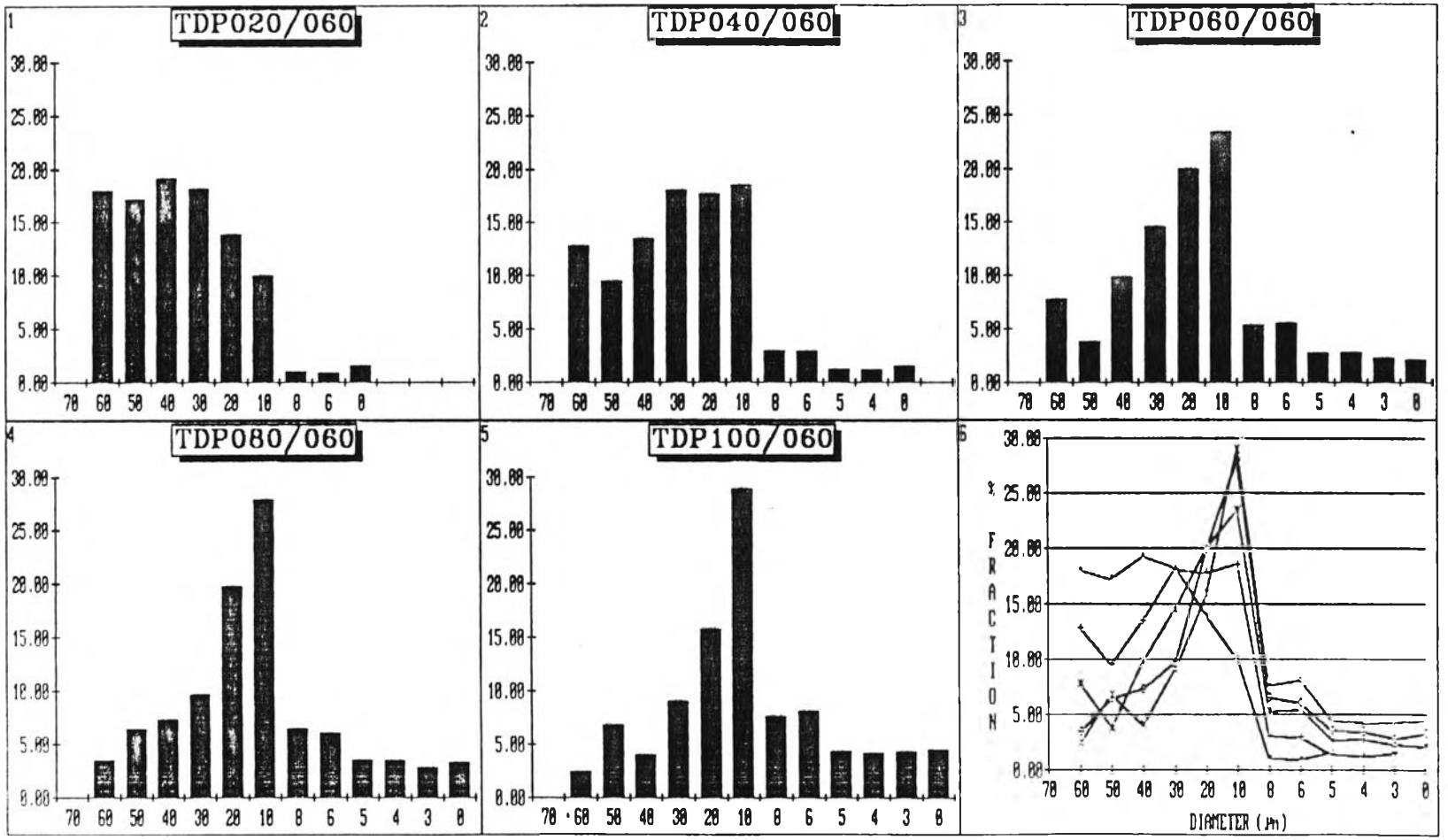
Effect of the homogenizing times from 30 to 150 sec. at the propeller speeds from 2,000 to 10,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 15 Histogram of Particle Size Distribution of TDP020/030-TDP100/030.

(The graphs were made from the data from Tables 79-1 - 79-5)

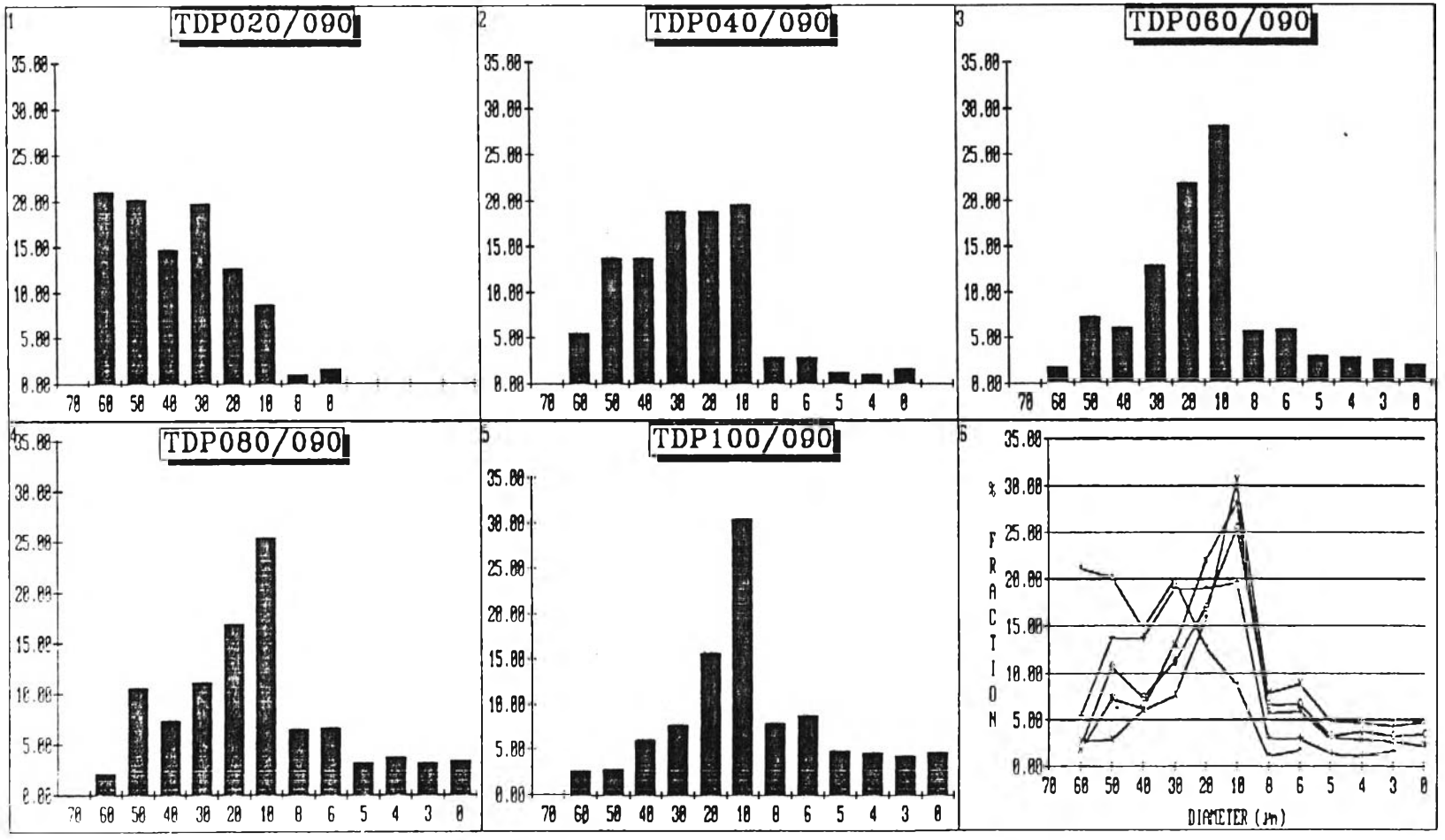
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 30 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 16 Histogram of Particle Size Distribution of TDP020/060-TDP100/060.

(The graphs were made from the data from Tables 80-1 - 80-5)

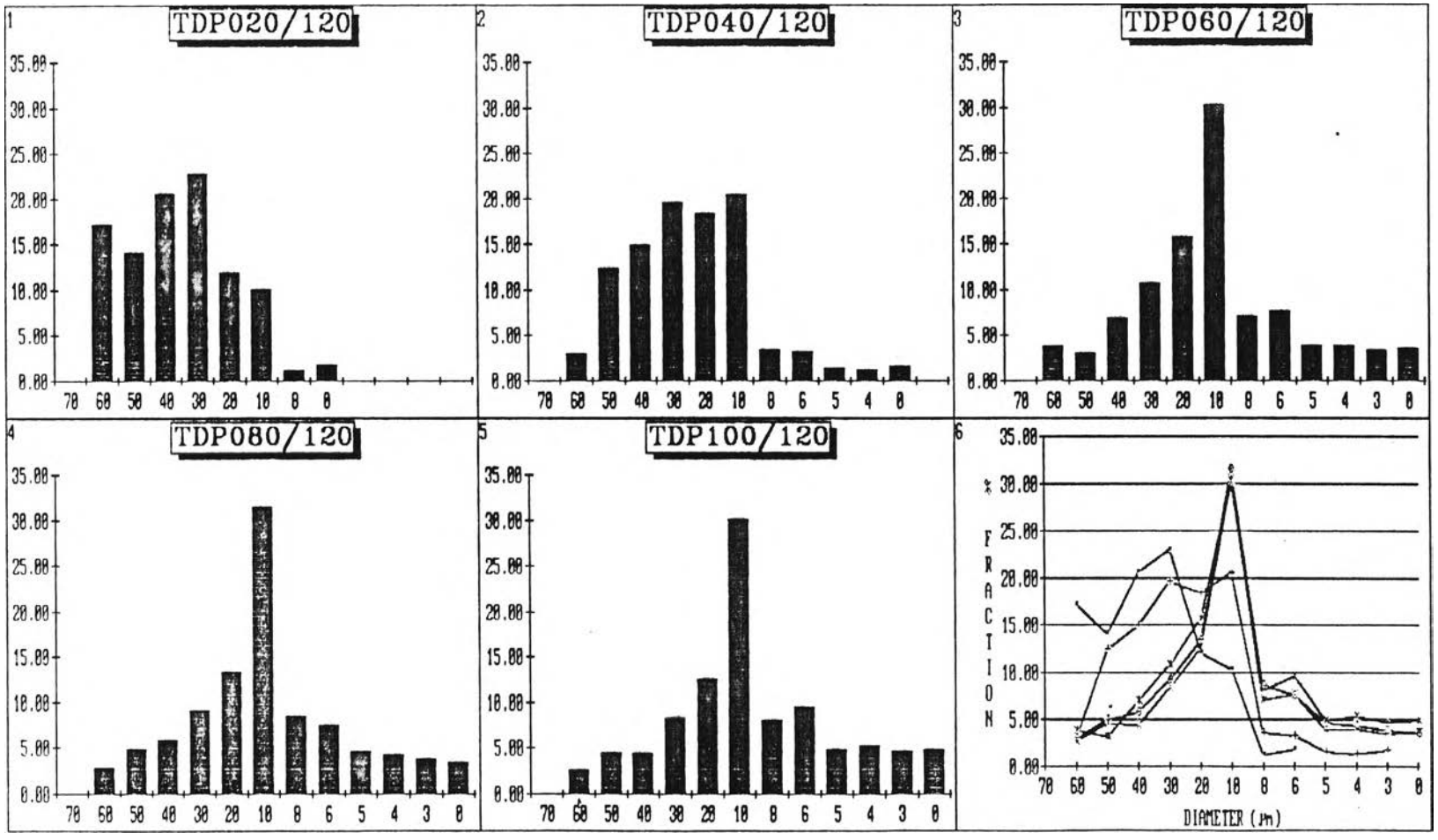
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 60 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 17 Histogram of Particle Size Distribution of TDP020/090-TDP100/090.

(The graphs were made from the data from Tables 81-1 - 81-5)

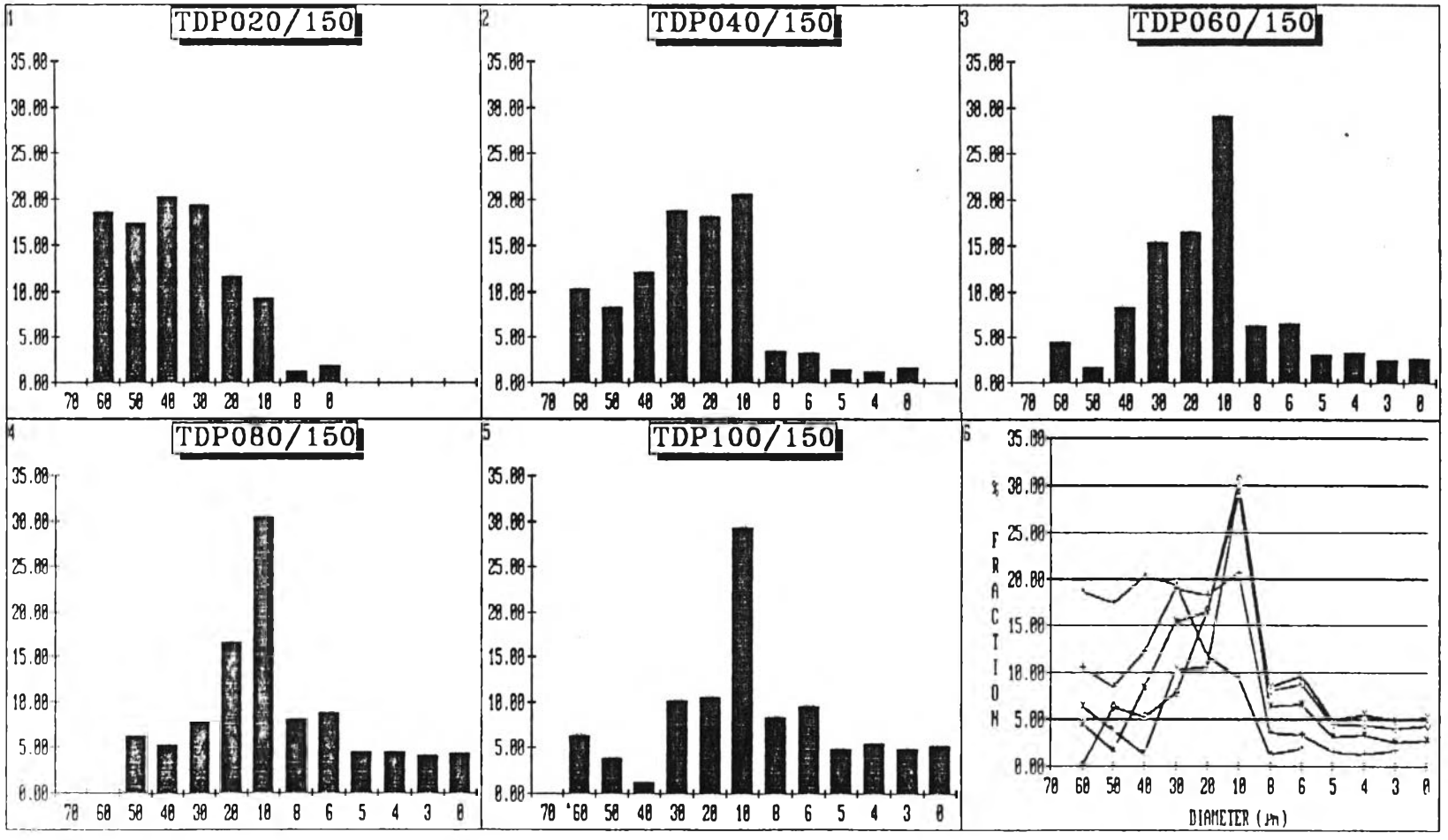
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 90 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 18 Histogram of Particle Size Distribution of TDP020/120-TDP100/120.

(The graphs were made from the data from Tables 82-1 - 82-5)

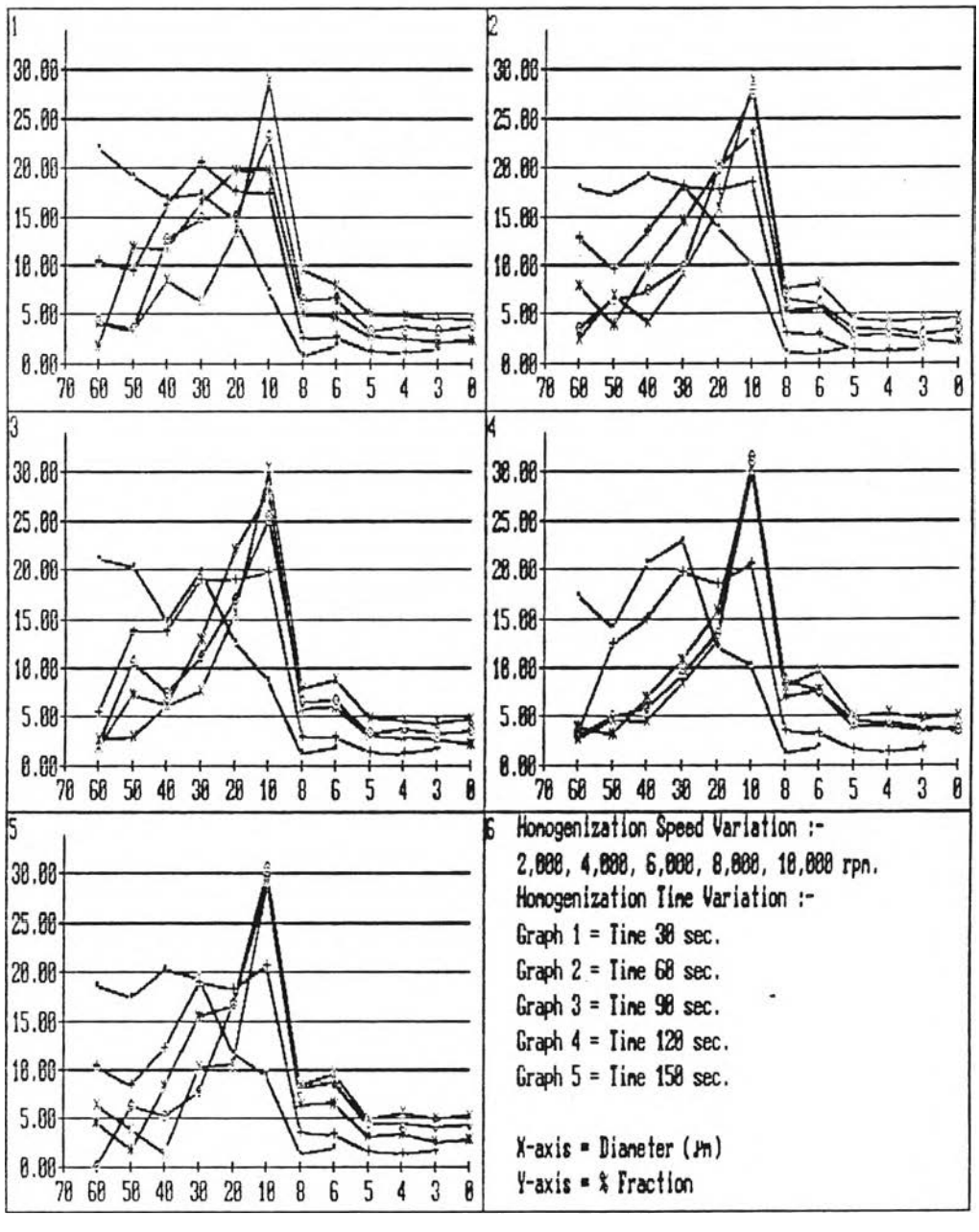
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 120 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 19 Histogram of Particle Size Distribution of TDP020/150-TDP100/150.

(The graphs were made from the data from Tables 83-1 - 83-5)

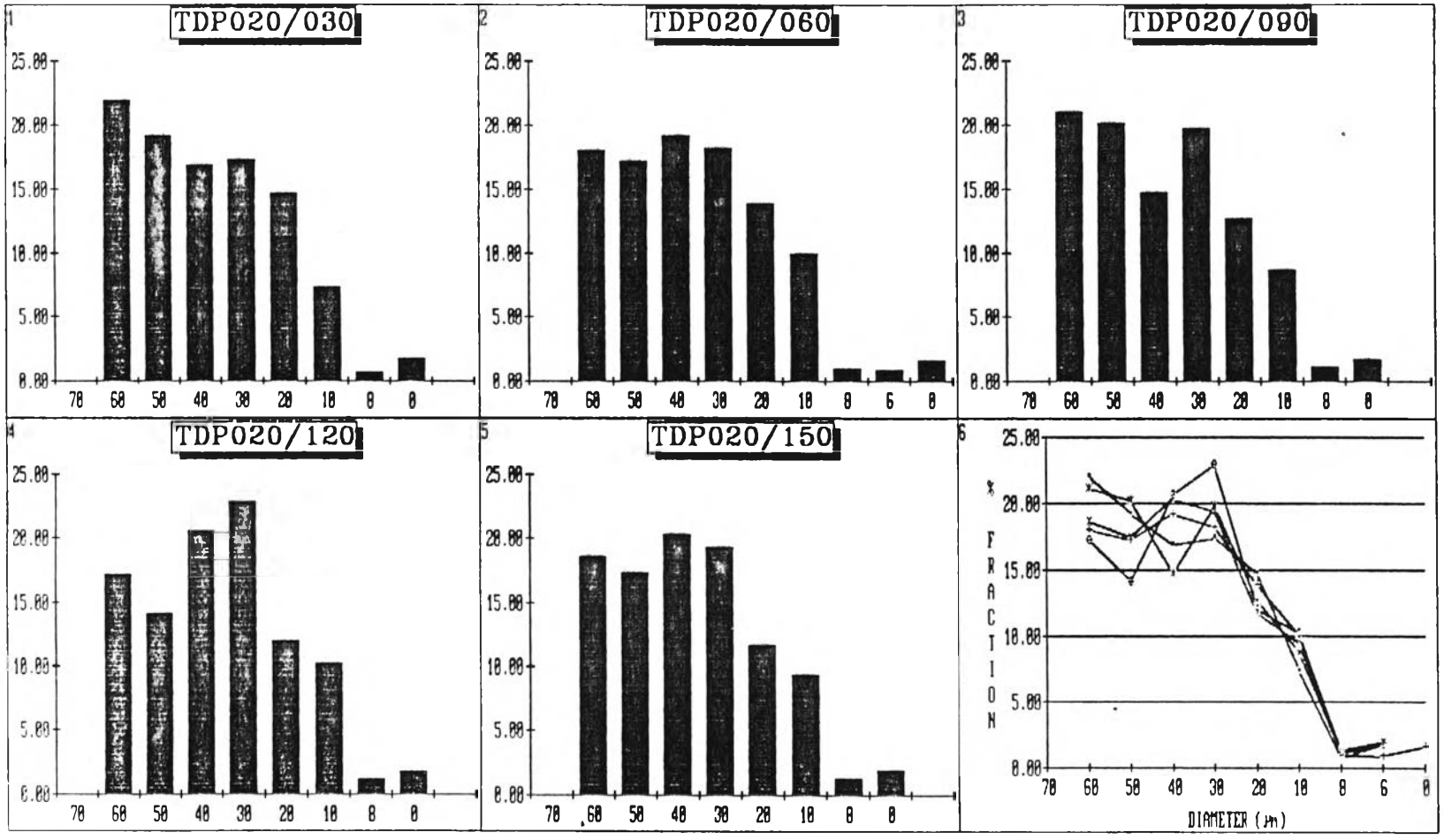
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing time 150 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 20 Summary of the Graph series 15 - 19 on Effect of Propeller Speed.

(The graphs were made from the data from Tables 79 - 83)

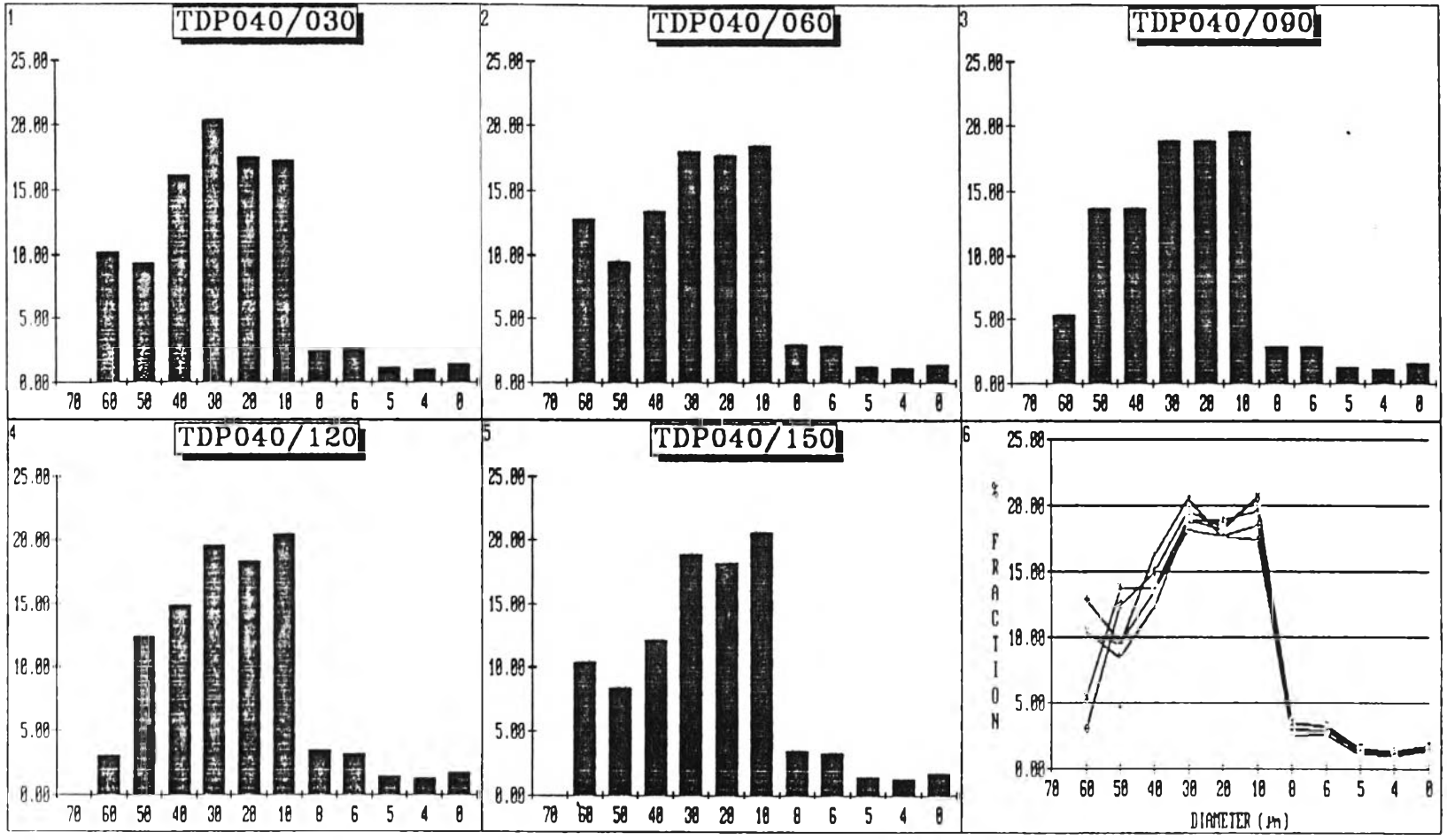
Effect of the propeller speeds from 2,000 to 10,000 rpm. at the homogenizing times from 30 to 150 sec. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 21 Histogram of Particle Size Distribution of TDP020/030-TDP020/150.

(The graphs were made from the data from Tables 79-1 - 83-1)

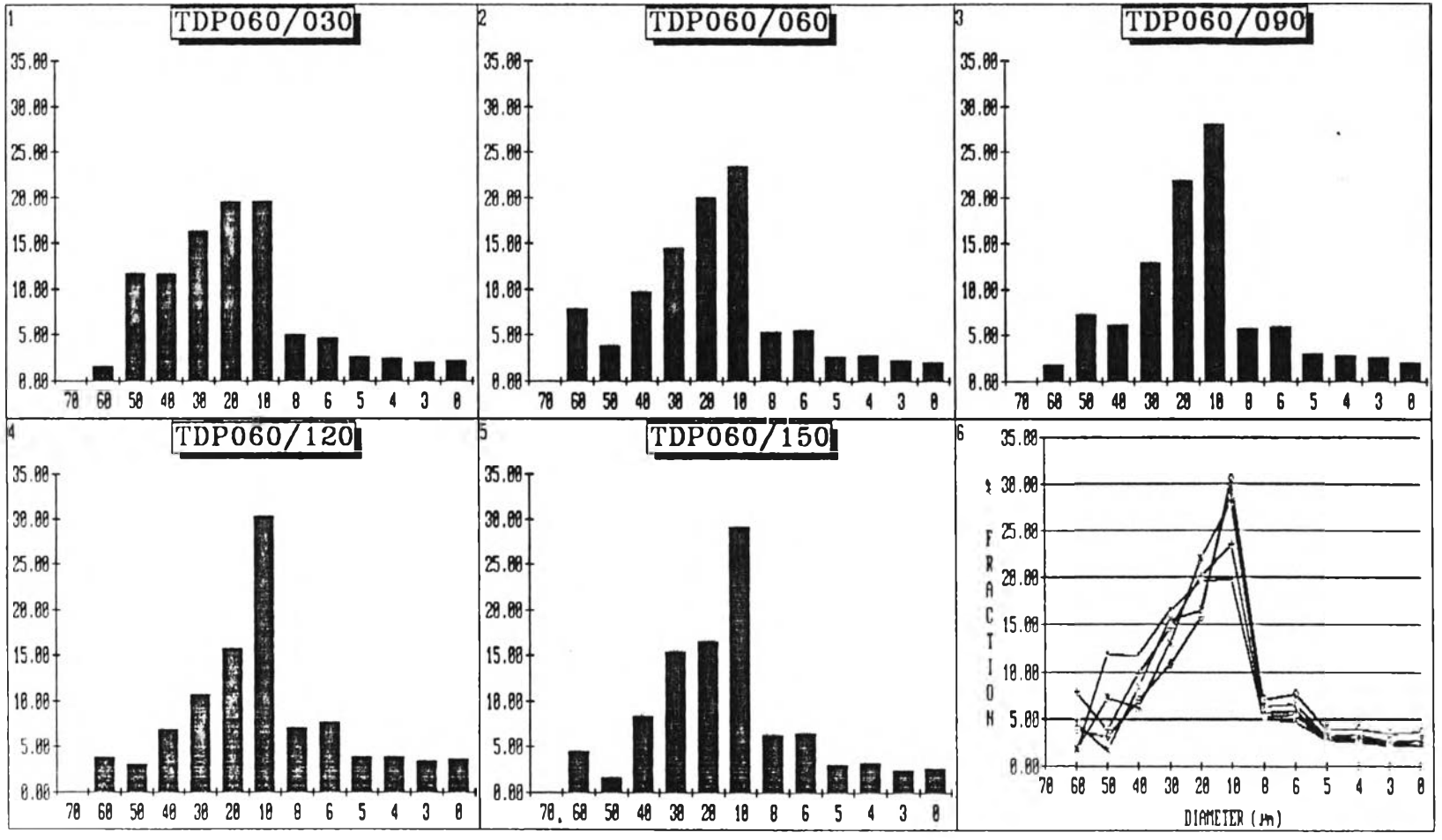
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 2,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 22 Histogram of Particle Size Distribution of TDP040/030-TDP040/150.

(The graphs were made from the data from Tables 79-2 - 83-2)

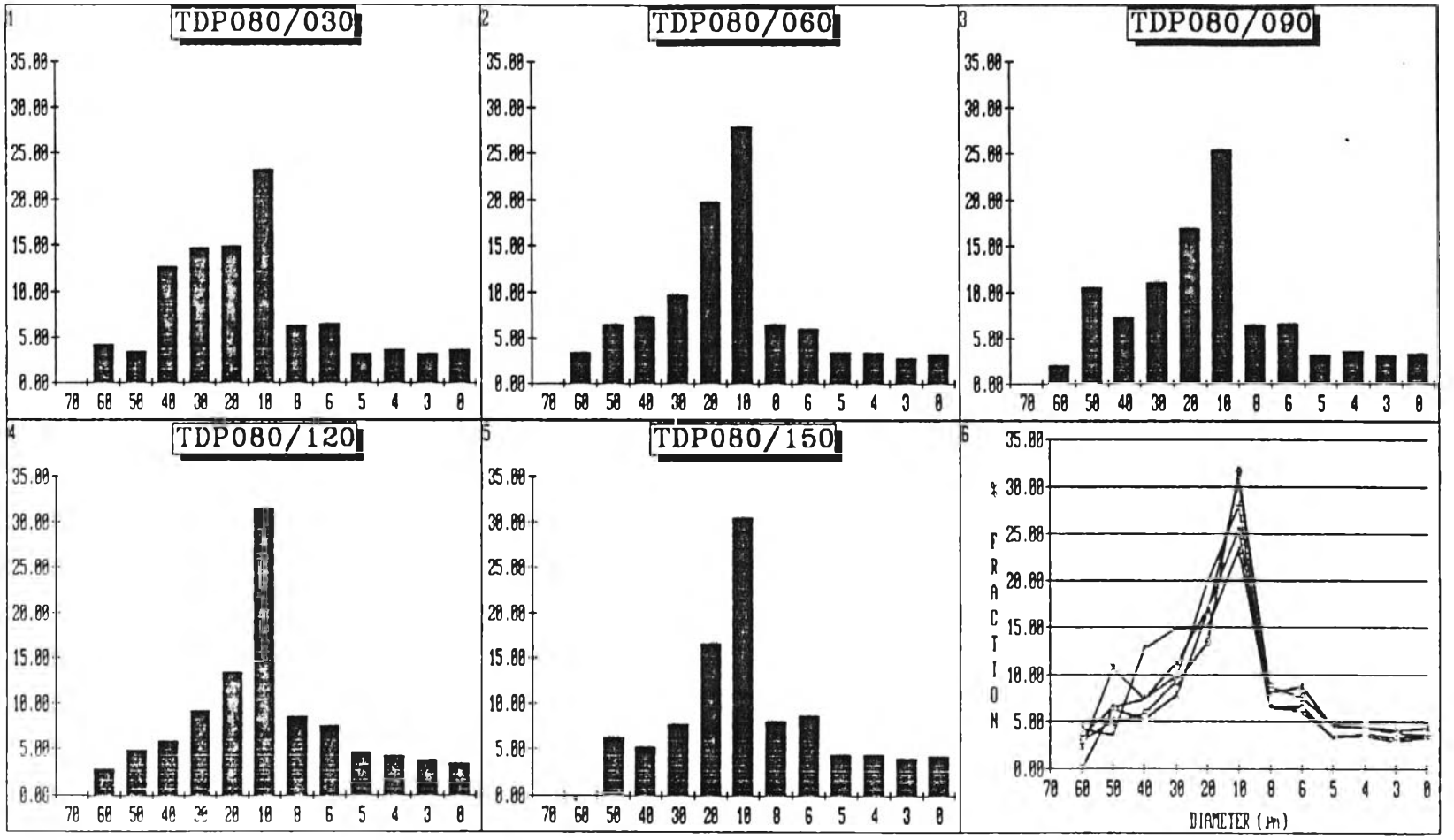
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 4,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 23 Histogram of Particle Size Distribution of TDP060/030-TDP060/150.

(The graphs were made from the data from Tables 79-3 - 83-3)

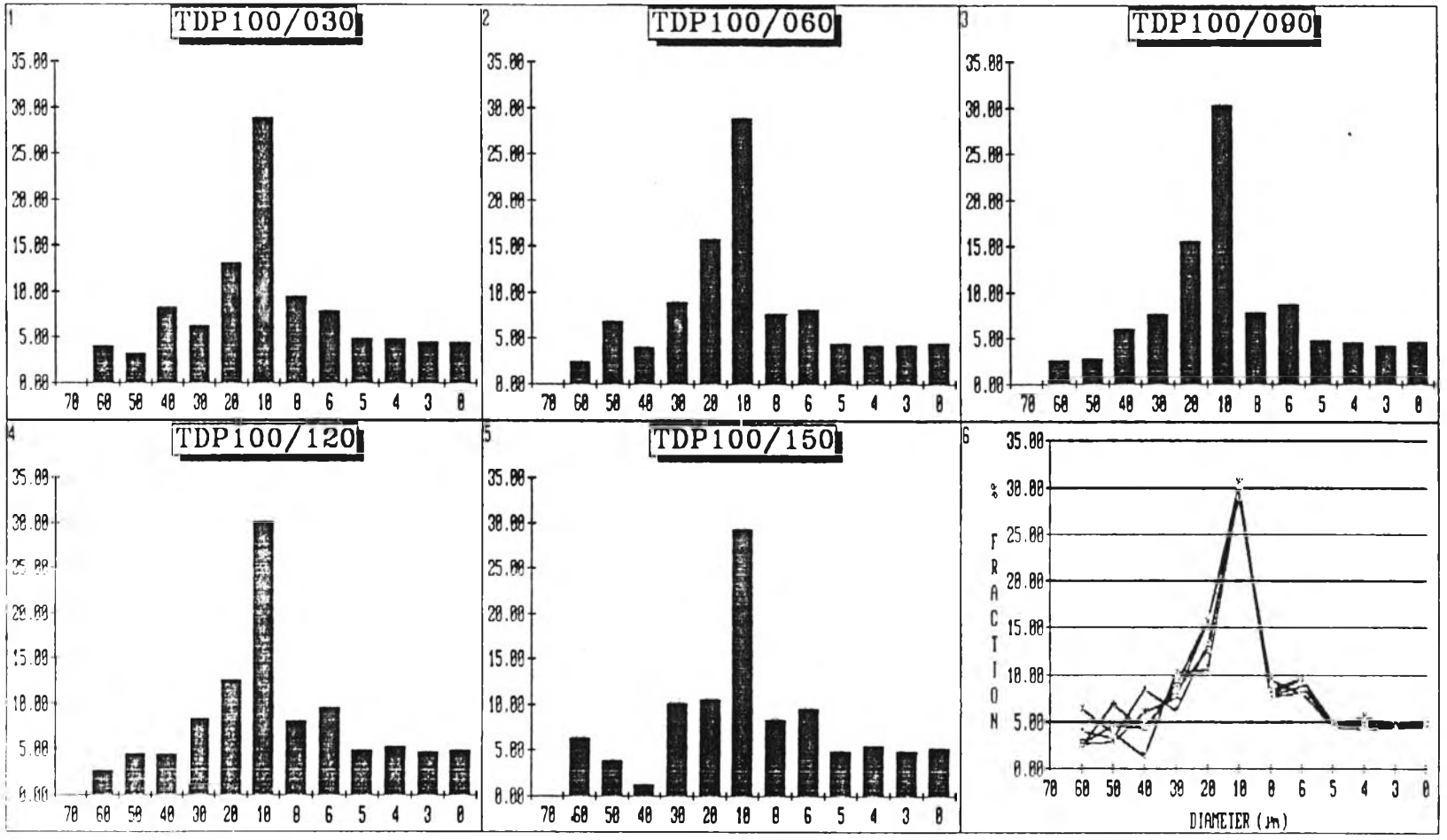
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 6,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 24 Histogram of Particle Size Distribution of TDP080/030-TDP080/150.

(The graphs were made from the data from Tables 79-4 - 83-4)

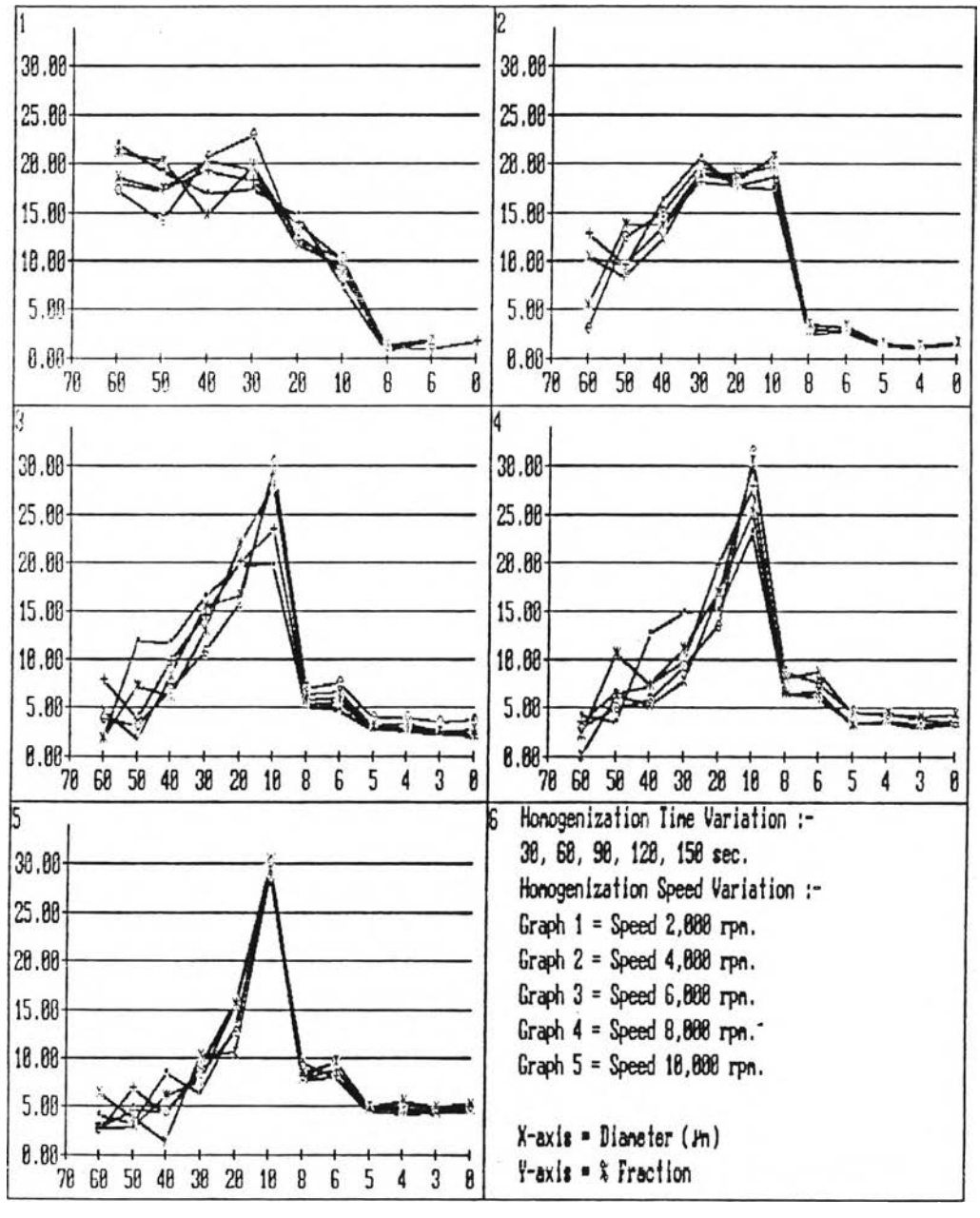
Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 8,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 25 Histogram of Particle Size Distribution of TDP100/030-TDP100/150.

(The graphs were made from the data from Tables 79-5 - 83-5)

Effect of the homogenizing times from 30 to 150 sec. at the propeller speed 10,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.



Graph series 26 Summary of the Graph series 21 - 25 on Effect of Homogenizing Time. (The graphs were made from the data from Tables series 79 - 83)

Effect of the homogenizing time from 30 to 150 sec. at the propeller speeds from 2,000 to 10,000 rpm. on the particle size distribution of dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules using poly(vinyl alcohol) as emulsifier.

Table 42 Average Diameter and % Unencapsulated Oil of SDP Series. Average Particle Size and Microencapsulation Efficiency of Poly(hexamethylene sebacamide) Microcapsules in Various Propeller Speeds and Homogenizing Times Using Poly(vinyl alcohol), 7.5% of the Total Oil Phase, as Emulsifier.

Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
SDP020/030	43.29	5.64
SDP020/060	40.71	4.98
SDP020/090	39.46	5.23
SDP020/120	41.22	5.50
SDP020/150	39.82	4.74
SDP040/030	33.02	3.79
SDP040/060	28.97	4.21
SDP040/090	27.77	3.42
SDP040/120	27.80	3.31
SDP040/150	26.96	3.50
SDP060/030	22.76	2.32
SDP060/060	21.29	1.97
SDP060/090	21.00	1.34
SDP060/120	19.22	1.09
SDP060/150	18.76	1.22
SDP080/030	19.36	1.56
SDP080/060	17.23	1.92
SDP080/090	16.81	1.47
SDP080/120	16.76	1.79

Table 42 Average Diameter and % Unencapsulated Oil of SDP Series. Average Particle Size and Microencapsulation Efficiency of Poly(hexamethylene sebacamide) Microcapsules in Various Propeller Speeds and Homogenizing Times Using Poly(vinyl alcohol), 7.5% of the Total Oil Phase, as Emulsifier.

Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
SDP080/150	16.89	1.64
SDP100/030	16.68	1.05
SDP100/060	15.68	1.87
SDP100/090	14.49	1.53
SDP100/120	14.83	1.27
SDP100/150	15.36	1.09

Table 43 Average Diameter and % Unencapsulated Oil of TDP Series. Average Particle Size and Microencapsulation Efficiency of Poly(para-phenylene terephthalamide) Microcapsules in Various Propeller Speeds and Homogenizing Times Using Poly(vinyl alcohol), 7.5% of the Total Oil Phase, as Emulsifier.

Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
TDP020/030	43.51	7.54
TDP020/060	41.39	6.77
TDP020/090	43.07	7.21
TDP020/120	40.98	6.98
TDP020/150	42.17	5.74

Table 43 Average Diameter and % Unencapsulated Oil of TDP Series. Average Particle Size and Microencapsulation Efficiency of Poly(para-phenylene terephthalamide) Microcapsules in Various Propeller Speeds and Homogenizing Times Using Poly(vinyl alcohol), 7.5% of the Total Oil Phase, as Emulsifier.

Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
TDP040/030	33.90	5.97
TDP040/060	33.81	5.11
TDP040/090	32.13	4.82
TDP040/120	30.75	5.31
TDP040/150	31.87	4.50
TDP060/030	27.54	3.32
TDP060/060	26.40	3.97
TDP060/090	23.40	2.94
TDP060/120	21.24	3.09
TDP060/150	22.96	2.12
TDP080/030	24.31	2.56
TDP080/060	23.04	2.92
TDP080/090	23.95	2.47
TDP080/120	20.42	1.99
TDP080/150	19.14	1.64
TDP100/030	20.08	2.05
TDP100/060	20.44	1.97
TDP100/090	19.06	2.13
TDP100/120	18.87	1.68
TDP100/150	19.57	1.29

2.9.5) Conclusions

1) The Effect of Propeller Speed

Based on the results presented by graph series 3 - 8 and 15 - 20 showed that the propeller speeds of the homogenizer are very influentail on the particle size distribution and average particle size of polyamide microcapsules. Increasing the propeller speeds decrease the average particle size and produce a broad distribution in diameter of the microcapsules.

2) The Effect of Homogenizing Time

Based on the results presented by graph series 9 - 14 and 21 - 26 showed that the homogenized times cannot affect the average particle size of polyamide microcapsules but has a very strong effect on the particle size distribution. From the Microphotograph series 5 - 9 and 10 - 14, show that increasing the homogenizing times produces a narrow particle distribution of the microcapsules.

2.10) EFFECT OF EMULSIFIER CONCENTRATION

2.10.1) Purpose

To study the effect of emulsifier concentrations on microscopic properties, particle size and size distribution and microencapsulation efficiency when monomer concentration, propeller speed and homogenizing time are fixed. Emulsifier concentrations vary from 2.5 to 12.5% of the total oil phase.

2.10.2) Synthesis Method

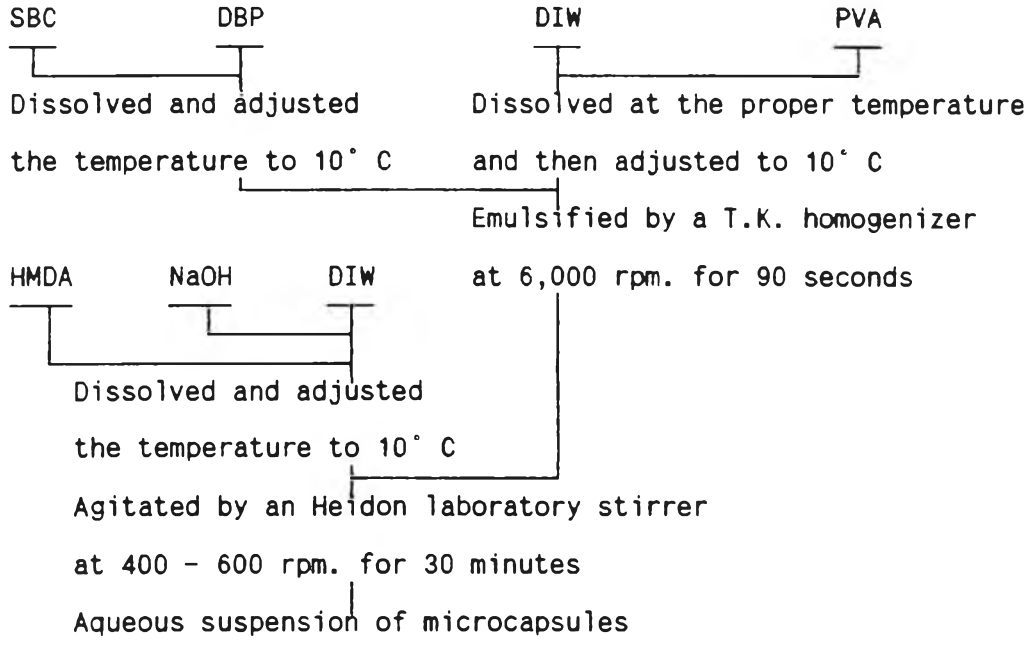
The stock solutions of diacid chloride, diamine and emulsifier, all of which were of various concentrations were prepared and kept in the water bath to control the temperature at 10°C for

sebacoyl chloride and 30°C for terephthaloyl chloride. 210.0 gm. of emulsifier and 90.0 gm. of diacid chloride solutions were poured into a T.K. homogenizer vessel. The mixture was then homogenized at the propeller speeds and homogenizing times arranged as shown in the Tree Diagram 5 to form an oil-in-water emulsion. The emulsion was poured into a 500 ml. beaker containing 200.0 gm. of diamine solution while stirring with an Heidon laboratory stirrer at the propeller speed of 400 - 600 rpm. Microencapsulation occurred by interfacial polycondensation at the interface of the diacid chloride solution droplets and the diamine solution which had the emulsifier solution as stabilizer.

2.10.2.1) Sebacoyl Chloride System

To prepare the formulation SDP075E, 6.75 gm. of poly(vinyl alcohol) was dissolved in 203.25 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution .PA was cooled down to 10°C and kept in a water bath to control the temperature. For the diacid chloride solution, 9.28 gm. of sebacoyl chloride was dissolved in 80.72 gm. of dibutyl phthalate. This was carried out at room temperature and were kept in the -water bath to control the temperature at 10°C. Likewise, for the diamine solution, 4.50 gm. of hexamethylene diamine and 3.01 of sodium hydroxide were added into a 500 ml. beaker containing 192.49 gm. of deionized water, both of which were prepared at room temperature and then adjusted the temperature to 10°C. The diamine solution was stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of propeller speeds. The emulsion was prepared by homogenizing the mixture of diacid chloride and emulsifier solutions at the propeller speeds and homogenizing times which were arranged as shown in the Tree Diagram 5. This emulsion was then poured into the diamine solution and was continuously agitated for 30 minutes to form poly(hexamethylene sebacamide) microcapsules containing dibutyl phthalate as encapsulated material.

Flow Chart 11 Synthesis Method of SBC for Studying Effect of Emulsifier Concentration.



2.10.2.2) Terephthaloyl Chloride System

To synthesize the formulation TDP075E, 6.75 gm. of poly(vinyl alcohol) was dissolved in 203.25 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 30°C and kept in a water bath to control the temperature. For the diacid chloride solution, 6.06 gm. of terephthaloyl chloride was dissolved in 83.94 gm. of dibutyl phthalate which was prepared at room temperature and kept in water bath to control the temperature at 30°C. Similarly, the diamine solution, 3.29 gm. of para-phenylene diamine and 2.37 of sodium hydroxide were added into a 500 ml. beaker containing 194.34 gm. of deionized water. They were prepared at room temperature and then adjusted the temperature to 30°C. The diamine solution was then stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of propeller speeds. The emulsion was prepared by homogenizing the mixture of diacid chloride and emulsifier solutions at the propeller speeds and homogenizing times which were arranged as shown in the Tree

Diagram 5. This emulsion was poured into the diamine solution and was continuously agitated for 30 minutes to form poly(para-phenylene terephthalamide) microcapsules containing dibutyl phthalate as encapsulated material.

Flow Chart 12 Synthesis Method of TPC for Studying Effect of Emulsifier Concentration.

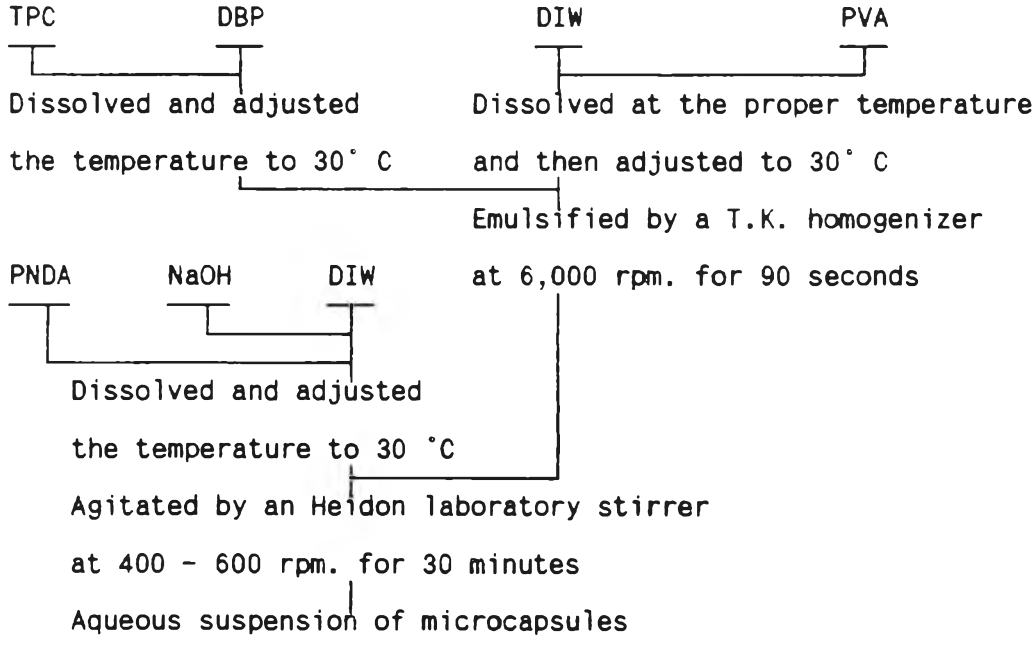


Table 44 Effect of Emulsifier Concentrations on Encapsulating of Dibutyl Phthalate by Poly(hexamethylene sebacamide) Microcapsules.

Assigned Name / Chemicals	SDP025E (gm.)	SDP050E (gm.)	SDP075E (gm.)	SDP100E (gm.)	SDP125E (gm.)
SBC	9.28	9.28	9.28	9.28	9.28
DBP	80.72	80.72	80.72	80.72	80.72
PVA	2.25	4.50	6.75	9.00	11.25
DIW	207.75	205.50	203.25	201.00	198.75

Table 44 Effect of Emulsifier Concentrations on Encapsulating of Dibutyl Phthalate by Poly(hexamethylene sebacamide) Microcapsules.

Assigned Name Chemicals	SDP025E (gm.)	SDP050E (gm.)	SDP075E (gm.)	SDP100E (gm.)	SDP125E (gm.)
HMDA	4.50	4.50	4.50	4.50	4.50
NaOH	3.01	3.01	3.01	3.01	3.01
DIW	192.49	192.49	192.49	192.49	192.49

Table 45 Effect of Emulsifier Concentrations on Encapsulating of Dibutyl Phthalate by Poly(para-phenylene terephthalamide) Microcapsules.

Assigned Name Chemicals	TDP025E (gm.)	TDP050E (gm.)	TDP075E (gm.)	TDP100E (gm.)	TDP125E (gm.)
TPC	6.06	6.06	6.06	6.06	6.06
DBP	83.94	83.94	83.94	83.94	83.94
PVA	2.25	4.50	6.75	9.00	11.25
DIW	207.75	205.50	203.25	201.00	198.75
PNDA	3.29	3.29	3.29	3.29	3.29
NaOH	2.37	2.37	2.37	2.37	2.37
DIW	194.34	194.34	194.34	194.34	194.34

Tree Diagram 5 Effect of Emulsifier Concentrations on Microencapsulation. Monomer, encapsulated oil, propeller speed and homogenizing time were constant.

Monomer	Oil	Speed rpm.	Time sec.	PVA conc.	Assigned Name
SBC + HMDA	DBP	6,000	90	2.5%	SDP025E
		6,000	90	5.0%	SDP050E
		6,000	90	7.5%	SDP075E
		6,000	90	10.0%	SDP100E
		6,000	90	12.5%	SDP125E
TPC + PNDA	DBP	6,000	90	2.5%	TDP025E
		6,000	90	5.0%	TDP050E
		6,000	90	7.5%	TDP075E
		6,000	90	10.0%	TDP100E
		6,000	90	12.5%	TDP125E

2.10.3) Analysis Methods

General appearance was observed by visual evaluation, volume of separation of the system after sedimentation for 24 hours was measured in a 100 ml. cylinder; microscopic properties were examined by a Zeiss optical microscope and a Joel scanning electron microscope; average particle size and particle size distribution were measured by a Shimadzu particle size analyzer and the microencapsulation efficiency was analyzed by a Shimadzu gas chromatograph. The detail of each method was already explained in the earlier experiments.

2.10.4) Results

2.10.4.1) General Properties

The appearance and the amount of microcapsule sedimentation were showed in Tables 46 an 47. Increasing the amount of poly(vinyl alcohol) produces a more stable emulsion microcapsules.

Table 46 Separation and Appearance of SDP025E-SDP125E.
Effect of Emulsifier Concentrations on Microencapsulation of Dibutyl Phthalate within the Poly(hexamethylene sebacamide) Microcapsules.

Assigned Name	Separation at 24 hours	Appearance by Visual Evaluation
SDP025E	7 ml.	milky white emulsion and uniform
SDP050E	3 ml.	milky white emulsion and uniform
SDP075E	1 ml.	milky white emulsion and uniform
SDP100E	0 ml.	milky white emulsion and uniform
SDP125E	0 ml.	milky white emulsion and uniform

Table 47 Separation and Appearance of TDP025E-TDP125E.
Effect of Emulsifier Concentrations on Microencapsulation of Dibutyl Phthalate within the Poly(para-phenylene terephthalamide) Microcapsules.

Assigned Name	Separation at 24 hours	Appearance by Visual Evaluation
TDP025E	8 ml.	milky brown emulsion and uniform
TDP050E	5 ml.	milky brown emulsion and uniform
TDP075E	2 ml.	milky brown emulsion and uniform
TDP100E	0 ml.	milky brown emulsion and uniform
TDP125E	0 ml.	milky brown emulsion and uniform

2.10.4.2) Microscopic Properties

Photomicrograph series 15 shows the effect of poly(vinyl alcohol) concentrations. Increasing the amount of

emulsifier produces the smaller size of poly(hexamethylene sebacamide) microcapsules. In the same manner, the effect of emulsifier concentrations on poly(para-phenylene terephthalamide) microcapsules as showed in Photomicrograph series 16.

2.10.4.3) Particle Size Distribution

1) Graph series 27 shows that increasing the amount of poly(vinyl alcohol) shifts the histogram of particle size distribution of poly(hexamethylene sebacamide) microcapsules to the smaller size. In the same manner, Graph series 28 shows the distribution of poly(para-phenylene terephthalamide) microcapsules.

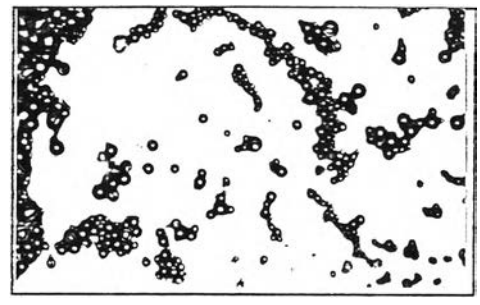
2) From Appendix III, Tables 89 - 90 show that increasing the amount of poly(vinyl alcohol) shifts the particle size distribution and average particle size of poly(hexamethylene sebacamide) microcapsules to the smaller size. Likewise, Tables 91 - 92 show the results of poly(para-phenylene terephthalamide) microcapsules.

2.10.4.4) Averge Particle Size and Encapsulation Efficiency

The concentration of poly(vinyl alcohol) has a very strong effect on the average particle size of microcapsules and microencapsulation efficiency. As showed in Tables 48 and 49, increasing the amount of poly(vinyl alcohol) decreases the average size of the microcapsules but increases the microencapsulation efficiency.

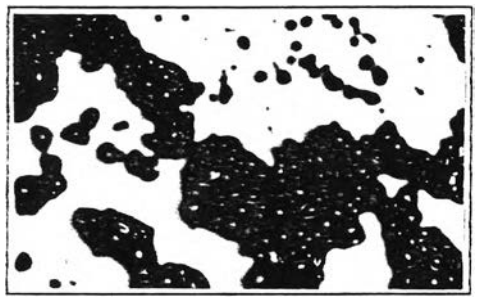
SDP025E

PVA 2.5 %



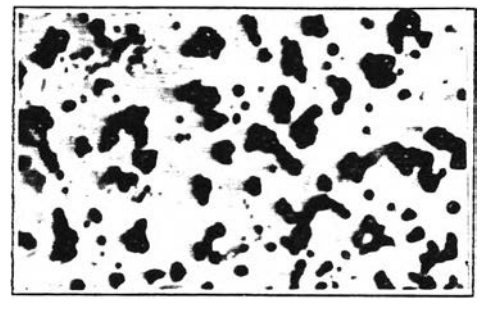
SDP100E

PVA 10.0 %



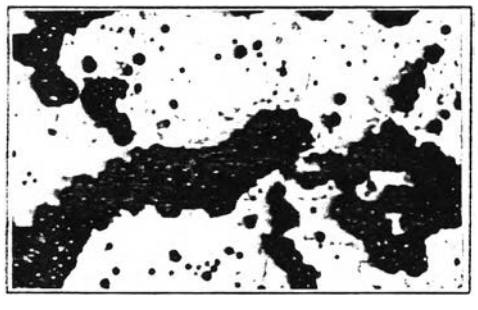
SDP050E

PVA 5.0 %



SDP125E

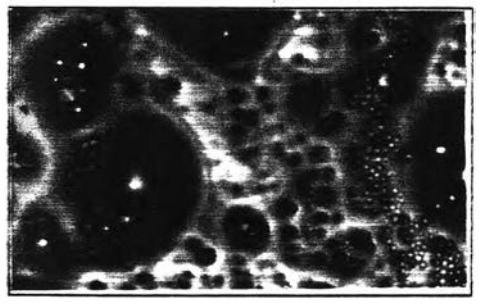
PVA 12.5 %



SDP075E

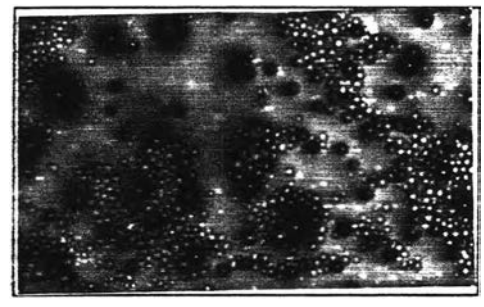
PVA 7.5 %

Photomicrograph series 15 Photomicrographs of SDP025E-SDP125E. Poly(hexamethylene sebacamide) as polymeric shell; dibutyl phthalate as encapsulated material; the propeller speed and homogenizing time fixed at 6.000 rpm. and 90 sec. and various concentrations of poly(vinyl alcohol), as emulsifier, were used. The photomicrographs were taken by the Zeiss optical microscope with a magnification of 100 times from which the prints were enlarged 2.5 times.



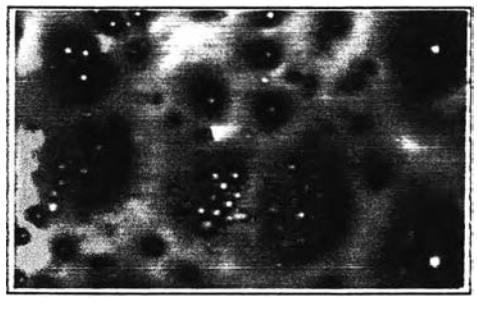
TDP025E

PVA 2.5 %



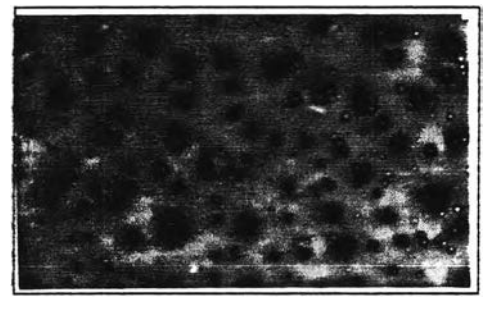
TDP100E

PVA 10.0 %



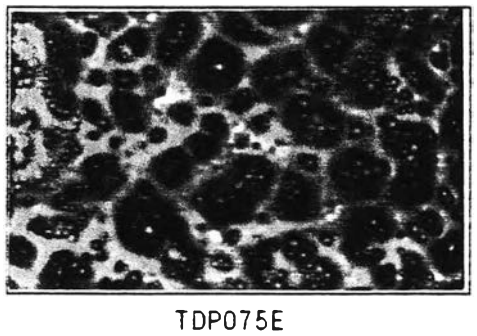
TDP050E

PVA 5.0 %



TDP125E

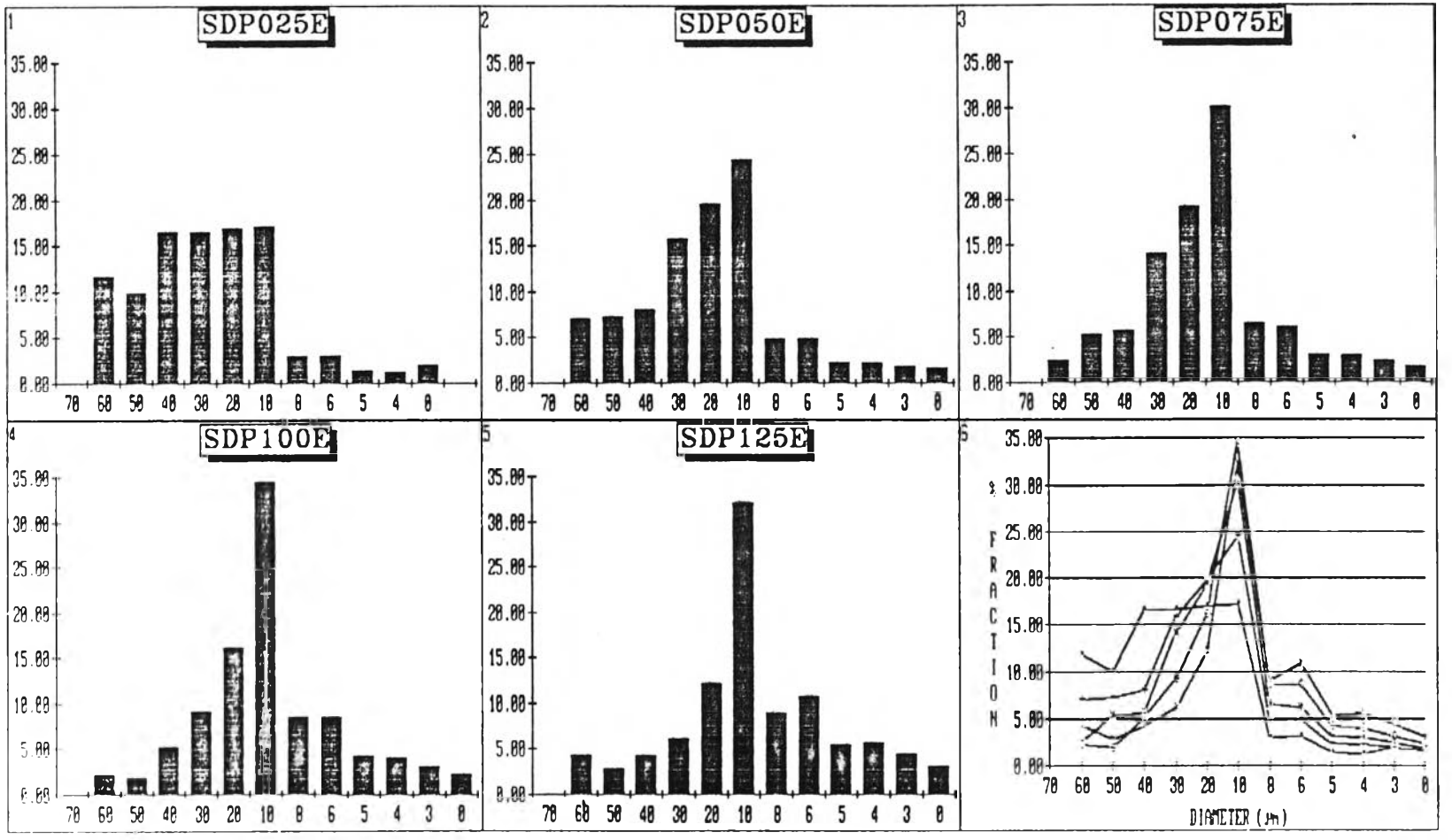
PVA 12.5 %



TDP075E

PVA 7.5 %

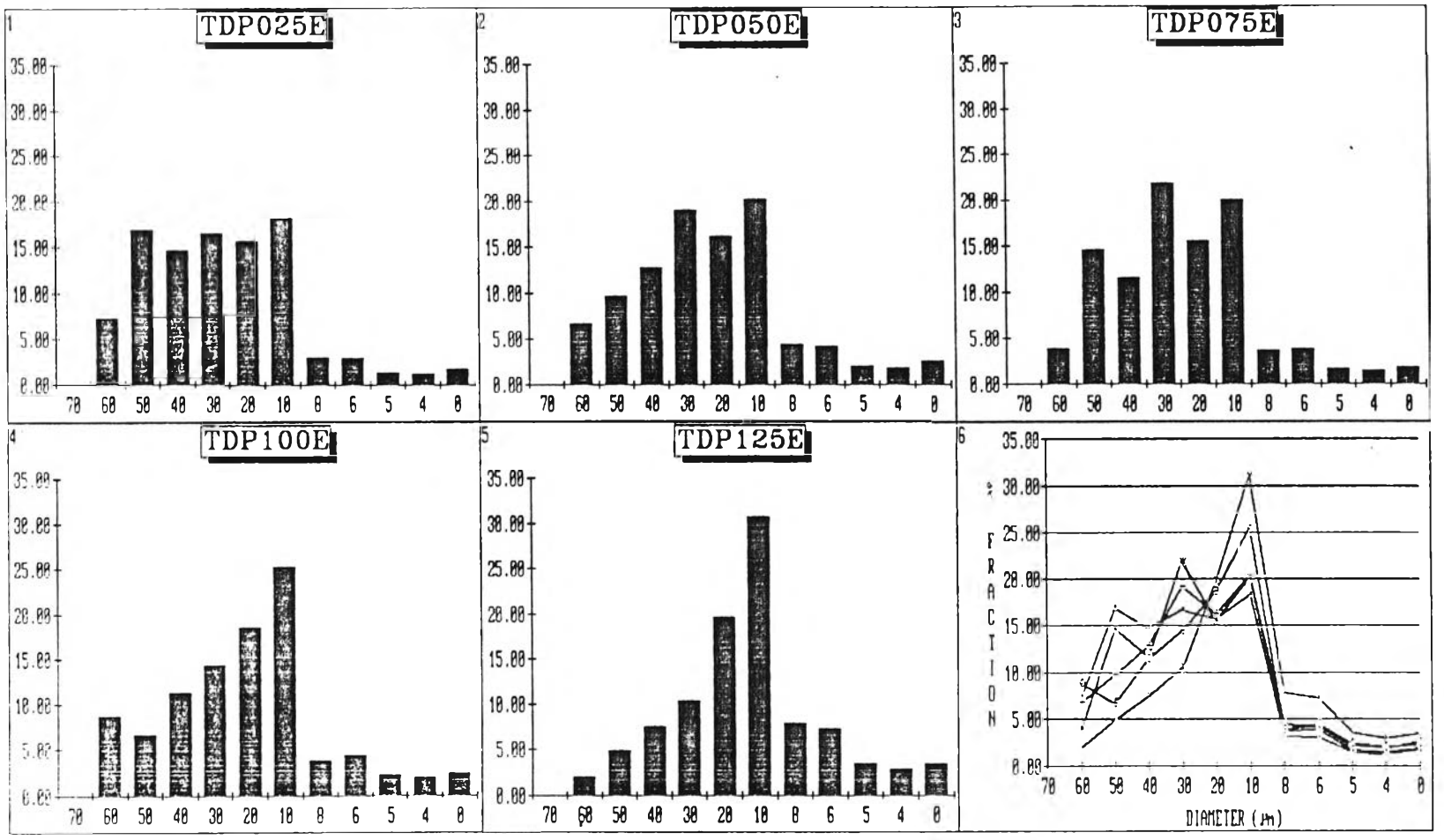
Photomicrograph series 16 Photomicrographs of TDP025E-TDP125E. Poly(para-phenylene terephthalamide) as polymeric shell; dibutyl phthalate as encapsulated material; the propeller speed and homogenizing time fixed at 6,000 rpm. and 90 sec. and various concentrations of poly(vinyl alcohol), as emulsifier, were used. The photomicrographs were taken by the Zeiss optical microscope with a magnification of 100 times from which the prints were enlarged 2.5 times.



Graph series 27 Histogram of Particle Size Distribution of SDP050E-SDP125E.

(The graphs were made from the data from Tables 89-1 - 89-5)

Effect of poly(vinyl alcohol) concentrations from 2.5, 5.0, 7.5, 10.0 and 12.5 % of the total oil phase on the particle size distribution for dibutyl phthalate being encapsulated by poly(hexamethylene sebacamide) microcapsules. Fixing the propeller speed at 6,000 rpm. and homogenizing time for 90 sec.



Graph series 28 Histogram of Particle Size Distribution of TDP050E-TDP125E.

(The graphs were made from the data from Tables 91-1 - 91-5)

Effect of poly(vinyl alcohol) concentrations from 2.5, 5.0, 7.5, 10.0 and 12.5 % of the total oil phase on the particle size distribution for dibutyl phthalate being encapsulated by poly(para-phenylene terephthalamide) microcapsules. Fixing the propeller speed at 6,000 rpm. and homogenizing time for 90 sec.

Table 48 Average Diameter and % Unencapsulated Oil of SDP025E-SDP125E. Effect of Emulsifier Concentration on Microencapsulation of Dibutyl Phthalate by Poly(hexamethylene sebacamide) Microcapsules.

Assigned name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
SDP025E	33.97	3.56
SDP050E	27.33	2.06
SDP075E	22.82	1.47
SDP100E	19.18	1.09
SDP125E	18.53	0.64

Table 49 Average Diameter and % Unencapsulated Oil of TDP025E-TDP125E. Effect of Emulsifier Concentration on Microencapsulation of Dibutyl Phthalate by Poly(para-phenylene terephthalamide) Microcapsules.

Assigned name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
TDP025E	33.81	4.56
TDP050E	31.11	3.92
TDP075E	30.20	2.77
TDP100E	28.92	1.89
TDP125E	22.16	0.97

2.10.5) Conclusions

Increasing the amount of poly(vinyl alcohol) decreases the average particle size, produces a more stable emulsion and increases the microencapsulation efficiency.

2.11) EFFECT OF MONOMER CONCENTRATION

2.11.1) Purpose

To study the effect of diacid chloride concentrations on microscopic properties, average particle size, particle size distribution and microencapsulation efficiency of the microcapsules when propeller speed, homogenizing time and emulsifier concentration are fixed. Sebacoyl chloride concentrations were varied from the ratios of 1:29, 2:28, 3:27, 4:26, and 5:25 (gm./gm.) of sebacoyl chloride to dibutyl phthalate. Likewise the ratios of 1.0:29.0, 1.5:28.5, 2.0:28.0, 2.5:27.5, and 3.0:27.0 of terephthaloyl chloride to dibutyl phthalate were made.

2.11.2) Synthesis Method

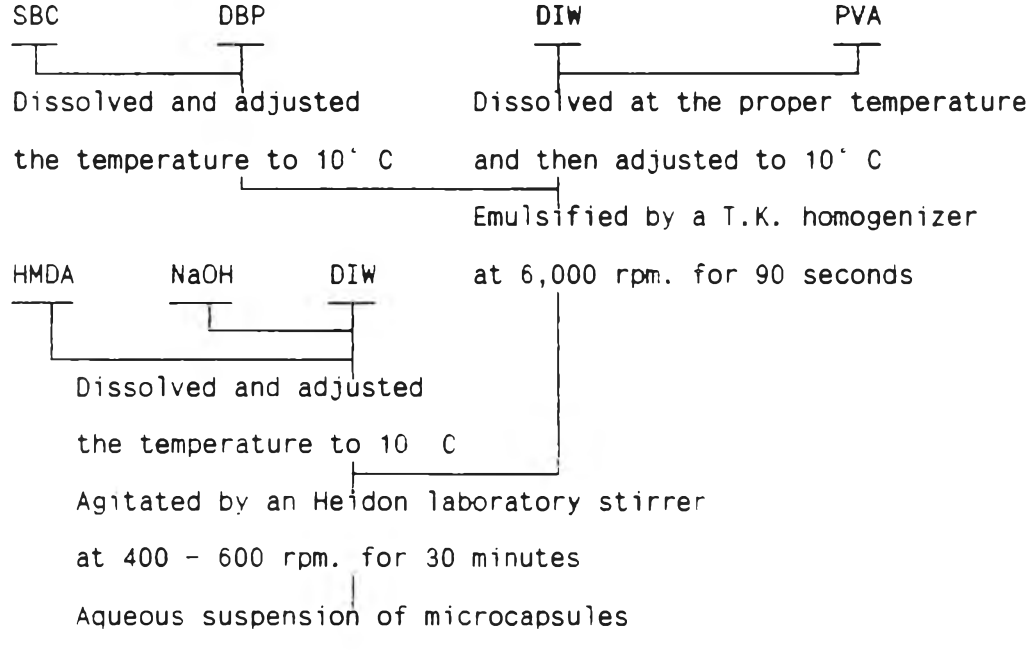
The stock solutions of diacid chloride, emulsifier and diamine were prepared and were kept in a water bath at the temperature of 10°C for the sebacoyl chloride solution and at 30°C for the terephthaloyl chloride solution. 210.0 gm. of the emulsifier solution and 90.0 gm. of the diacid chloride solution were poured into the T.K. homogenizer vessel. The mixture was homogenized at the propeller speed and homogenizing time, show as follows in the Tree Diagram 6, to form oil-in-water emulsion. The emulsion was then poured into a 500 ml. beaker containing 200.0 gm. of the diamine solution while being stirred by an Heidon laboratory stirrer at 400 - 600 rpm. of the propeller speed. Microencapsulation was formed by interfacial polycondensation at the interfacial droplets of the diacid chloride and diamine solutions having the emulsifier solution as stabilizer.

2.11.2.1) Sebacoyl Chloride Process

Formulation SDP030/270 was synthesized as follows : 6.75 gm. of poly(vinyl alcohol) was dissolved in 203.25 gm. of

deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 10°C and was kept in water bath to control the temperature. To prepare the diacid chloride solution, 9.28 gm. of sebacoyl chloride was dissolved in 80.72 gm. of dibutyl phthalate at room temperature and were kept in water bath to control temperature at 10°C. For diamine solution, 4.50 gm. of hexamethylene diamine and 3.01 of sodium hydroxide were added into a 500 ml. beaker containing 192.49 gm. of deionized water at room temperature and then adjusted the temperature to 10°C. The diamine solution was then stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of the propeller speed. The emulsion was prepared by homogenizing the mixture of the diacid chloride and emulsifier solutions at the propeller speed and homogenizing time arranged as follows in the Tree Diagram 6. This emulsion was poured into the diamine solution and was continuously agitated for 30 minutes to form poly(hexamethylene sebacamide) microcapsules in which dibutyl phthalate was encapsulated. The other formulations as follows in Table 50 were prepared in the same method.

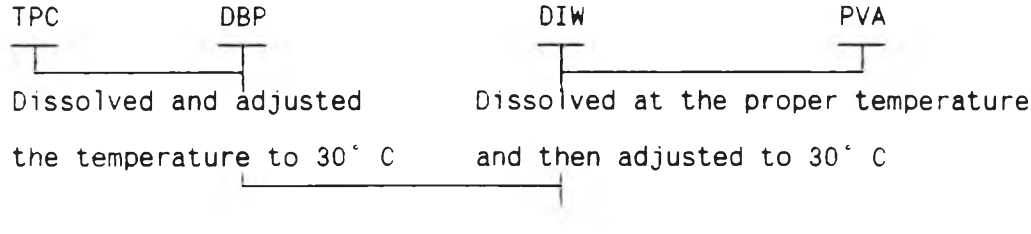
Flow Chart 13 Synthesis Method of SBC for Studying Effect of Monomer Concentration.



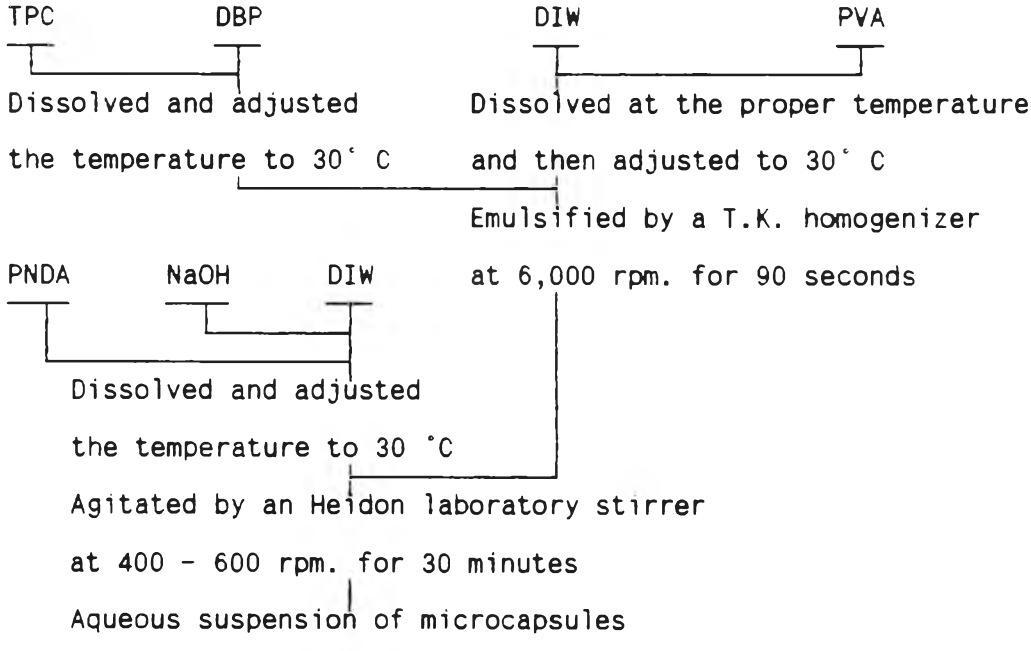
2.11.2.2) Terephthaloyl Chloride Process

Formulation TDP020/280, was synthesized as follows : 6.75 gm. of poly(vinyl alcohol) was dissolved in 203.25 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 30°C and was kept in water bath to control the temperature. To prepare the diacid chloride solution, 6.06 gm. of terephthaloyl chloride was dissolved in 83.94 gm. of dibutyl phthalate at room temperature and were kept in water bath to control temperature at 30°C. For diamine solution, 3.29 gm. of para-phenylene diamine and 2.37 of sodium hydroxide were added into a 500 ml. beaker containing 194.34 gm. of deionized water at room temperature and then adjusted the temperature to 30°C. The diamine solution was then stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of the propeller speed. The emulsion was prepared by homogenizing the mixture of the diacid chloride and emulsifier solutions at the propeller speed and homogenizing time arranged as follows in the Tree Diagram 6. This emulsion was poured into the diamine solution and was continuously agitated for 30 minutes to form poly(para-phenylene terephthalamide) microcapsules in which dibutyl phthalate was encapsulated. The other formulations as follows in the Table 51 were prepared in the same method.

Flow Chart 14 Synthesis Method of TPC for Studying Effect of Monomer Concentration.



Flow Chart 14 Synthesis Method of TPC for Studying Effect of Monomer Concentration.



Tree Diagram 6 Diacid Chloride Concentrations When Fixing the Encapsulated Oil, Emulsifier, Propeller Speed and Homogenizing Time Constant.

Monomer	Oil	Speed rpm.	Time sec.	PVA conc.	SBC/DBP	Assigned Name
SBC + HMDA	DBP	6,000	90	7.5	1.0/29.0	SDP010/290
					2.0/28.0	SDP020/280
					3.0/27.0	SDP030/270
					4.0/26.0	SDP040/260
					5.0/25.0	SDP050/250
					TPC/DBP	
TPC + PNDA	DBP	6,000	90	7.5	1.0/29.0	TDP010/290
					1.5/28.5	TDP015/285
					2.0/28.0	TDP020/280
					2.5/27.5	TDP025/275
					3.0/27.0	TDP030/270

Table 50 Formulation of SDP010/290-SDP050/250.

Dibutyl Phthalate Encapsulated by Poly(hexamethylene sebacamide) Microcapsules Formulated with Various Concentrations of Sebacoyl Chloride.

Assigned Name / Chemicals	SDP010/290 (gm.)	SDP020/280 (gm.)	SDP030/270 (gm.)	SDP040/260 (gm.)	SDP050/250 (gm.)
SBC	3.09	6.19	9.28	12.37	15.47
DBP	86.91	83.81	80.72	77.63	74.53
PVA	6.75	6.75	6.75	6.75	6.75
DIW	203.25	203.25	203.25	203.25	203.25
HMDA	1.50	3.00	4.50	6.00	7.50
NaOH	1.00	2.01	3.01	4.01	5.02
DIW	197.50	194.99	192.49	189.99	187.48

Table 51 Formulation of TDP010/290-TDP030/270.

Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules Formulated with Various Concentrations of Terephthaloyl Chloride.

Assigned Name / Chemicals	TDP010/290 (gm.)	TDP015/285 (gm.)	TDP020/280 (gm.)	TDP025/275 (gm.)	TDP030/270 (gm.)
TPC	3.03	4.55	6.06	7.56	9.09
DBP	86.97	85.45	83.94	82.44	80.91
PVA	6.75	6.75	6.75	6.75	6.75
DIW	203.25	203.25	203.25	203.25	203.25

Table 51 Formulation of TDP010/290-TDP030/270.
Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules Formulated with Various Concentrations of Terephthaloyl Chloride.

Assigned Name / Chemicals	TDP010/290 (gm.)	TDP015/285 (gm.)	TDP020/280 (gm.)	TDP025/275 (gm.)	TDP030/270 (gm.)
PNDA	1.64	2.47	3.29	4.10	4.94
NaOH	1.18	1.78	2.37	2.95	3.55
DIW	197.18	195.75	194.34	192.95	191.51

2.11.3) Analysis Methods

General appearances of the microcapsules were observed by visual evaluation, the volume of separation assessed as sedimentation after being kept for 24 hours was measured in a 100 ml. cylinder. Microscopic properties were examined by a Zeiss optical microscope and a Joel scanning electron microscope; average particle size and particle size distribution were measured by a Shimadzu particle size analyzer and the microencapsulation efficiency was analyzed by a Shimadzu gas chromatograph. The detail of each methods was explained in the previous experiments.

2.11.4) Results

2.11.4.1) General Properties

The amount of sediment and appearances of the microcapsules were showed in Tables 52 and 53.

Table 52 Separation and Appearance of SDP010/290-SDP050/250. Dibutyl Phthalate Encapsulated by Poly(hexamethylene sebacamide) Microcapsules with Various Concentrations of Sebacoyl Chloride.

Assigned Name	Separation after 24 hours	Appearances by Visual Evaluation
SDP010/290	2 ml.	milky white emulsion and uniform
SDP020/280	3 ml.	milky white emulsion and uniform
SDP030/270	5 ml.	milky white emulsion and uniform
SDP040/260	6 ml.	milky white emulsion and uniform
SDP050/250	6 ml.	milky white emulsion and uniform

Table 53 Separation and Appearance of TDP010/290-TDP030/270. Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules with Various Concentrations of Terephthaloyl Chloride.

Assigned Name	Separation after 24 hours	Appearances by Visual Evaluation
TDP010/290	3 ml.	milky brown emulsion and uniform
TDP015/285	3 ml.	milky brown emulsion and uniform
TDP020/280	5 ml.	milky brown emulsion and uniform
TDP025/275	6 ml.	milky brown emulsion and uniform
TDP030/270	7 ml.	milky brown emulsion and uniform

2.11.4.2) Microscopic Properties

Photomicrograph series 17 show that any changes, neither increase nor and decrease in the amount of sebacoyl chloride do not affect the average diameter and size distribution of

poly(hexamethylene sebacamide) microcapsules. But changes in the concentration had a very strong influence in the shape of the microcapsules. When sebacoyl chloride was used at the low concentrations, the surface of polyamide shell was soft and thin due to the heat evolved from the exothermic reaction which caused the surface to pucker and wrinkle. Photomicrograph series 18 show the same trends of the average diameter and size distribution of poly(para-phenylene terephthalamide) microcapsules, however, at the low concentrations of terephthaloyl chloride, the effect of concentration was obvious as a lot of broken microcapsules were observed.

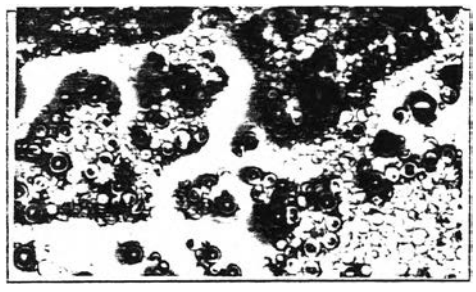
2.11.4.3) Particle Size Distribution

1) Graph series 29 shows that increasing the amount of sebacoyl chloride does not shift the histogram of particle size distribution of poly(hexamethylene sebacamide) microcapsules to the smaller size. In the same manner, the effect of concentration of terephthaloyl chloride on poly(para-phenylene terephthalamide) microcapsules is elucidated in Graph series 30.

2) From Appendix III, Tables 93 - 94 show that increasing the amount of sebacoyl chloride does not shift the particle size distribution and average particle size of poly(hexamethylene sebacamide) microcapsules to the smaller size. Likewise, the effect of concentration of terephthaloyl chloride on poly(para-phenylene terephthalamide) microcapsules is elucidated in Tables 95 - 96.

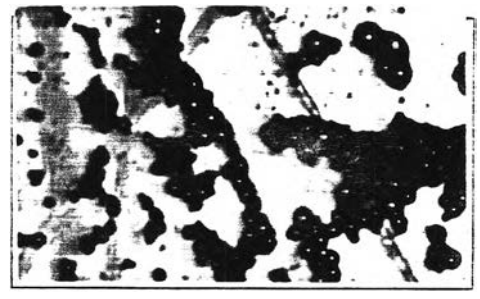
2.11.4.4) Average Particle Size and Encapsulation Efficiency

Tables 54 and 55 confirmed that the concentrations of diacid chloride did not affect the size of



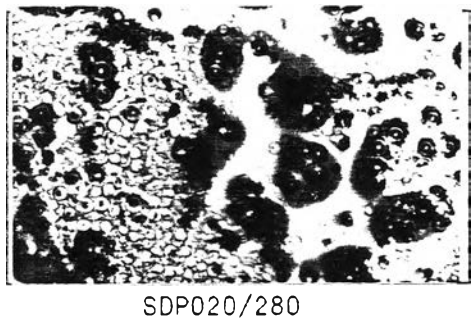
SDP010/290

SBC:DBP = 1:29



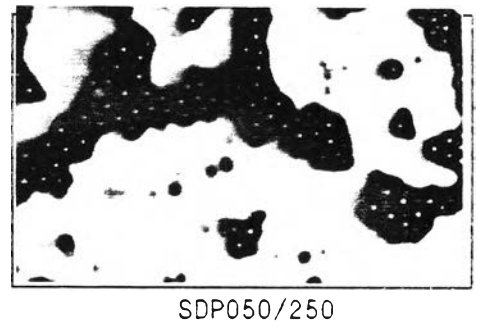
SDP040/260

SBC:DBP = 4:26



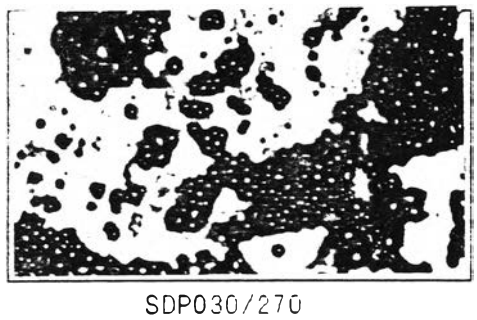
SDP020/280

SBC:DBP = 2:28



SDP050/250

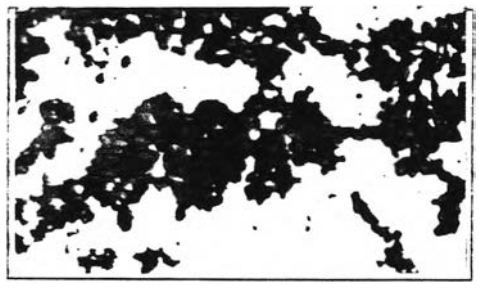
SBC:DBP = 5:25



SDP030/270

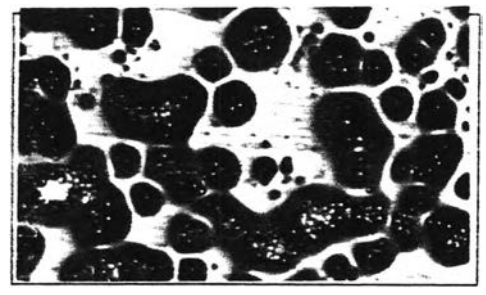
SBC:DBP = 3:27

Photomicrograph series 17 Photomicrographs of SDP010/290-SDP050/250. Effect of ratio of the diacid chloride/encapsulated oil on microencapsulation : Poly(hexamethylene sebacamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; the propeller speed and homogenizing time fixed at 6,000 rpm. and for 90 sec. respectively; the concentration of poly(vinyl alcohol), as emulsifier, at 7.5 % of the total oil phase. A Zeiss optical microscope was used to take the photomicrographs with magnification of 100 times. The prints were enlarged 2.5 times.



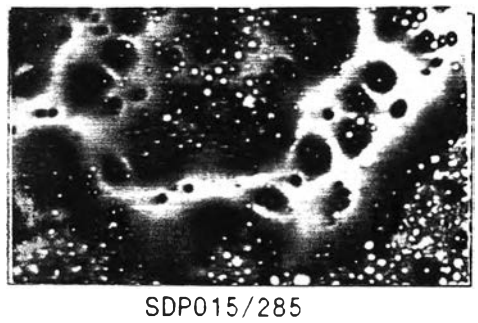
TDP010/290

TPC:DBP = 1.0:29.0



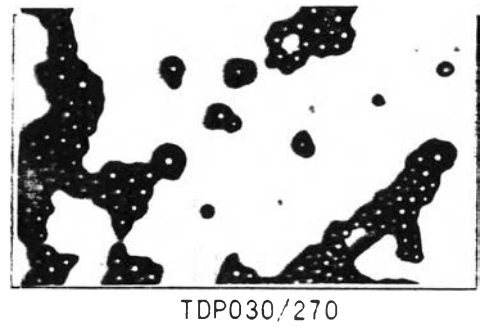
TDP025/275

TPC:DBP = 2.5:27.5



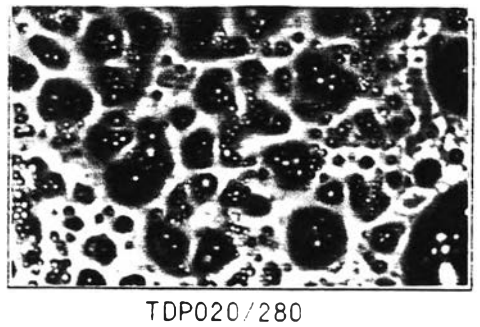
SDP015/285

TPC:DBP = 1.5:28.5



TDP030/270

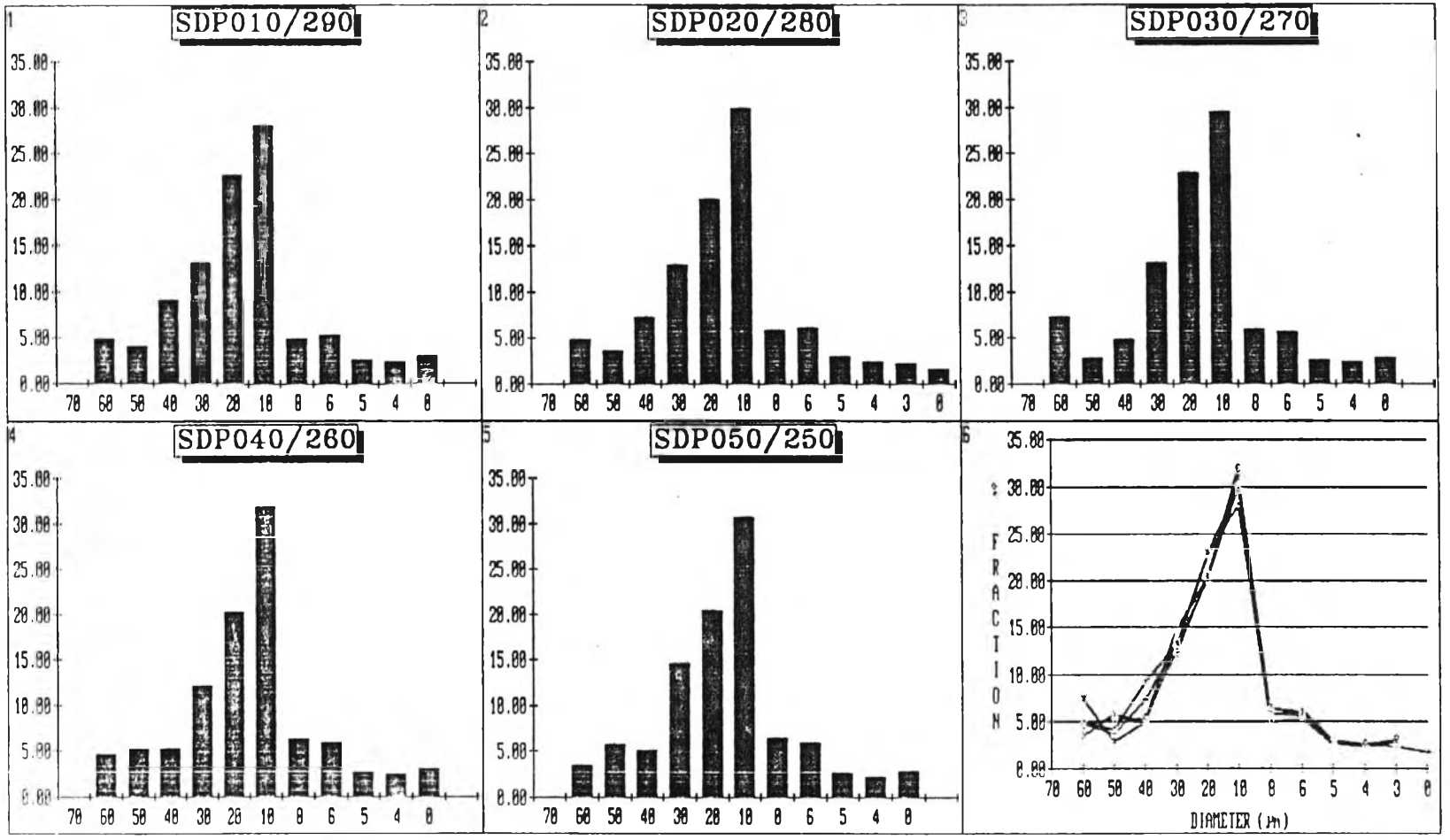
TPC:DBP = 3.0:27.0



TDP020/280

TPC:DBP = 2.0:28.0

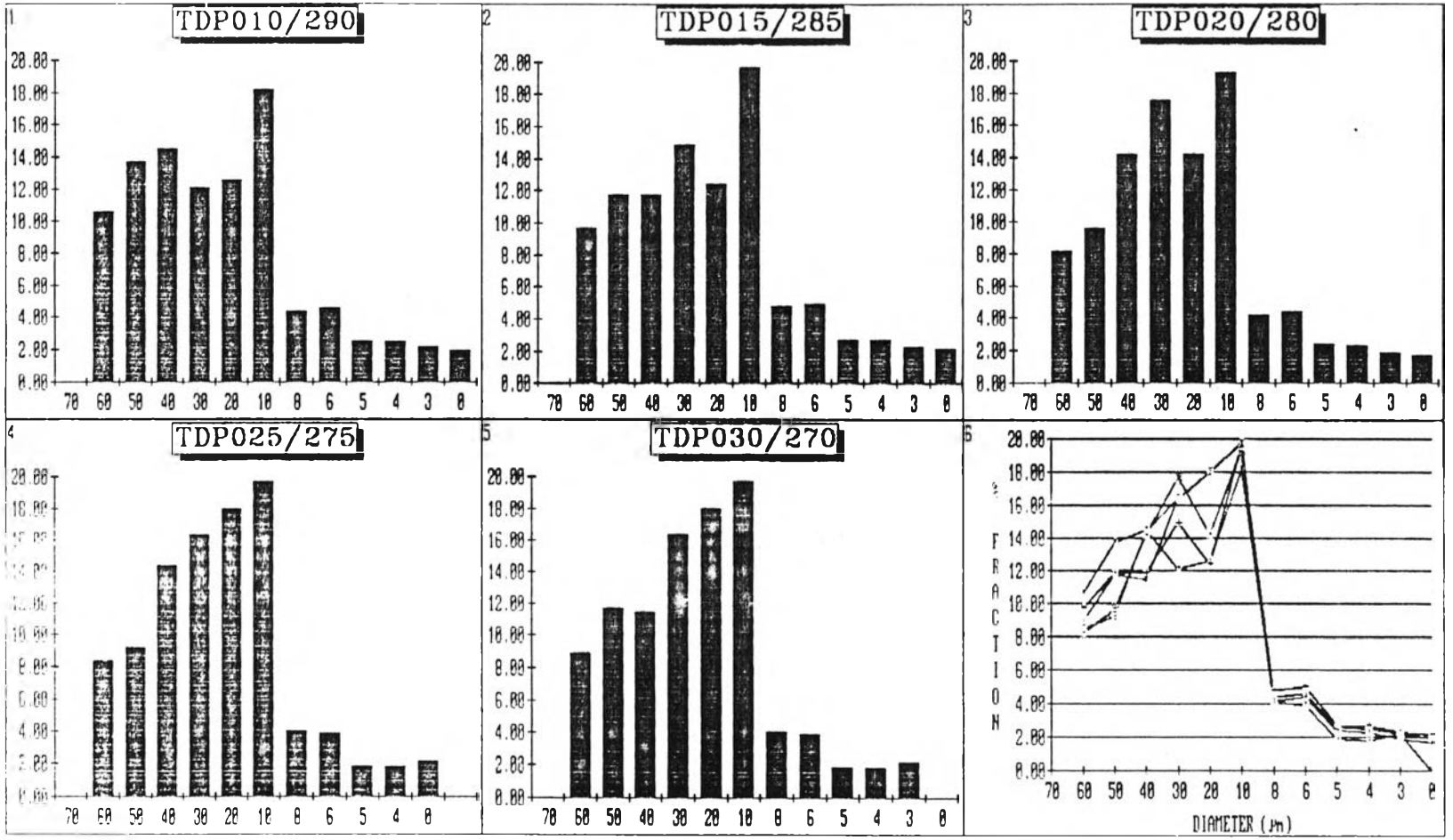
Photomicrograph series 18 Photomicrographs of TDP010/290-TDP030/270. Effect of ratio of the diacid chloride/encapsulated oil on microencapsulation : Poly(para-phenylene terephthalamide) as polymeric microcapsule shell; dibutyl phthalate as encapsulated material; the propeller speed and homogenizing time fixed at 6,000 rpm. and for 90 sec. respectively; the concentration of poly(vinyl alcohol), as emulsifier, at 7.5 % of the total oil phase. A Zeiss optical microscope was used to take the photomicrographs with magnification of 100 times. The prints were enlarged 2.5 times.



Graph series 29 Histogram of Particle Size Distribution of SDP010/290-SDP050/250.

(The graphs were made from the data from Tables 93-1 - 93-5)

Effect of sebacoyl chloride : dibutyl phthalate ratio from 1:29, 2:28, 3:27, 4:26 and 5:25 on particle size distribution of dibutyl phthalate encapsulated by poly(hexamethylene sebacamide) microcapsules when fixing the propeller speed at 6,000 rpm., homogenizing time for 90 sec. and poly(vinyl alcohol) concentration at 7.5 % of the total oil phase .



Graph series 30 Histogram of Particle Size Distribution of TDP010/290-TDP030/270.

(The graphs were made from the data from Tables 95-1 - 95-5)

Effect of terephthaloyl chloride : dibutyl phthalate ratio from 1.0:29.0, 1.5:28.5, 2.0:28.0, 2.5:27.5 and 3.0:27.0 on particle size distribution of dibutyl phthalate encapsulated by poly(para-phenylene terephthalamide) microcapsules when fixing the propeller speed at 6,000 rpm., homogenizing time for 90 sec. and poly(vinyl alcohol) concentration at 7.5 % of the total oil phase.

microcapsules but it did change microencapsulation efficiency. Increasing the diacid chloride concentrations produced the thick and strong polyamide film which could completely encapsulate the droplets of dibutyl phthalate. Poly(hexamethylene sebacamide) as microcapsule shell was more capable in terms of encapsulation than was poly(para-phenylene terephthalamide) because of the rigidity and brittleness of the latter.

Table 54 Average Diameter and % Unencapsulated Oil of SDP010/290-SDP050/250.

Dibutyl Phthalate Encapsulated by Poly(hexamethylene sebacamide) Microcapsules Using Various Concentrations of Sebacoyl Chloride.

Assigned Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
SDP010/290	25.14	6.74
SDP020/280	23.71	5.36
SDP030/270	24.51	3.67
SDP040/260	23.77	2.79
SDP050/250	23.80	1.84

Table 55 Average Diameter and % Unencapsulated Oil of TP010/290-TP03/270.

Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules Using Various Concentrations of Terephthaloyl Chloride.

Assigned Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
TDP010/290	32.15	8.63
TDP015/285	30.54	5.29

Table 55 Average Diameter and % Unencapsulated Oil of TP010/290-TP03/270.

Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules Using Various Concentrations of Terephthaloyl Chloride.

Assigned Name	Average Diameter of Microcapsules (μm)	% Unencapsulated Dibutyl Phthalate
TDP020/280	30.62	3.88
TDP025/275	31.10	2.79
TDP030/270	31.45	2.08

2.11.5) Conclusions

Of all concentrations of the diacid chloride, increasing the concentration of diacid chloride increased microencapsulation efficiency and the microcapsule's shell which a new polymer formed during the polycondensation became thicker accordingly. However the average particle size of the microcapsules was not affected by the influences of the diacid chloride concentration.

2.12) COMBINATION OF PROTECTIVE COLLOID AND SURFACE ACTIVE AGENT FORMULATION

2.12.1) Purpose

To study the combination effect of the protective colloid in the presence of surface active agent which affects the synthesis and the properties of microcapsule. Poly(vinyl alcohol) and sodium dodecyl benzene sulfonate were selected because of their non-coagulation nature.

2.12.2) Synthesis Method

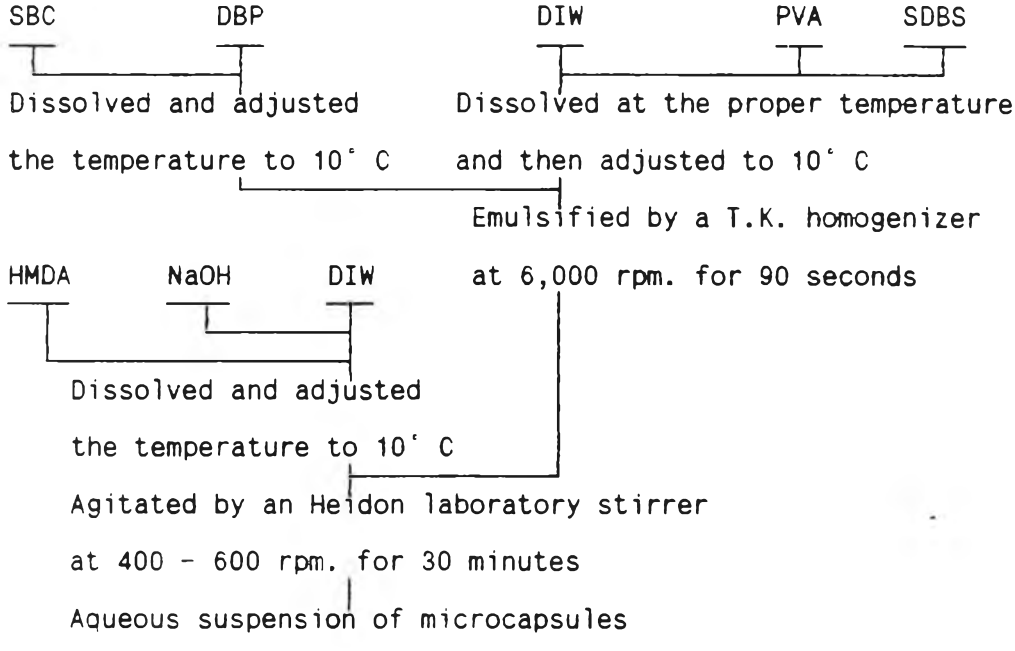
The stock solutions of the diacid chloride, emulsifier and diamine were prepared and kept in a water bath so as to control the temperature at 10°C in case of sebacoyl chloride and 30°C for terephthaloyl chloride. 210.0 gm. of the emulsifier solution and 90.0 gm. of the diacid chloride solution were poured into a T.K. homogenizer vessel. The mixture was homogenized at the propeller speed and homogenizing time which were set as shown in the Tree Diagram 7 to form oil-in-water emulsion. The emulsion was then poured into a 500 ml. beaker containing 200.0 gm. of the diamine solution under continuous stirring with an Heidon laboratory stirrer at 400 - 600 rpm of the propeller speed. Microencapsulation was formed through interfacial polycondensation at the interface of the diacid chloride solution and the diamine solution which contained the emulsifier solution as stabilizer.

2.12.2.1) PVA/SDBS in Sebacoyl Chloride

For the formulation of SD-PVSD75/20, 6.75 gm. of poly(vinyl alcohol) and 5.14 gm. of sodium dodecyl benzene sulfonate were dissolved in 198.11 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 10°C and kept in water bath so as to control the temperature. To prepare the diacid chloride solution, 9.28 gm. of sebacoyl chloride was dissolved in 80.72 gm. of dibutyl phthalate at room temperature and kept in the water bath to control the temperature at 10°C. Likewise for the diamine solution, 4.50 gm. of hexamethylene diamine and 3.01 gm. of sodium hydroxide were added into a 500 ml. beaker containing 192.49 gm. of deionized water at room temperature and then adjusted the temperature to 10°C. The diamine solution was stirred with an Heidon laboratory stirrer at 400 - 600 rpm. of the propeller

speed. The emulsion was prepared by homogenizing the mixture of the diacid chloride and the emulsifier solutions at the propeller speed and homogenizing time which were shown in the Tree Diagram 7. This emulsion was then poured into the diamine solution and continuously agitated for 30 minutes to form poly(hexamethylene sebacamide) microcapsules encapsulating dibutyl phthalate. The other formulations as follows in the Table 56 were prepared in the same method.

Flow Chart 15 Synthesis Method of SBC for Studying Effect of Emulsifier Combination.

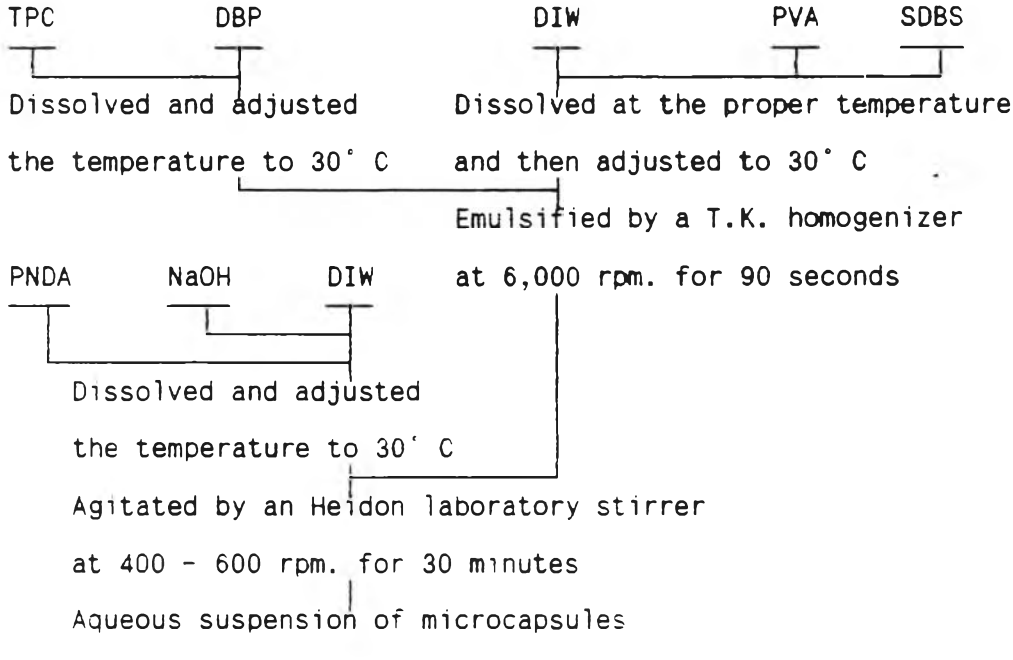


2.12.2.2) PVA/SDBS in Terephthaloyl Chloride

For the formulation of TD-PVSD75/20, 6.75 gm. of poly(vinyl alcohol) and 5.14 gm. of sodium dodecyl benzene sulfonate were dissolved in 198.11 gm. of deionized water at the temperature of 80°C for 60 minutes then this emulsifier solution was cooled down to 30°C and kept in a water bath to control the temperature. To prepare diacid chloride solution, 6.06 gm. of terephthaloyl chloride was dissolved in 83.94 gm. of dibutyl phthalate at room temperature and kept in the water bath to control the temperature at 30°C. Likewise for

the diamine solution, 3.29 gm. of para-phenylene diamine and 2.37 gm. of sodium hydroxide were added into a 500 ml. beaker containing 194.34 gm. of deionized water, was prepared at room temperature and then adjusted the temperature to 30°C. The diamine solution was stirred by an Heidon laboratory stirrer at 400 - 600 rpm. of propeller speed. The emulsion was prepared by homogenizing the mixture of the diacid chloride and the emulsifier solutions at the propeller speed and homogenized time which were shown in the Tree Diagram 7. This emulsion was poured into the diamine solution and continuously agitated for 30 minutes to form poly(para-phenylene terephthalamide) microcapsules encapsulating dibutyl phthalate. The other formulations as follows in the Table 57 were prepared in the same method.

Flow Chart 16 Synthesis Method of TPC for Studying Effect of Emulsifier Combination.



Tree Diagram 7 Effect of Emulsifier Combination on Microencapsulation.

Monomer	Oil	Emulsifier PVA/SDBS	Speed rpm.	Time sec.	Assigned Name
SBC + HMDA	DBP	7.5/1.0	6,000	90	SD-PVSD75/10
		7.5/2.0	6,000	90	SD-PVSD75/20
		7.5/3.0	6,000	90	SD-PVSD75/30
TPC + PNDA	DBP	7.5/1.0	6,000	90	TD-PVSD75/10
		7.5/2.0	6,000	90	TD-PVSD75/20
		7.5/3.0	6,000	90	TD-PVSD75/30

Table 56 Formulation of SD-PVSD75/10, SD-PVSD75/20 and SD-PVSD75/30. Effect of Protective Colloid and Surface Active Agent Combination on Dibutyl Phthalate Encapsulated by Poly(hexamethylene sebacamide) Microcapsules.

Name / Chemicals	SD-PVSD75/10 (gm.)	SD-PVSD75/20 (gm.)	SD-PVSD75/30 (gm.)
SBC	9.28	9.28	9.28
DBP	80.72	80.72	80.72
PVA	6.75	6.75	6.75
SDBS	2.57	5.14	7.71
DIW	200.68	198.11	195.54
HMDA	4.50	4.50	4.50
NaOH	3.01	3.01	3.01
DIW	192.49	192.49	192.49

Table 57 Formulation of TD-PVSD75/10, TD-PVSD75/20 and TD-PVSD75/30. Effect of Protective Colloid and Surface Active Agent Combination on Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules.

Name / Chemicals	TD-PVSD75/10 (gm.)	TD-PVSD75/20 (gm.)	TD-PVSD75/30 (gm.)
TPC	6.06	6.06	6.06
DBP	83.94	83.94	83.94
PVA	6.75	6.75	6.75
SDBS	2.57	5.14	7.71
DIW	200.68	198.11	195.54
PNDA	3.29	3.29	3.29
NaOH	2.37	2.37	2.37
DIW	194.34	194.34	194.34

2.12.3) Analysis Methods

General appearances of the microcapsules were evaluated by visual assessment; volume of separation after keeping for 24 hours was measured in a 100 ml. cylinder; microscopic properties were examined by a Zeiss optical microscope and a Joel scanning electron microscope; average particle size and particle size distribution was measured by a Shimadzu particle size analyzer and the microencapsulation efficiency was analyzed by a Shimadzu gas chromatograph. The details of each methods were explained in the previous experiments.

2.12.4) Results

2.12.4.1) General Properties

The effect of sodium dodecyl benzene sulfonate on the amount of sediment and visualized appearances are showed in Tables 58 and 59 as follows :-

Table 58 Separation and Appearance of SD-PVSD Series.
Effect of Concentration of Sodium Dodecyl Benzene Sulfonate in the Presence of Poly(vinyl alcohol) on Microencapsulation of Dibutyl Phthalate Encapsulated by Poly(hexamethylene sebacamide) Microcapsules.

Assigned Name	Separation after 24 hours	Appearances by Visual Evaluation
SD-PVSD75/00	5 ml.	milky white emulsion and uniform
SD-PVSD75/10	0 ml.	milky white emulsion and uniform
SD-PVSD75/20	0 ml.	milky white emulsion and uniform
SD-PVSD75/30	0 ml.	milky white emulsion and uniform

Table 59 Separation and Appearance of TD-PVSD Series.
Effect of Concentration of Sodium Dodecyl Benzene Sulfonate in the Presence of Poly(vinyl alcohol) on Microencapsulation of Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules.

Assigned Name	Separation after 24 hours	Appearances by Visual Evaluation
TD-PVSD75/00	7 ml.	milky brown emulsion and uniform
TD-PVSD75/10	1 ml.	milky brown emulsion and uniform

Table 59 Separation and Appearance of TD-PVSD Series.
Effect of Concentration of Sodium Dodecyl Benzene Sulfonate in the Presence of Poly(vinyl alcohol) on Microencapsulation of Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules.

Assigned Name	Separation after 24 hours	Appearances by Visual Evaluation
TD-PVSD75/20	0 ml.	milky brown emulsion and uniform
TD-PVSD75/30	0 ml.	milky brown emulsion and uniform

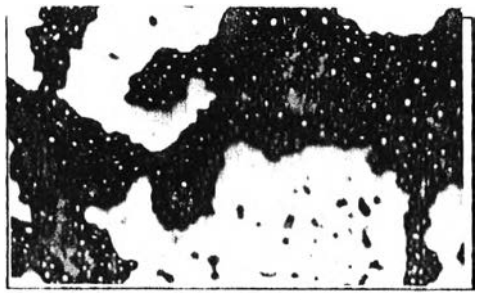
2.12.4.2) Microscopic Properties

Photomicrograph series 19 and 20 show the effects of the concentration of sodium dodecyl benzene sulfonate on microscopic properties.

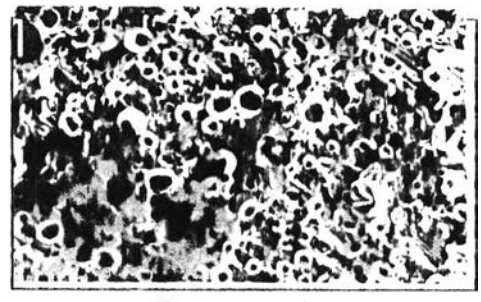
2.12.4.3) Particle Size Distribution

1) Graph series 31 shows the results of poly(hexamethylene sebacamide) microcapsules. Graph series 32 shows the results of poly(para-phenylene terephthalamide) microcapsules. The results of these are of different pattern in histogram compared to those obtained from the system without the addition of sodium dodecyl benzene sulfonate.

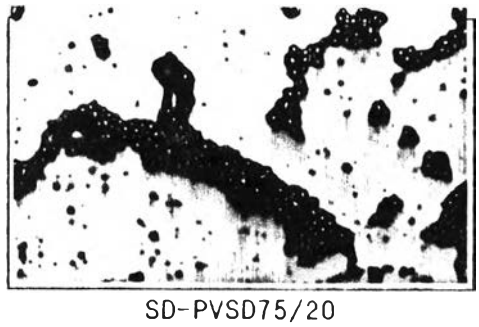
2) From Appendix III, Tables 97 and 98 show that increasing the concentration of sodium dodecyl benzene sulfonate shifts the particle size distribution and average particle size to the smaller size. The results are in the same trends for both poly(hexamethylene sebacamide) and poly(para-phenylene terephthalamide) microcapsules.



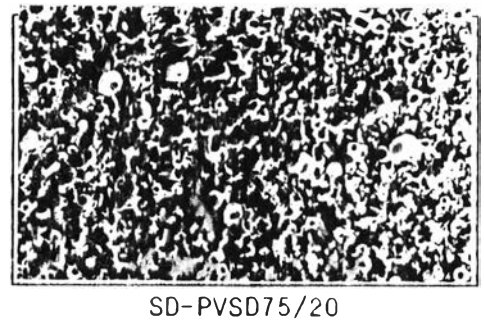
SD-PVSD75/10



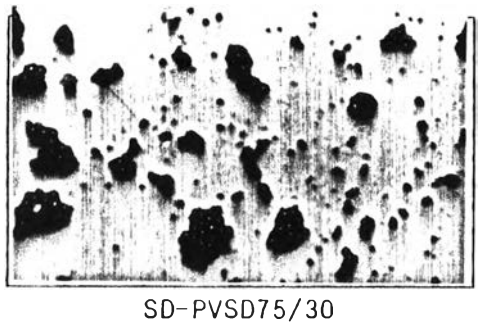
SD-PVSD75/10



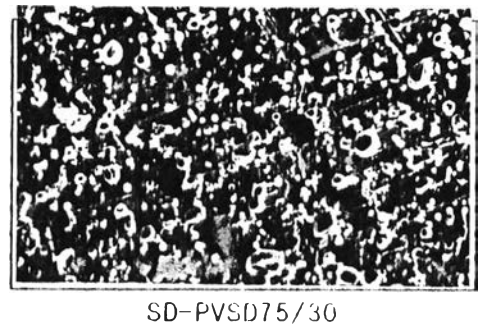
SD-PVSD75/20



SD-PVSD75/20

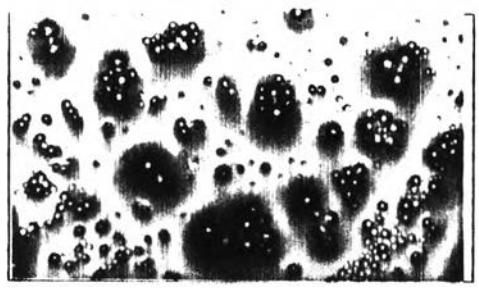


SD-PVSD75/30



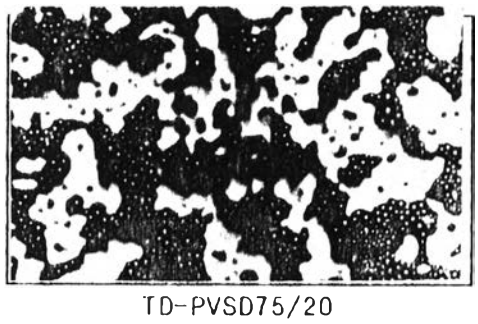
SD-PVSD75/30

Photomicrograph series 19 Photomicrographs of SD-PVSD75/10~SD-PVSD75/30. Effect of protective colloid and surface active agent on encapsulated dibutyl phthalate by poly(hexamethylene sebacamide): Poly(hexamethylene sebacamide) as polymeric microcapsule shell, dibutyl phthalate as encapsulated material, the propeller speed and homogenizing time fixed at 6,000 rpm. and for 90 sec., respectively, the concentration of poly(vinyl alcohol) at 7.5% as emulsifier and the concentration of sodium dodecyl benzene sulfonate at 1.0, 2.0 and 3.0% of the total oil phase. Photomicrographs at the left were taken from the Zeiss optical microscope with 250 times magnification and prints enlargement of 2.5 times while those at the right were from the Joel scanning electron microscope.

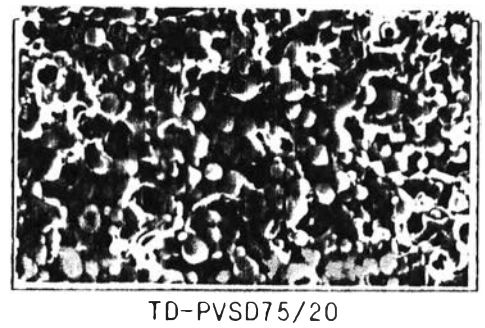


TD-PVSD75/10

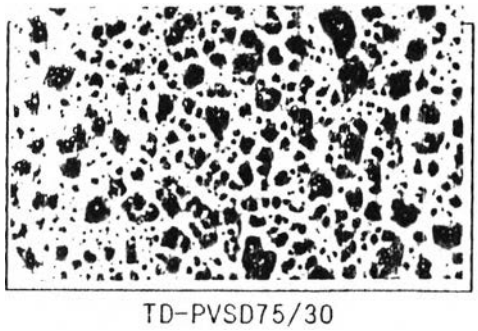
TD-PVSD75/10



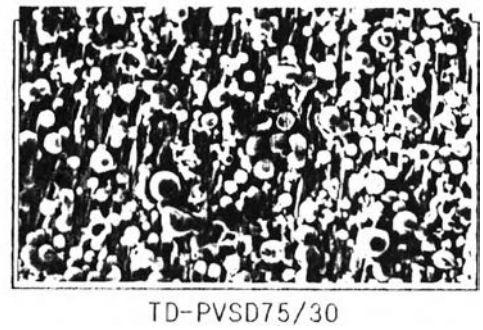
TD-PVSD75/20



TD-PVSD75/20

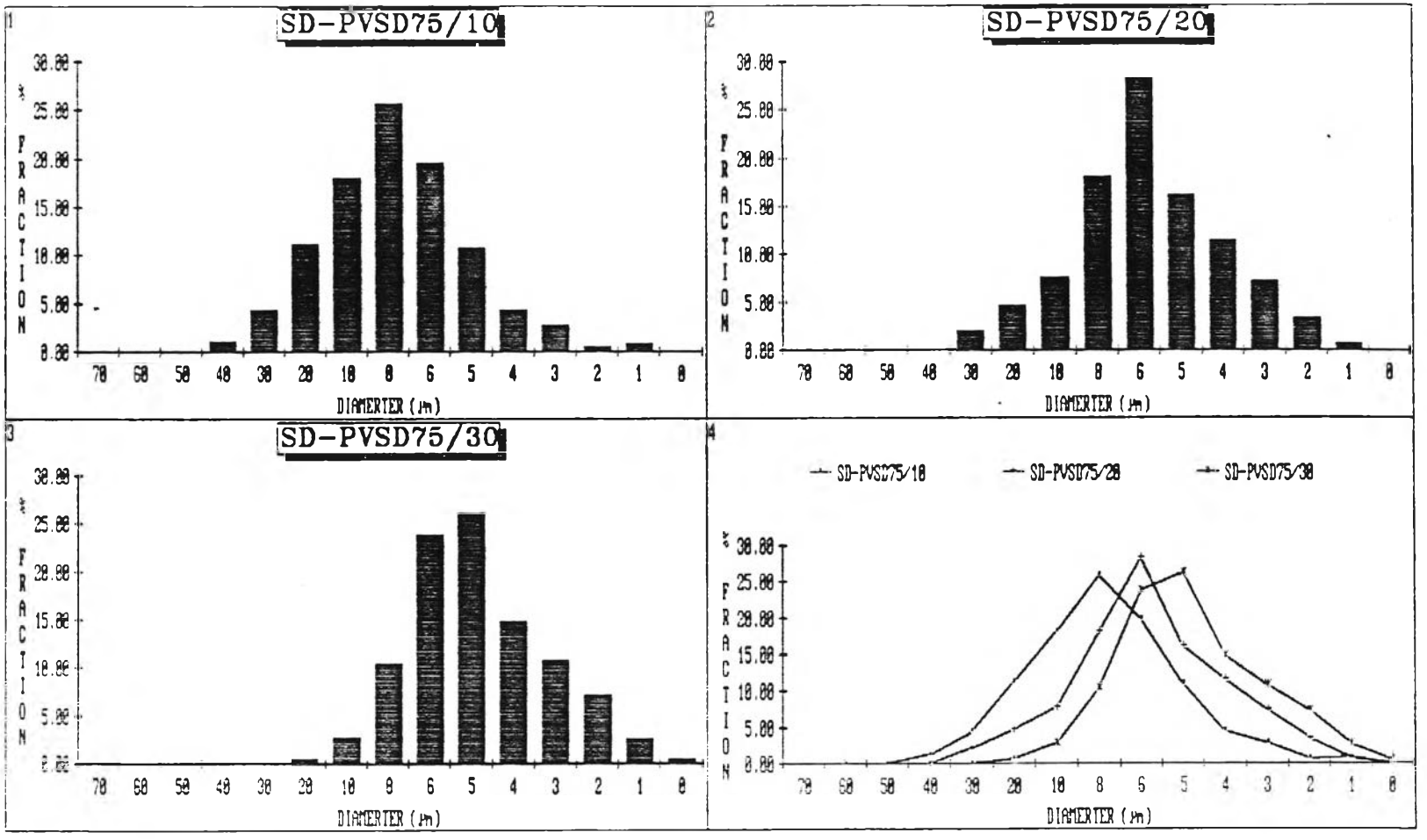


TD-PVSD75/30



TD-PVSD75/30

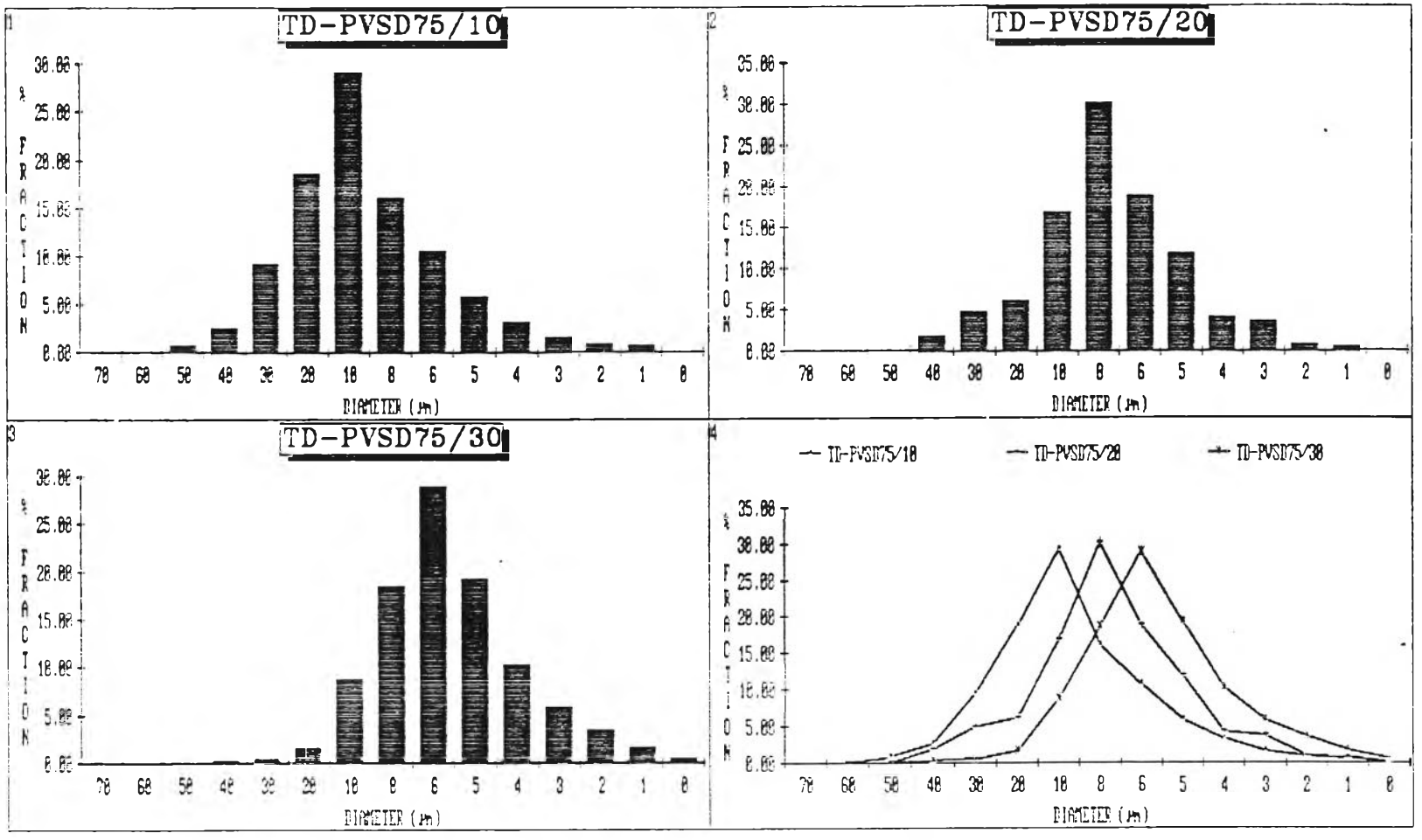
Photomicrograph series 20 Photomicrographs of TD-PVSD75/10~TD-PVSD75/30. Effect of protective colloid and surface active agent on encapsulated dibutyl phthalate by poly(para-phenylene terephthalamide): Poly(para-phenylene terephthalamide) as polymeric microcapsule shell, dibutyl phthalate as encapsulated material, the propeller speed and homogenizing time fixed at 6,000 rpm. and for 90 sec., respectively, the concentration of poly(vinyl alcohol) at 7.5% as emulsifier and the concentration of sodium dodecyl benzene sulfonate at 1.0, 2.0 and 3.0% of the total oil phase. Photomicrographs at the left were taken from the Zeiss optical microscope with 250 times magnification and prints enlargement of 2.5 times while those at the right were from the Joel scanning electron microscope.



Graph series 31 Histogram of Particle Size Distribution of SD-PVSD75/10~SD-PVSD75/30.

(The graphs were made from the data from Tables 97-1 - 97-3)

Effect of sodium dodecyl benzene sulfonate concentration varied from 1.0, 2.0 and 3.0 % combinating with 7.5 % of poly(vinyl alcohol) as emulsifier of the total oil phase when fixing propeller speed at 6,000 rpm. and homogenization time at 90 sec. on particle size distribution of dibutyl phthalate encapsulating poly(hexamethylene sebacamide) microcapsules.



Graph series 32 Histogram of Particle Size Distribution of TD-PVSD75/10~TD-PVSD75/30.

(The graphs were made from the data from Tables 98-1 - 98-3)

Effect of sodium dodecyl benzene sulfonate concentration varied from 1.0, 2.0 and 3.0 % combinating with 7.5 % of poly(vinyl alcohol) as emulsifier of the total oil phase when fixing propeller speed at 6,000 rpm. and homogenization time at 90 sec. on particle size distribution of dibutyl phthalate encapsulating poly(para-phenylene terephthalamide) microcapsules.

2.12.4.4) Average Particle Size and Encapsulation Efficiency

Tables 60 and 61 show that increasing the concentrations of sodium dodecyl benzene sulfonate decrease the average size of polyamide microcapsules but at high concentration of sodium dodecyl benzene sulfonate, the microencapsulation efficiency decrease.

Table 60 Average Diameter and % Unencapsulated Oil Of SD-PVSD Series. Effect of the Concentration of Sodium Dodecyl Benzene Sulfonate in the Presence of Poly(vinyl alcohol) on Dibutyl Phthalate Encapsulated by Poly(hexamethylene sebacamide) Microcapsules.

Assigned Name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
SD-PVSD75/00	21.00	1.34
SD-PVSD75/10	12.22	1.06
SD-PVSD75/20	8.43	4.98
SD-PVSD75/30	5.88	11.67

Table 61 Average Diameter and % Unencapsulated Oil Of TD-PVSD Series. Effect of the Concentration of Sodium Dodecyl Benzene Sulfonate in the Presence of Poly(vinyl alcohol) on Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules.

Assigned Name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
TD-PVSD75/00	23.40	2.94
TD-PVSD75/10	16.72	2.17

Table 61 Average Diameter and % Unencapsulated Oil Of TD-PVSD Series. Effect of the Concentration of Sodium Dodecyl Benzene Sulfonate in the Presence of Poly(vinyl alcohol) on Dibutyl Phthalate Encapsulated by Poly(para-phenylene terephthalamide) Microcapsules.

Assigned Name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
TD-PVSD75/20	11.65	9.29
TD-PVSD75/30	7.57	13.85

2.12.5) Conclusions

Increasing the amount of sodium dodecyl benzene sulfonate reduces the average particle size diameter and gives more uniformity of particle diameters. The high concentrations of sodium dodecyl benzene sulfonate decrease accordingly the microencapsulation efficiency.

2.13) EFFECT OF THE APPROPRIATE MONOMER PAIRS ON MICROENCAPSULATION

2.13.1) Purpose

To study the effect of different monomer pairs, by altering the conventional counter monomer containing diamine moiety, on microencapsulation via polycondensation.

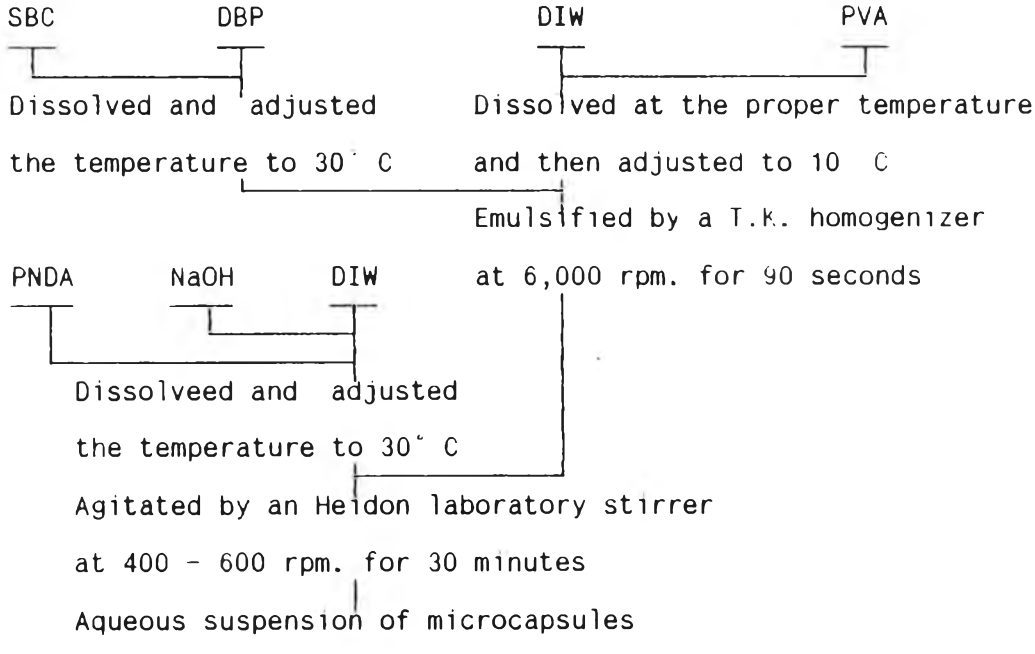
2.13.2) Synthesis Method

The stock solutions of diacid chloride and diamine were prepared as follows in Table 92 and they were kept in water bath to control the temperature at 30°C. 210.0 gm. of poly(vinyl alcohol) solution at 30°C and 90.0 gm. of diacid chloride solution were

subsequently poured into a T.K. homogenizer vessel. The mixture was then homogenized at 6,000 rpm. of the propeller speed and 90 sec. of the homogenizing time which showed in Tree Diagram 8 to form oil in water emulsion. The emulsion was poured into a 500 ml. beaker containing 200.0 gm. of diamine solution under stirring by an Heidon laboratory stirrer at 400 - 600 rpm of the propeller speed. Flow Charts 17, 18 and 19 were prepared to elucidate the effect of the appropriate monomer pairs on microencapsulation. Microencapsulation was formed though by interfacial polycondensation at the interface of the diacid chloride droplets and the diamine solution which have an emulsifier as stabilizer.

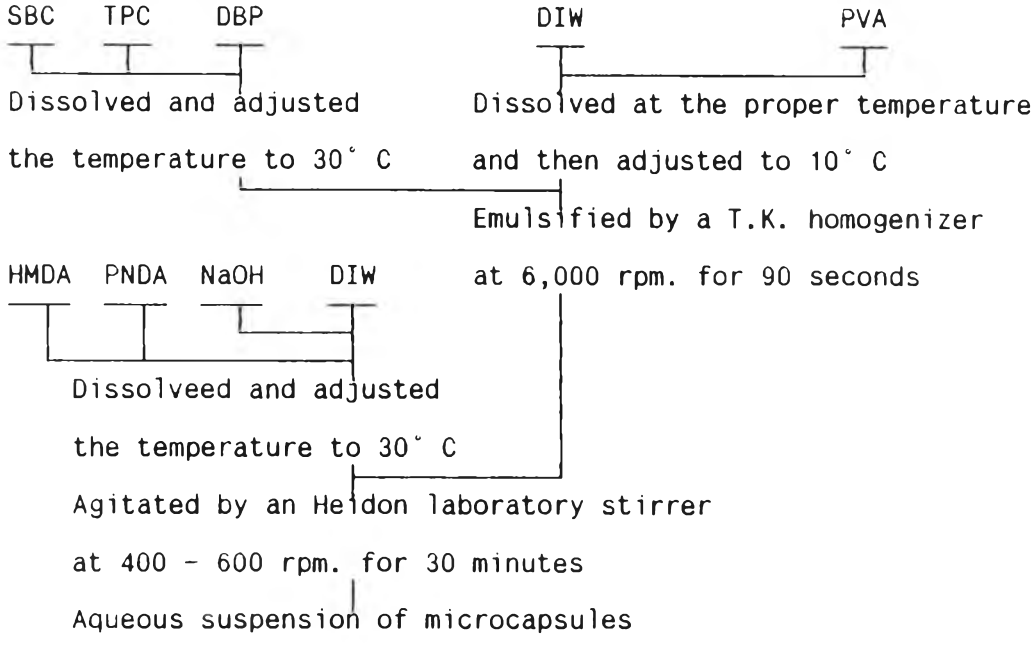
2.13.2.1) SBC/PNDA Pair

Flow Chart 17 Synthesis Method of SBC/PNDA Monomer Pair.



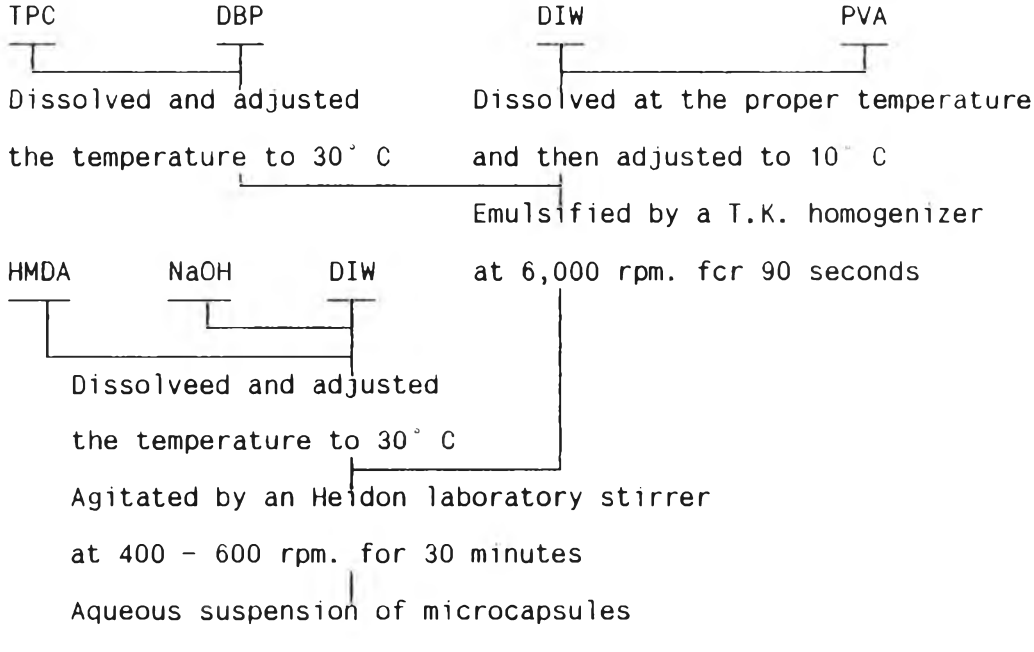
2.13.2.2) STC/HMPN Pair

Flow Chart 18 Synthesis Method of STC/HMPN Monomer Pair.



2.13.2.3) TPC/HMDA Pair

Flow Chart 19 Synthesis Method of TPC/HMDA Monomer Pair.



Tree Diagram 8 Monomer Pairs for the Encapsulation of Dibutyl Phthalate by Polyamide Microcapsules Using Poly(vinyl alcohol) as Emulsifier.

Monomer	Oil	Emulsifier	Speed rpm.	Time sec.	Assigned Name
SBC + PNDA	DBP	PVA	6,000	90	SBC/PNDA
SBC+TPC + HMDA+PNDA	DBP	PVA	6,000	90	STC/HMPN
TPC + HMDA	DBP	PVA	6,000	90	TPC/HMDA

Table 62 Formulations of the Studied Monomer Pairs.

Assigned Name / Chemicals	SBC/PNDA (gm.)	STC/HMPN (gm.)	TPC/HMDA (gm.)
SBC	9.28	6.19	-.--
TPC	-.--	3.03	6.06
DBP	80.72	80.78	83.94
PVA	6.75	6.75	6.75
DIW	203.25	203.25	203.25
HMDA	-.--	3.01	3.55
PNDA	4.19	1.65	-.--
NaOH	3.01	3.19	2.37
DIW	192.49	192.15	194.34

2.13.3) Analysis Method

All the analysis methods were discussed in the earlier experiments.

2.13.4) Results

2.13.4.1) General Properties

Table 63 Effect of Monomer Pairs on Visual Appearance in Microencapsulation of Dibutyl Phthalate.

Assigned Name	Separation after 24 hours	Appearance by Visual Evaluation
SBC/PNDA	1.5 ml.	milky brown emulsion and uniform
STC/HMPN	1.0 ml.	milky yellow emulsion and uniform
TPC/HMDA	2.0 ml.	milky white emulsion and uniform

2.13.4.2) Microscopic Properties

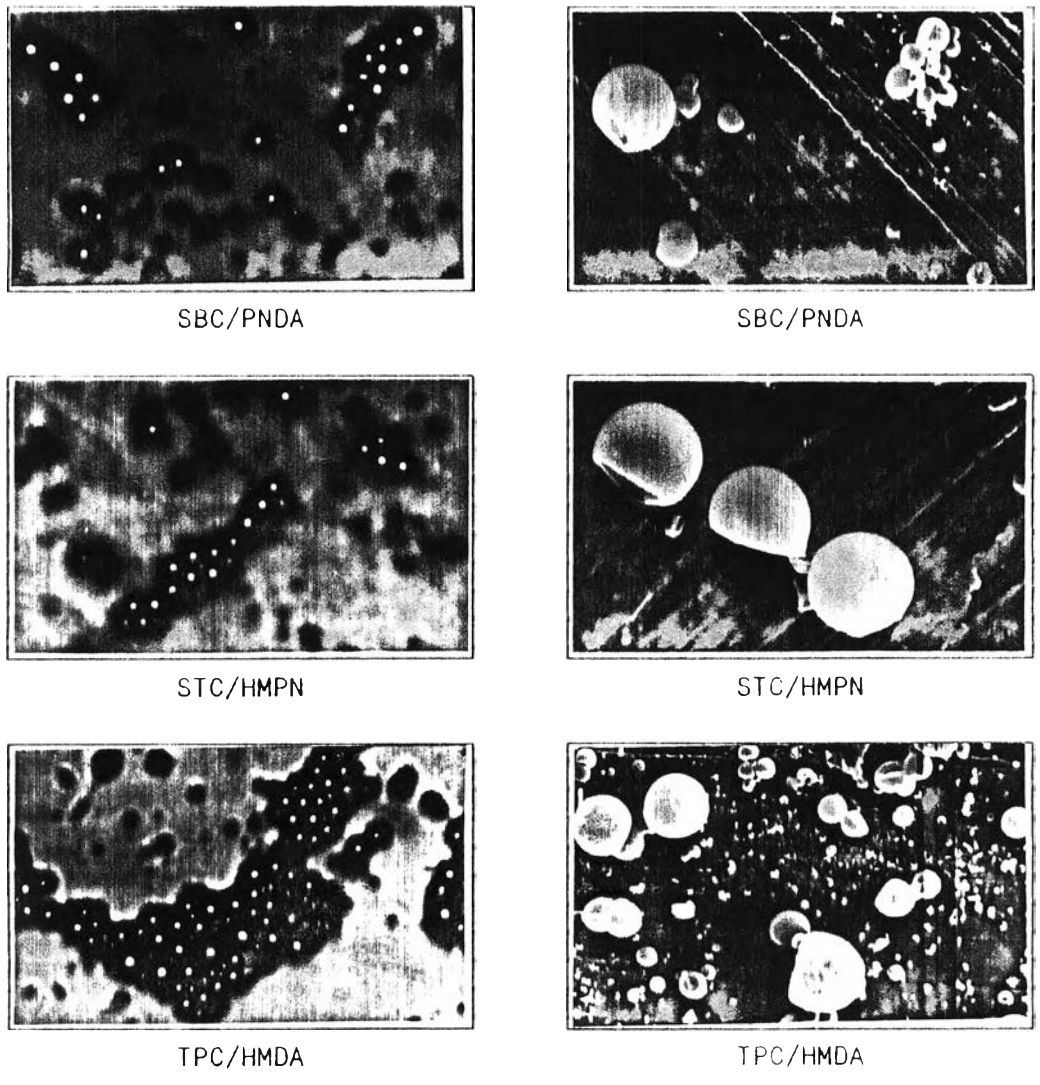
Photomicrograph series 21 showed the microscopic properties, the details of which were depicted and explained in the respective photomicrographs.

2.13.4.3) Particle Size Distribution

Graph series 33 and Table series 99 in Appendix III show the histogram of particle size distribution and average particle size of polyamide microcapsules. Each monomer pair has an individual average particle size and a specific pattern of histogram.

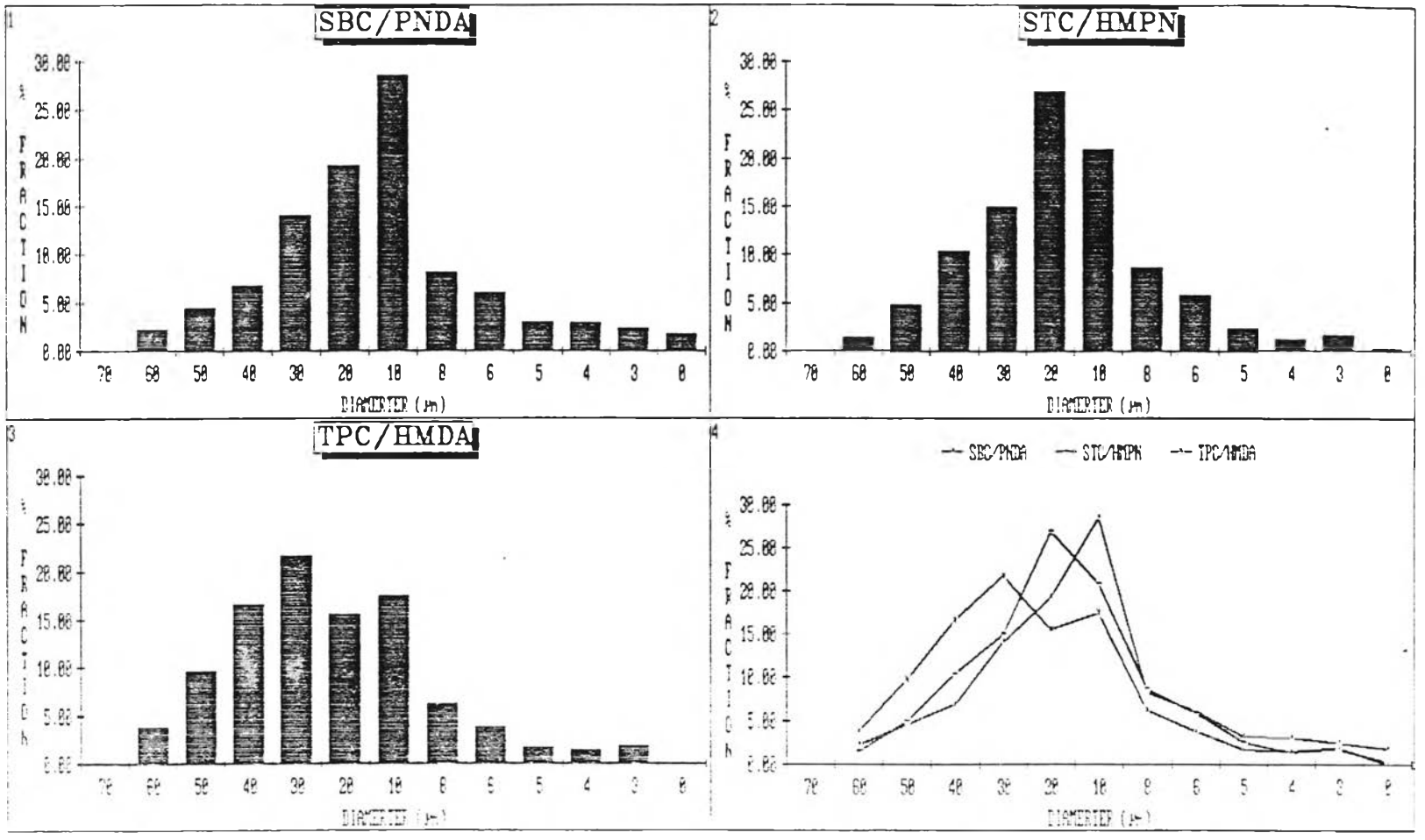
2.13.4.4) Average Particle Size and Encapsulation Efficiency

Table 64 show the average particle size and microencapsulation efficiency of polyamide microcapsules.



Photomicrograph series 21 Photomicrographs of SBC/PNDA, STC/HMPN and TPC/HMDA.

Effect of the appropriate monomer pairs on microcapsulation of poly amides. The types of monomer pairs are specified in each micrograph; dibutyl phthalate as encapsulated material while 7.5 % poly(vinyl alcohol) as emulsifiers, the propeller speed at 6,000 rpm. and the homogenizing time at 90 sec. The photomicrographs on the left-hand side were taken by a Zeiss optical microscope under 250 times magnification from which the prints were enlarged 2.5 times. The prints on the right-hand side were taken by Joel scanning electron microscope under 500 times magnification.



Graph series 33 Histogram of Particle Size Distribution of SBC/PNDA, STC/HMPN and TPC/HMDA.

(The graphs were made from the data from Tables 99-1 - 99-3)

Effect of the monomer pairs on particle size distribution of dibutyl phthalate encapsulated by polyamide microcapsules. The conditions were fixed at 7.5 % poly(vinyl alcohol) as emulsifier, 6,000 rpm. propeller speed and 90 sec. homogenizing time.

Table 64 Effect of Monomer Pairs on Average Diameter and Efficiency of Microencapsulation of Dibutyl Phthalate.

Assigned Name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
SBC/PNDA	22.58	1.78
STC/HMPN	24.92	1.26
TPC/HMDA	30.45	1.84

2.13.5) Conclusions

It is evidenced that one can use the appropriate monomer pair, the diacid chlorides and the diamines, for the synthesis of microcapsules which are condensation polymers such as polyamide in this case. Other classes of monomers should be carefully selected in terms of factors mentioned in the previous sections. Considering the case of using terephthaloyl chloride, average particle diameter is somewhat bigger than of sebacoyl chloride.

2.14) OVERALL OPTIMIZATION OF THE SYSTEM

2.14.1) Purpose

Based on the results concluded from all previous experiment, the optimal conditions were used to synthesize the microcapsules. This experiment was carried out so as to check the validity and effectiveness of the conditions obtained from above mentioned experiments.

2.14.2) Synthesis Method

The stock solutions of the diacid chloride, emulsifier and diamine were prepared by dissolving 6.19 gm. of sebacoyl chloride

and 3.03 gm. of terephthaloyl chloride in 80.78 gm. of dibutyl phthalate as oil phase; 6.75 gm. of poly(vinyl alcohol) and 2.57 gm. of sodium dodecyl benzene sulfonate in 200.68 gm. of deionized water at 80 C for 60 min. as emulsifier phase and 3.01 gm. of hexamethylene diamine, 1.65 gm. of para-phenylene diamine and 3.19 gm. of sodium hydroxide in 192.15 gm. of deionized water as aqueous phase. The oil and diamine phases were kept in a water bath to control the temperature at 30 C; and at 10 C. for the emulsifier phase. 210.0 gm. of emulsifier solution and 90.0 gm. of the diacid chloride solution were poured into a T.K. homogenizer vessel. The mixture was homogenized at 8,000 rpm. of propeller speed and 90 sec. of homogenizing time. to form oil-in-water emulsion. The emulsion was poured into a 500 ml. beaker containing 200.0 gm. of the diamine solution being stirred with an Heidon laboratory stirrer at 400 - 600 rpm of propeller speed. Microencapsulation occurred by interfacial polycondensation at the interface of the diacid chloride droplets and the diamine solution which contained the emulsifier solution as stabilizer.

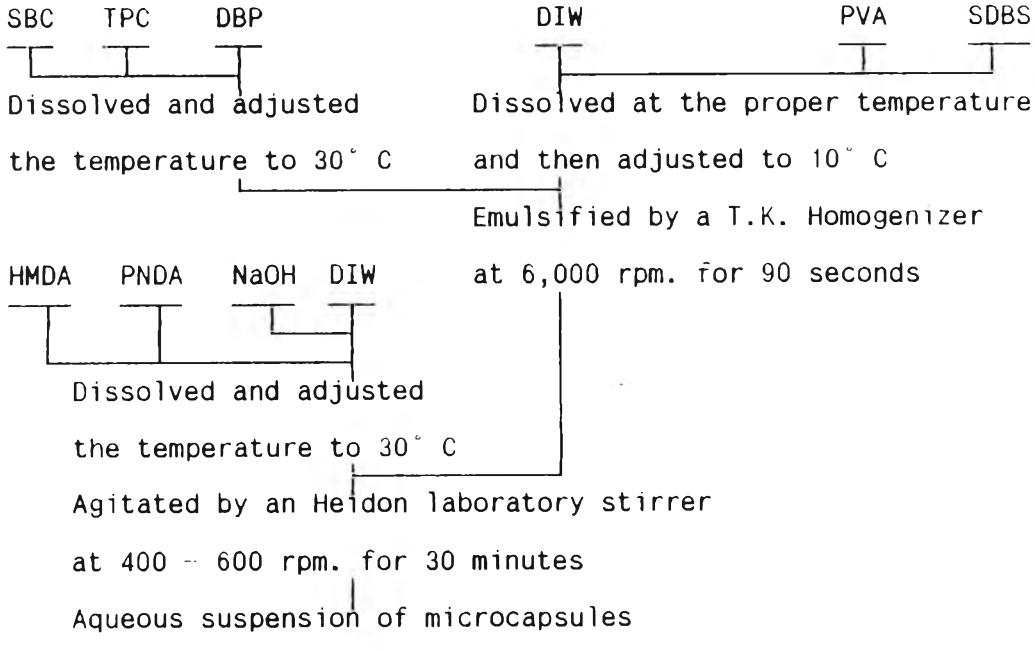
Table 65 Overall Optimization Formulation for the Synthesis of Polyamide Microcapsules.

Chemical Name	Code Name	Quantity (gm)
Sebacoyl chloride	SBC	6.19
Terephthaloyl chloride	TPC	3.03
Dibutyl phthalate	DBP	80.78
Poly(vinyl alcohol)	PVA	6.75
Sodium dodecyl benzene sulfonate	SDBS	2.57
Deionized water	DIW	200.68

Table 65 Overall Optimization Formulation for the Synthesis of Polyamide Microcapsules.

Chemical Name	Code Name	Quantity (gm)
Hexametylene diamine	HMDA	3.01
Para-phenylene diamine	PNDA	1.65
Sodium hydroxide	NaOH	3.19
Deionized water	DIW	192.15

Flow Chart 20 Optimization of Synthesis Method of Polyamide Microcapsules.



2.14.3) Analysis Method

The same analytical techniques were used to evaluate the results as mentioned in the previous experiments.

2.14.4) Results

2.14.4.1) General Properties

Table 66 Visual Evaluation of the Polyamide Microcapsules.

Assigned Name	Separation after 24 hours	Appearance by Visual Evaluation
STC/HMPN/PVSD	0 ml.	milky yellow emulsion and uniform

2.14.4.2) Microscopic Properties

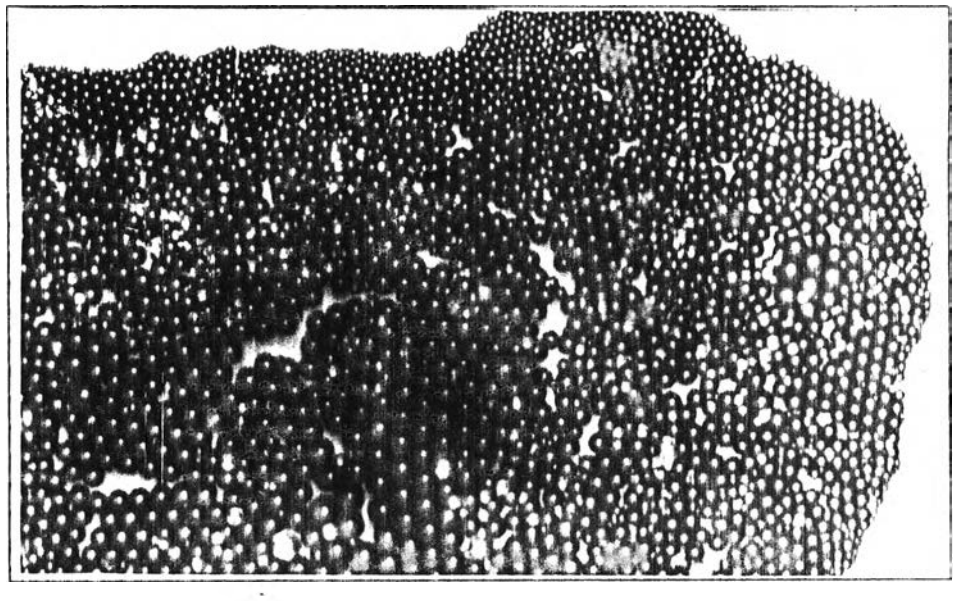
Photomicrograph series 22 show the polyamide microcapsules which have very spherical and perfect shape. The wrinkle and broken microcapsules problem that found in the previous experiment was solved.

2.14.4.3) Particle Size Distribution

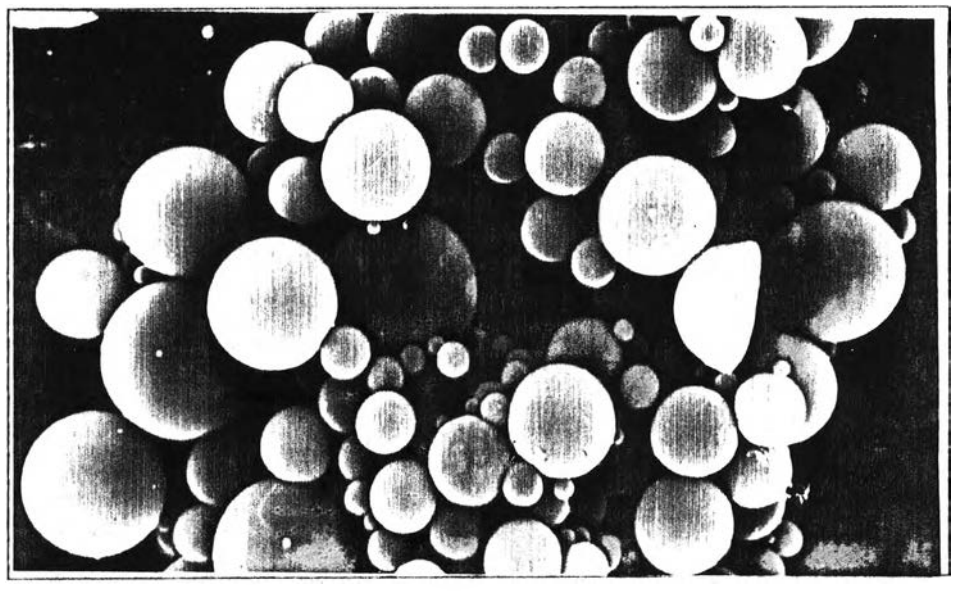
Table 67 and Graph series 33 show the size distribution of polyamide microcapsules.

Table 67 Average Diameter and Particle Size Distribution of STC/HMPN/PVSD.

Diameter (μm) Micrometer	Average Diameter	Percentage Cumulative	Percentage Different	Diameter Coefficient
70.00	*.**	0.0	0.00	0.00
60.00	65.00	0.0	0.00	0.00
50.00	55.00	0.8	0.80	44.00
40.00	45.00	3.4	2.60	117.00
30.00	35.00	12.8	9.40	329.00



Optical Micrograph of STC/HMPN/PVSD



Scanning Electron Micrograph of STC/HMPN/PVSD

Photomicrograph series 22 Photomicrograph of STC/HMPN/PVSD. Microscopic Appearence of STC/HMPN/PVSD Synthesized from the Optimization Data from the Earlier Experiments. The photomicrographs on the top side were taken by a Zeiss optical microscope under 250 times magnification from which the prints were enlarged 2.5 times. The prints on the bottom side were taken by Joel scanning electron microscope under 500 times magnification.

Table 67 Average Diameter and Particle Size Distribution of STC/HMPN/PVSD.

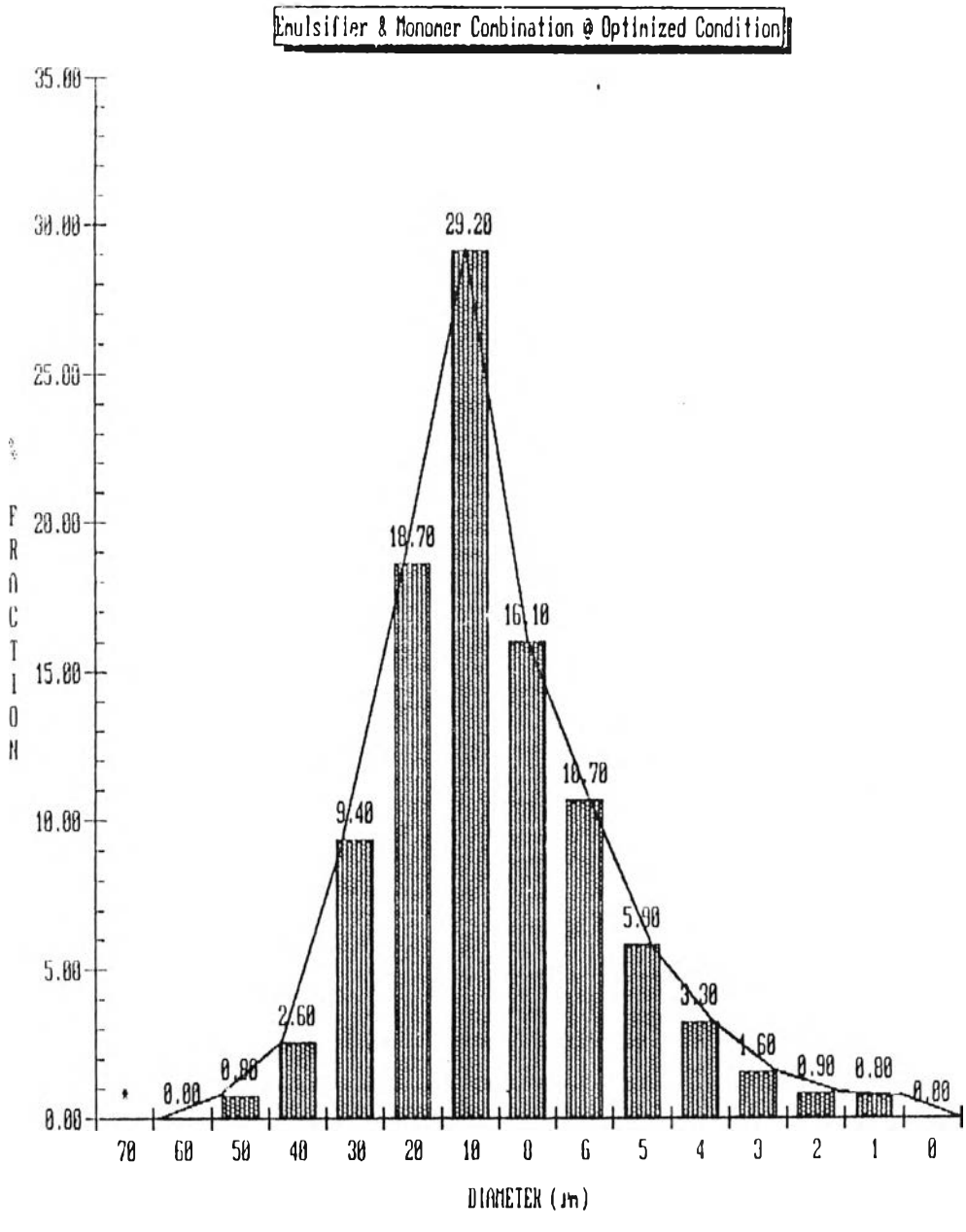
Diameter (μm) Micrometer	Average Diameter	Percentage Cumulative	Percentage Different	Diameter Coefficient
20.00	25.00	31.5	18.70	467.50
10.00	15.00	60.7	29.20	438.00
8.00	9.00	76.8	16.10	144.90
6.00	7.C0	87.5	10.70	74.90
5.00	5.50	93.4	5.90	32.45
4.00	4.50	96.7	3.30	14.85
3.00	3.50	98.3	1.60	5.60
2.00	2.50	99.2	0.90	2.25
1.00	1.50	100.0	0.80	1.20
0.00	0.50	100.0	0.00	0.00
			Average Particle Size (μm)	16.72

2.14.4.4) Average Particle Size and Encapsulation Efficiency

Table 68 shows the average diameter and microencapsulation efficiency of polyamide microcapsules synthesized by potimization condition.

Table 68 Average Particle Size and Encapsulation Efficiency of the Polyamide Microcapsules.

Assigned Name	Average Diameter (μm) of Microcapsules	% Unencapsulated Dibutyl Phthalate
STC/HMPN/PVSD	16.72	1.74



Graph series 34 Histogram of Particle Size Distribution of STC/HMPN/PVSD.

(The graphs were made from the data from Table 67)

Particle size distribution of the polyamide microcapsules synthesized by using the optimum conditions from the previous experiments.

2.14.5) Conclusions

The overall optimum conditions used in the synthesis of the microcapsules were acceptable since the general properties of the microcapsules were stable in emulsion form, the wrinkle and broken microcapsules could not be discoveried in this experiment.