Effect of Adsorption Layer on Emulsion Stability and Shell Growth in Microencapsulation by Interfacial Polycondensation Polymerization

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Chapter I

Introduction

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1. General Introduction

Interfacial polycondensation polymerization is one of the methods of microencapsulation studied for a long time. And it is an useful method for microencapsulating the core material of the liquid phase [1-4]

In the interfacial polycondensation polymerization, there are two stages in this microencapsulation process.

The first stage is the emulsification process. The O/W or the W/O dispersion must be prepared, where the oil soluble monomer or the water soluble monomer must be dissolved in the core liquid phase beforehand. The homogenizer is used for dispersion generally.

The second stage is the polycondensation reaction process. The water soluble monomer (or the oil soluble monomer) is added into the continuous phase after preparation of the liquid-liquid dispersion. It is important that emulsion is stable in this process. A few surfactants are always added to the continuous and/or the dispersed phases [1,5].

The advantages of microcapsules prepared by interfacial polycondensation polymerization shows the following things.

- Polymerization reacts at normal temperature and normal pressure easily. And reaction proceeds in the organic solvent inside the interface

- Reaction speed is very fast in comparison with uniform phase. And it is easy to control the reaction speed.

- It is able to make a microcapsule of various macromolecule membranes under various conditions.

- Because polymerization reacts on the liquid-liquid interface, it is easy to get a capsule of core-shell structure

• The refinement of a microcapsule is easy, too.

Using these advantages, the microcapsule have been studied, and reported.

In the field of record materials, a microcapsule for pressure sensitive carbon paper, a pressure sensitive microcapsule toner, a capsule containing magnetite are studied[5,6].

In the field of cosmetics and pharmaceutics industries, microencapsulated enzyme, an artificial cell, insulin capsule, an artificial pancreas and microencapsulated yeast cell were studied[5,7].

In the field of agriculture and food industries, perfume microcapsule, pheromone microcapsule, hormone microcapsule, anti-bacteria microcapsule, freshness keeping microcapsule, anti-mildew microcapsule and herbicide microcapsule were studied[5, 8-15].

2. Review of Previous Works

2-1 A formation process of microcapsule shell

The microcapsule shell consists of a polymer formed by a polycondensation reaction at the oil/water interface. There are some reports about the shell formation and the growth in microcapsule production [2,11, 16-21]. At or close to the organic solvent side of the interface, the reaction takes place and polymer precipitates. The production of the membranes consists of two stages.

In the early stages of polymerization the dense top-layer is formed, which is followed by the growth of the porous sub-layer. After the initial formation of the shell, the polycondensation reaction is controlled by diffusion of water soluble monomer through the shell. Because of the high reaction rate between water soluble monomer and oil soluble monomer, the consumption rate of the monomer inside a microcapsule is limited by the transfer rate of water soluble monomer from aqueous phase into the organic phase. According to Fick's first law, the rate of water soluble monomer transport depends on the reciprocal value of the shell thickness [2,16]. As the thickness of the microcapsule shell

increases with the reaction time, the water soluble monomer transport rate decreases during the reaction. Many of these studies relate to growth of a capsule of a microencapsulation process, but there are few studies about the effect of the surfactant adsorption layer on the formation process of microcapsule shell. It is important to investigate how each factor influences the shell formation

2-2   Release property of Microcapsules

There is a growing interest in the application of a controlled-release system, especially microcapsules to deliver active materials at a controlled rate. The microcapsule can be one of the most useful devices to release agent in a more effective, longer, and safer manner. Release property is limited by transmission speed of oil ingredient.

In the case of the shell material provided by polymerization reaction, we are able to control release property by change polymerization degree, a shell material, bridging degree and polymer composition. In addition, size of a microcapsule gives influence the release property of microcapsules too. It is important to examine how each factor controls release of a core material. [9-11, 22]

2-3   The role of surfactant in interfacial polycondensation polymerization

A few surfactants are always added to the continuous and/or the dispersed phases.

Interfacial tension decreases with the concentration of surfactant. It is important that emulsion is stable.

In others, in aqueous system, surfactants, having both hydrophobic and hydrophilic property, are able to form hydrogen bonding with water and capable of reducing considerable amount of unbound water reacting rapidly with oil soluble monomer.

But very few effects of surfactants in microencapsulation by interfacial polycondensation polymerization has been published so far.

3. Scope of This Thesis

There are many studies that materials and bridging of a capsule wall give influence to diffusion of a material. However, there are few studies about the effect of the surfactant adsorption layer on the formation process of microcapsule shell. It may be supposed that polycondensation reaction is affected by the surfactant adsorption layer.

The objective of the present thesis is to explain the effect of the surfactant adsorption layer on the formation process of microcapsule shell and the effect of the monomer concentration on the formation process of microcapsule shell.

The scope of each chapter is following:

Chapter I provides a general view of the useful method of the microencapsulation by interfacial polycondensation polymerization.

In the second part of this chapter, the background of the thesis as well as a review of the previous work are given. The third part of this chapter descrived the scope of the thesis.

Chapter II deals with the effect of water-soluble polymer on stability of limonene droplets.

In order to obtain the fundamental information required to prepare microcapsules by interfacial polycondensation polymerization, oil-in-water emulsions were prepared by dispersing limonene oil in the aqueous solution of poly(vinyl alcohol) (PVA) with different degrees of polymerization and saponification. Emulsion prepared was characterized by measuring the droplet diameters and the physical properties of emulsion.

Emulsion stability was estimated by measuring the transient height of the oil phase layer and the interfacial excess concentration for each PVA. PVA with higher surface activity showed the lower occupied interfacial area due to the larger excess concentration and resulted in the stabilized emulsion.

Chapter III deals with the effect of the surfactant adsorption layer on the growth rate of the polyurea capsule shell. Microcapsules containing limonene oil as core material were prepared by interfacial polycondensation polymerization between isocyanate and amine. In the experiment, emulsions were made by dispersing limonene oil in the aqueous solution of

poly(vinyl alcohol) with different degrees of saponification and then, microencapsulation was started. It was investigated how the adsorption layer of poly(vinyl alcohol) affected the growth rate of microcapsule shell. The growth rate of the microcapsule shell was estimated by measuring the transient shell thickness of microcapsules which were sampled out at anytime of microencapsulation process. It was found that the growth rate of microcapsule shell was different due to adsorption amount on the interface of poly(vinyl alcohol).

Chapter IV deals with mechanical strength of polyurea capsules.

It was investigated how the adsorption layer of poly(vinyl alcohol) on the surface of limonene droplets affected the growth rate of microcapsule shell and the mechanical strength of the microcapsule. The growth rate of the microcapsule shell was estimated by measuring the transient shell thickness of microcapsules which were sampled out at anytime of microencapsulation process. At the same time, the mechanical strength of microcapsules was measured by Micro Compression Testing Machine.

Chapter V deals with the effect of the concentration of the monomer on the growth rate of the polyurea capsule shell and permeability of an oil ingredient.

It is the main purpose to clarify whether growth rate of shell depends on the diffusion resistance of monomer through the shell or not.

Therefore we examined the effect of the monomer concentration and investigated the observation of microcapsule and the growth rate of the microcapsule shell thickness.

And the released amount of limonene ingredient as core material was measured.

Chapter VI summarizes the conclusion of the thesis .

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Chapter II

The Effect of Water-Soluble Polymer on Stability of Limonene Droplets

1. Introduction

Interfacial polycondensation polymerization is well known as a useful method for microencapsulating the core material of the liquid phase [1-4]. In this microencapsulation process, (O/W) or (W/O) emulsion must be prepared at first, where the oil soluble monomer or the water soluble monomer must be dissolved in the core liquid phase beforehand. And then, the water soluble monomer (or the oil soluble monomer) is added into the continuous phase after preparation of emulsion.

In this microencapsulation process, generally, it is necessary to prepare stable emulsion. Especially, in order to stably prepare droplets with the diameter smaller than 100 micron, a few surfactants are always added to the continuous and/or the dispersed phase. As the surfactant adsorbs to form the adsorption layer on the liquid-liquid interface, it may be supposed that polycondensation reaction is affected by this adsorption layer more or less. Accordingly, in order to prepare the superior smaller capsules and to control the shell thickness, it is necessary to investigate how surfactant adsorbs on the interface and the adsorption layer affects microencapsulation.

For this purpose, poly(vinyl alcohol) (PVA) which is one of water soluble macromolecules was adopted as stabilizer, because there are many homologues with various degrees of polymerization and saponification, which may show different interfacial activity, and their characteristics have been investigated in detail [5]. The core material was (R)-(+)limonene oil which has the various functions such as a flavor, pheromone to a species of insects and the good solvent of expanded polystyrene in recycle of plastics [6].

The purpose of this paper is to investigate the effects of adsorption behavior and the

adsorption layer of PVA on stability of limonene droplets in the continuous water phase and to obtain the fundamental information required for encapsulating the fine oil droplets.

2. Experimental

2.1 Materials

Poly(vinyl alcohols) (PVA, Kuraray Co.) with different degrees of polymerization and saponification were used as water soluble stabilizer. Their characters are shown in Table II-1. (R)-(+) limonene(Kanto Chemical Co.) and distilled water were used as the dispersed phase and as the continuous phase , respectively.

2.2 Preparation of emulsion

Emulsion was prepared as follows. The constant volume ($3.5 \times 10^{-6} \text{ m}^3$) of limonene was poured into the continuous water phase of the volume of $50 \times 10^{-6} \text{ m}^3$, where PVA of the given concentration was dissolved. Then, this mixture was stirred for 15 min under the condition of the revolution speed of 50 s^{-1} at 23 ℃ using a homogenizer (Biomixer BM-2M, Nippon Seiki Co.). Emulsion was prepared by changing the PVA species and the concentration of PVA.

2.3 Measurement of physical properties of emulsion

Surface tension of the PVA solution and interfacial tension between limonene and the PVA solution were measured with Surface Tension meter(K-12, Cross Co.) at 23℃. The viscosity of liquids concerned was measured with the Vibration Viscometer(Viscomate VM-1A-L, Yamaichi Denki Kogyo Co.) at 23 ℃.

2.4 Evaluation of emulsion stability

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Emulsion stability was evaluated as follows. Emulsion prepared was poured into the test tube of the effective volume of 50×10^{-6} m^3 with the inner diameter of 3×10^{-2} m. As dispersed droplets continue to float up to the surface, the four layers appear, namely, the transparent layer in which few droplets have dispersed, the dispersion layer in which droplets uniformly disperse, the creaming layer in which droplets are concentrated but don't coalesce, the oil phase layer in which droplets disappear due to coalescence. As the creaming layer appears as the deep white layer due to concentrated droplets above the dispersion layer which is light white in color. We can distinguish the creaming layer from the dispersion layer easily. The heights of the creaming layer and the oil phase layer change continuously, because droplets in the creaming layer coalesce with the oil phase. Here, emulsion stability was evaluated by measuring the changing rate of the height of the oil phase layer. Furthermore, droplets were sampled out from the dispersion layer at the constant time interval and their photographs were taken by an optical microscope. The droplet diameters were measured from these photographs by the previous manner [7].

Table II-1   Kinds of PVA and their characters

Kinds of PVA	Saponification degree	Polymerization degree
PVA 11	98~99	1700
PVA 12	94.5~95.5	1700
PVA 21	87~89	300
PVA 13	↑	1700
PVA 14	↑	↑
PVA 15	↑	↑
PVA 23	↑	3500
PVA 22	80~83	500

PVA13, PVA14 and PVA15 are the same polymerization degree and the same saponification degrees. However, the distribution of the acetyl group in a molecule of each PVA is different.

The distribution of the acetyl group for PVA13 is the most random and that for PVA15 is the most block. That for PVA14 is between them of PVA13 and PVA15

3. Results and discussion

3.1 Viscosity of the PVA solution

Figure II-1 shows the dependence of the viscosity of the PVA solution on the concentration of PVA. The viscosity was found to be almost constant at the concentration less than 0.1 wt% for each PVA species. From this result, it may be supposed that there is few interaction between macromolecule chains in the concentration range less than 0.1 wt %.

3.2 Surface and interfacial excess concentrations

Figure II-2(a) shows the dependence of surface tension of the PVA solution on the concentration of PVA. Surface tension decreases with increasing the concentration of PVA. At the same concentration, surface tension becomes lower with decrease in the degree of saponification and polymerization. These results are the same as those for surface tension measured previously [8].

Figure II-2(b) shows the dependence of interfacial tension against the limonene oil phase on the concentration of PVA. From this, the following results are obtained. Namely, interfacial tension decreases with the concentration of PVA. At the same degree of saponification, interfacial tension decreases with decrease in the degree of polymerization. PVA which has the acetyl groups in block polymerization gives lower interfacial tension even at the same degrees of saponification and polymerization. For example, PVA11 which has the highest degrees of saponification among the PVA species adopted here gives interfacial tension higher than the other PVA species. Also, PVA22 which has the lowest degrees of saponification gives interfacial tension lower than the other PVA species.

From these results, the interfacial excess concentrations(Γ) for each PVA were evaluated according to the Gibbs equation; $\Gamma = -(d/RT)(d\gamma/dc)$ [9]. For this evaluation, a polynomial correlating interfacial tension with the concentration of PVA

was derived by the curve-fitting method using the least squares method. The value of slope, $d\gamma/dc$, at each concentration of PVA was calculated by differentiating this polynomial with the concentration of PVA and then interpolating its concentration. Figure II-3 shows the dependence of the interfacial excess concentrations on the concentration of PVA. The interfacial excess concentrations increase according to interfacial activity of PVA. Namely, the interfacial excess concentrations increase with the concentration of PVA, but they are extremely different according to the PVA species. The interfacial excess concentrations at the concentration of $C_{PVA} = 1.0 \times 10^{-3}$ wt% for PVA11 and PVA22 are 9.0×10^{-5} and 1.05×10^{-3} mol/m^2, respectively. The values of the interfacial excess concentrations for the other PVA species are between them and become larger with decrease in the degree of saponification and polymerization.

3.3 Interfacial area occupied by a molecule of PVA

Figure II-4 shows the dependence of the interfacial area occupied by one molecule of PVA on the concentration of PVA. The interfacial areas decrease with the concentration of PVA and then, become constant. Their dependence on the concentration is extremely different according to the PVA species. For example, the interfacial areas at the concentration of $C_{PVA} = 1.0 \times 10^{-3}$ wt% for PVA22 and PVA 11 are 1.08×10^{-9} and 1.25×10^{-8} μm^2/molecule, respectively. It is found that the values of the interfacial areas for the other PVA species are between them. PVA22 with higher surface activity shows the lower interfacial area due to the larger excess concentration.
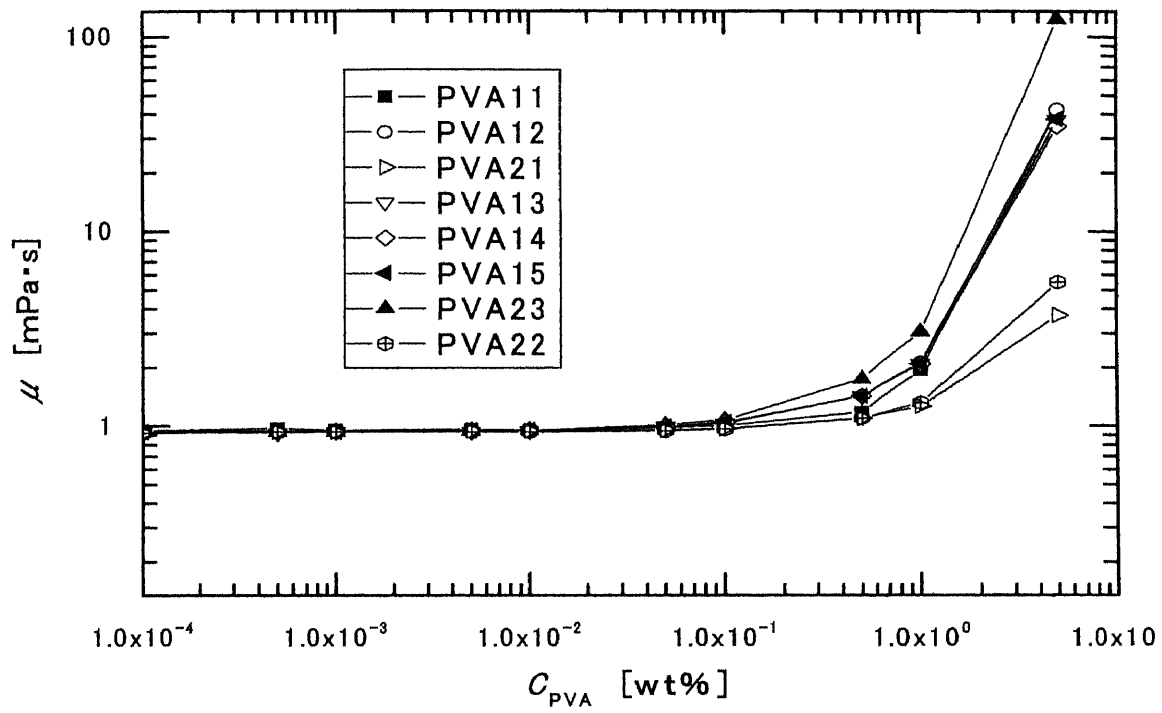
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Figure II-1   Dependence of viscosity of PVA solution on concentration of PVA (23℃)
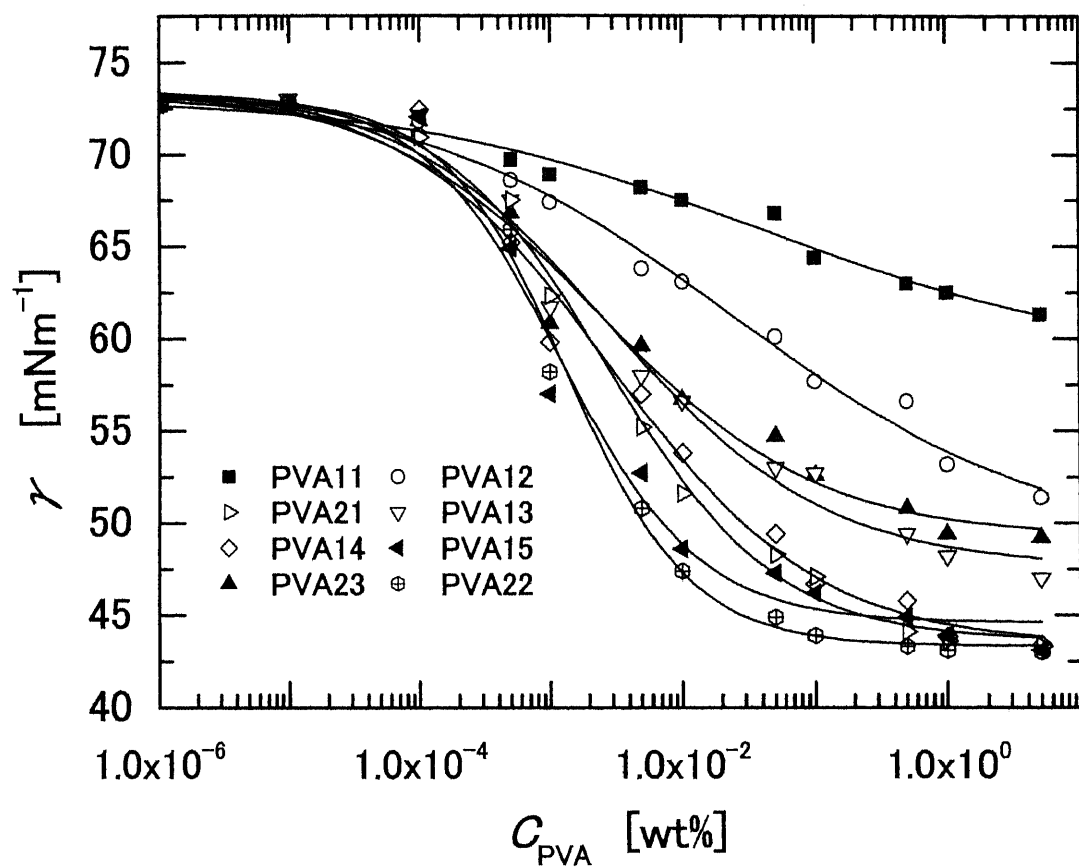
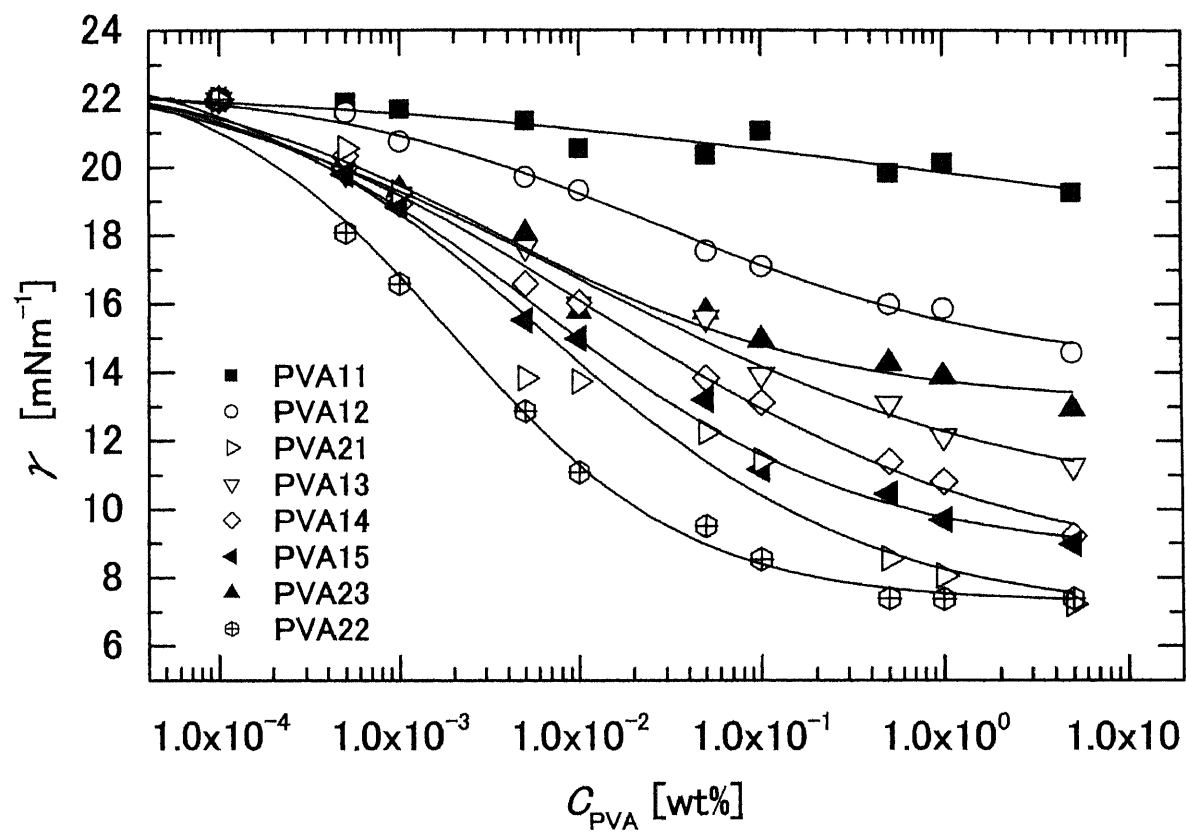Figure II-2(a)   Dependence of surface tension on concentration of PVA   (23℃)

Figure II -2(b)   Dependence of interfacial tension on concentration of PVA against the
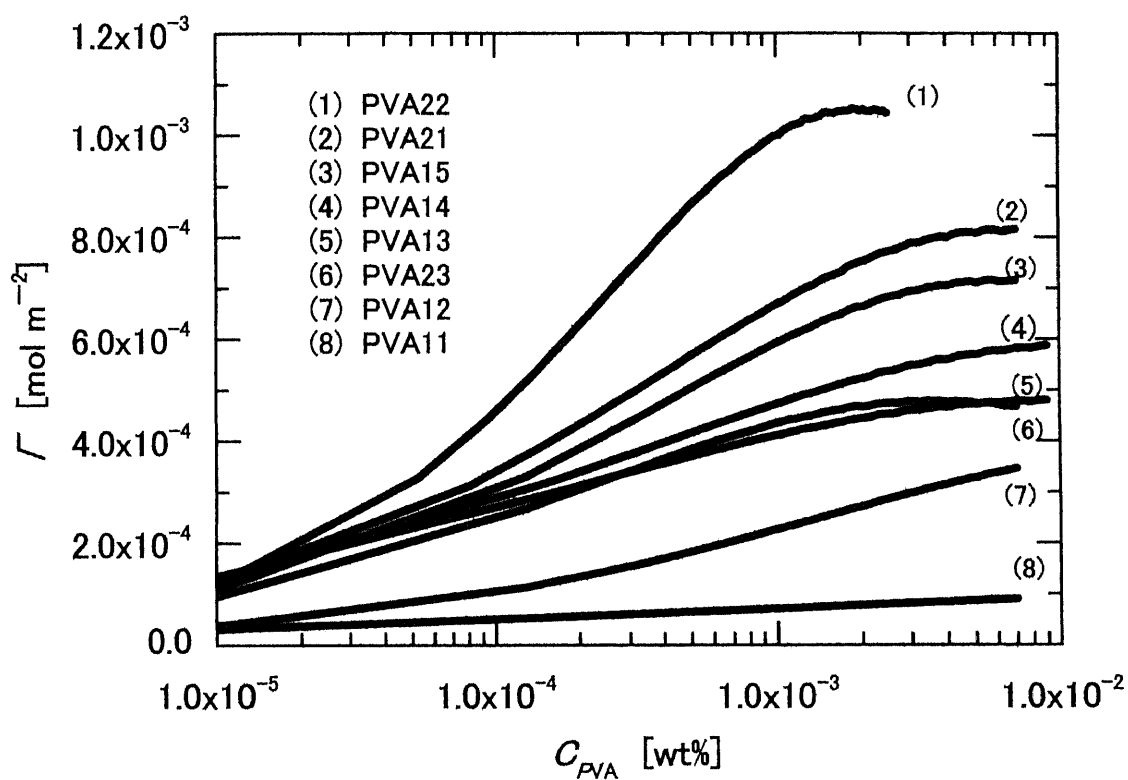Limonene oil phase

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Figure II-3 Dependence of interfacial excess concentration on concentration of PVA
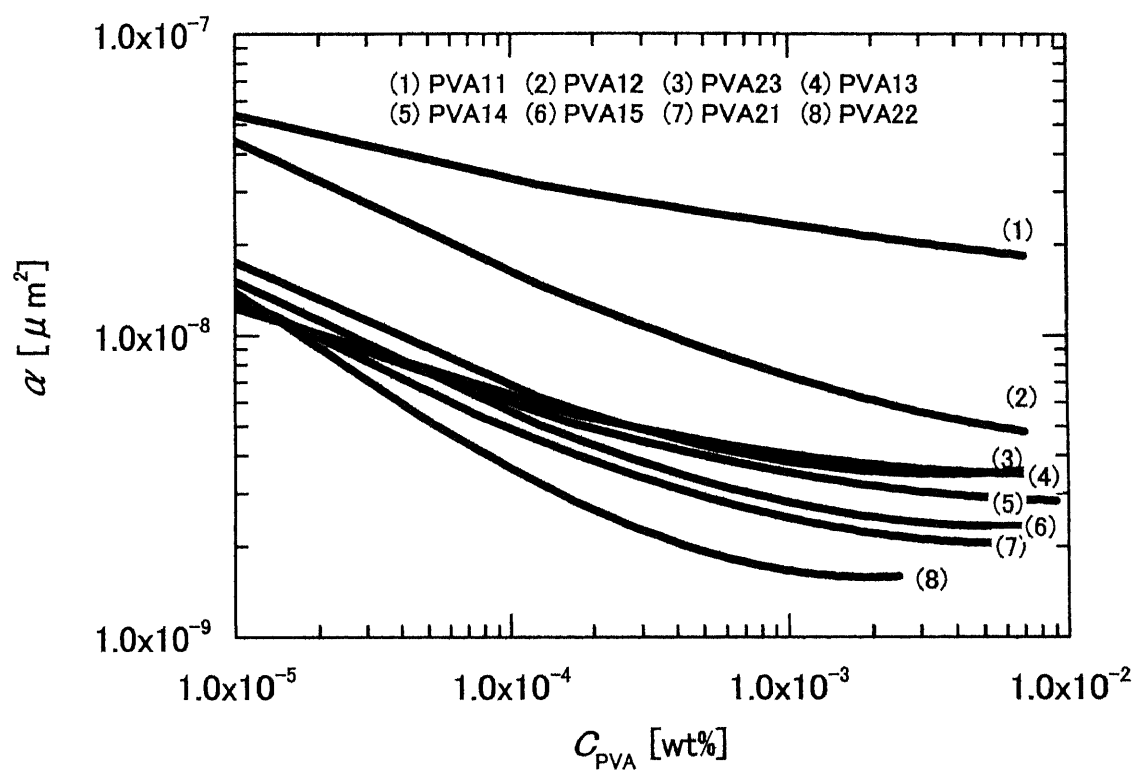
Figure II-4   Interfacial area occupide by one PVA molecule

3.4 Emulsion stability

Figure II-5 shows the photographs of emulsion for PVA15, which were taken at the elapsing time of 24 h and 21 days after preparation. In Figure II-5(b), the oil phase and creaming layers are shown clearly. In Figure II-5(a), the oil phase and creaming layers for the concentration of each PVA can't be distinguished each other at the elapsing time of 24 h. However, at the elapsing time of three weeks, only the oil phase layer can be seen at the concentration of 1.0×10^{-3} wt% and the creaming layer remains at the concentration of more than 1.0×10^{-2} wt%. The same transient features as in Figure II-5 were observed for the other PVA species. The change of four layers in emulsion is different according to the PVA species. Figure II-6 shows the transient features of the height of the oil phase layer, which is determined directly from Figure II-5(a).

PVA15 shows good stability at the concentration of $C_{PVA}=1.0 \times 10^{-3}$ wt% and however, results in rapid formation of the oil phase layer at the concentration of $C_{PVA}=1.0 \times 10^{-4}$ wt%. On the other hand, PVA11 results in rapid formation of the oil phase layer even at the concentration of $C_{PVA}=1.0 \times 10^{-3}$ wt%, but PVA22 gives relative higher stability at the concentration of $C_{PVA}=1.0 \times 10^{-3}$ wt%. The degree of emulsion stability for the other PVA species is found to be between them of PVA15 and PVA11.

Here, the height of the oil phase layer may be supposed to change according to Eq.(1) [10].

$$dH/dt = k(H_\infty - H)$$
(1)

On integrating Eqs. (1), (2) can be derived.

$$\ln\{(H_\infty - H)/(H_\infty - H_C)\} = -kt$$
(2)

Where H_∞ and H_C are the final height and the initial height, respectively and k is the coalescence rate constant. The effects of both of the PVA species and the concentration on emulsion stability are evaluated by the value of k at each experimental condition.

Figure II-7 shows the plots of $\ln(H_\infty - H)/(H_\infty - H_C)$ against t according to Eq.(2). These plots result in the straight lines in the initial changing region where droplets may be thought to actively coalesce with the oil phase. From Figure II-7, the values of k for the concentration of each PVA can be obtained. **Figure II-8** shows the dependence of k-values on the interfacial excess concentration. It is found that the values of k strongly depend on the interfacial excess concentration. The values of k are found to be the largest for PVA11 and the smallest for PVA22 at the concentration of $C_{PVA}=1.0\times10^{-3}$ wt%. The dependence of k on the concentration of PVA is as follows. The values of k for PVA11 increases from 9.5×10^{-2} at $C_{PVA}=1.0\times10^{-3}$ to 1.8×10^{-1} at $C_{PVA}=1.0\times10^{-4}$ wt%. and the values of k for PVA22 increases from 6.6×10^{-3} at $C_{PVA}=1.0\times10^{-3}$ to 6.3×10^{-2} at $C_{PVA}=1.0\times10^{-4}$ wt%.

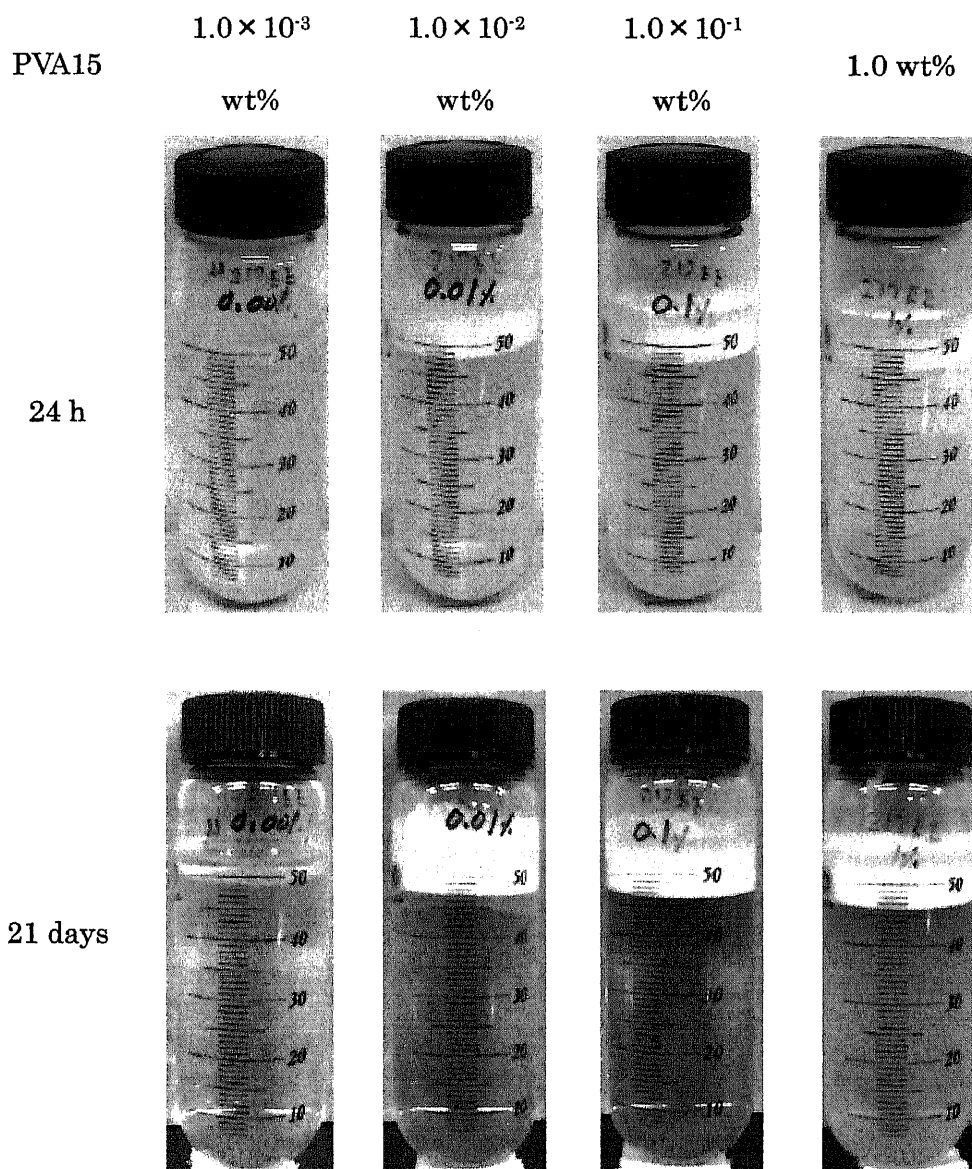From these results, it is found that the largest interfacial excess concentration gives the lowest coalescence rate.

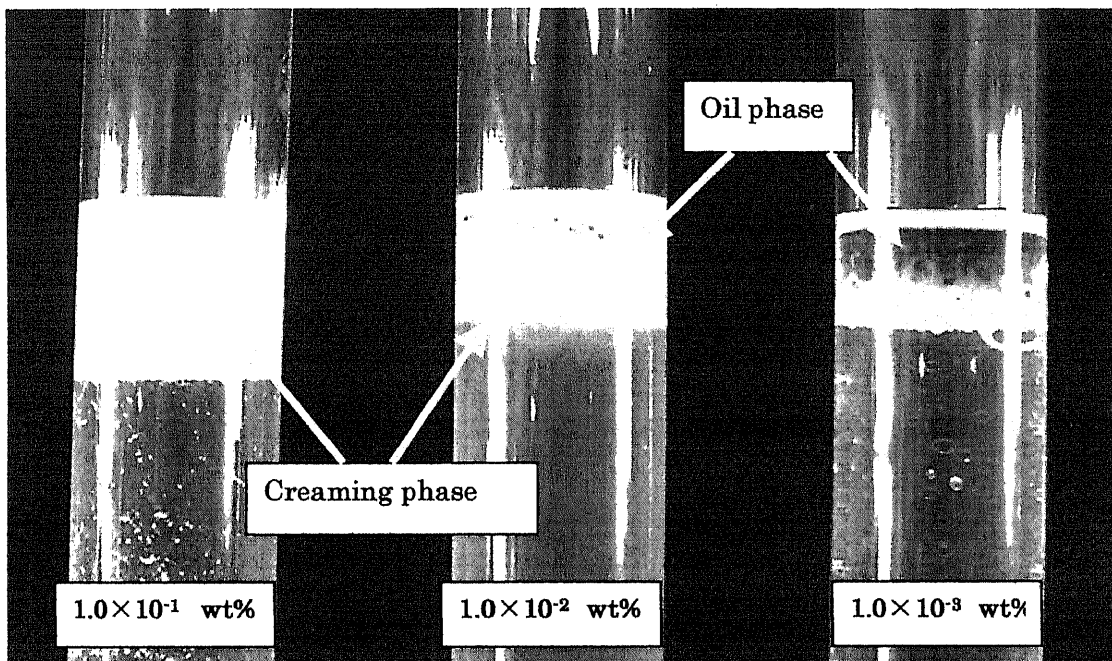Figure II-5(a)   Photographs of transient feature of emulsion prepared by PVA

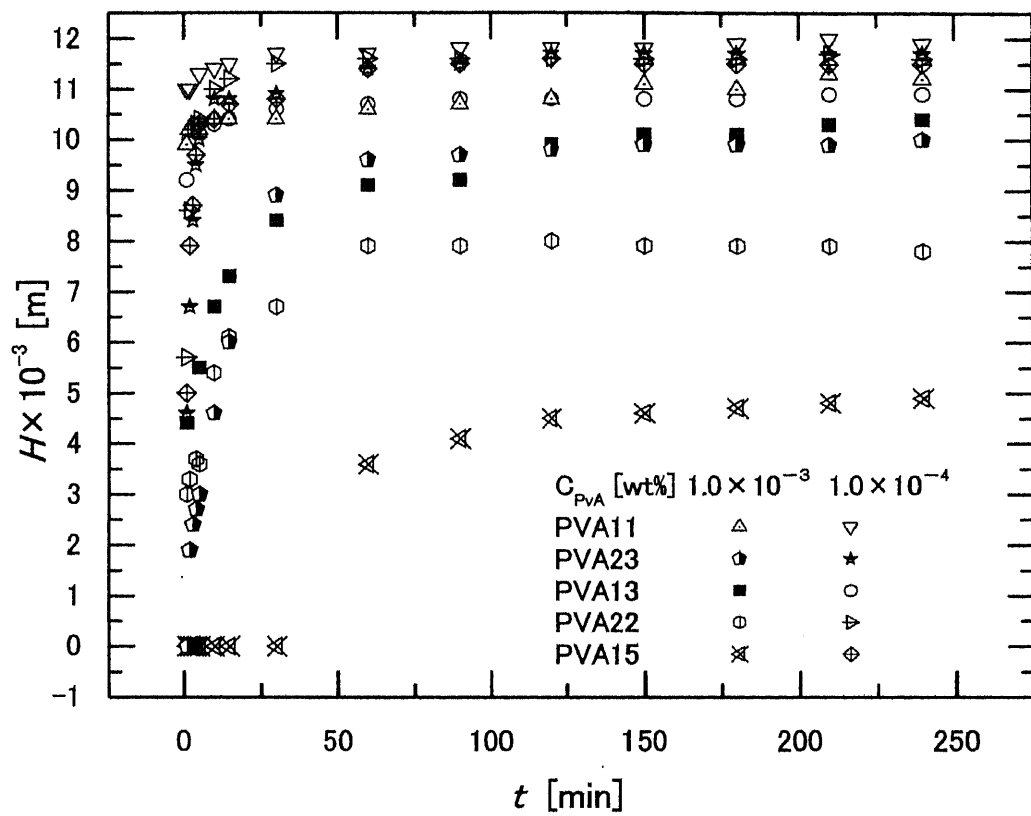Figure II-5(b)   Photographs of transient feature of emulsion prepared by PVA

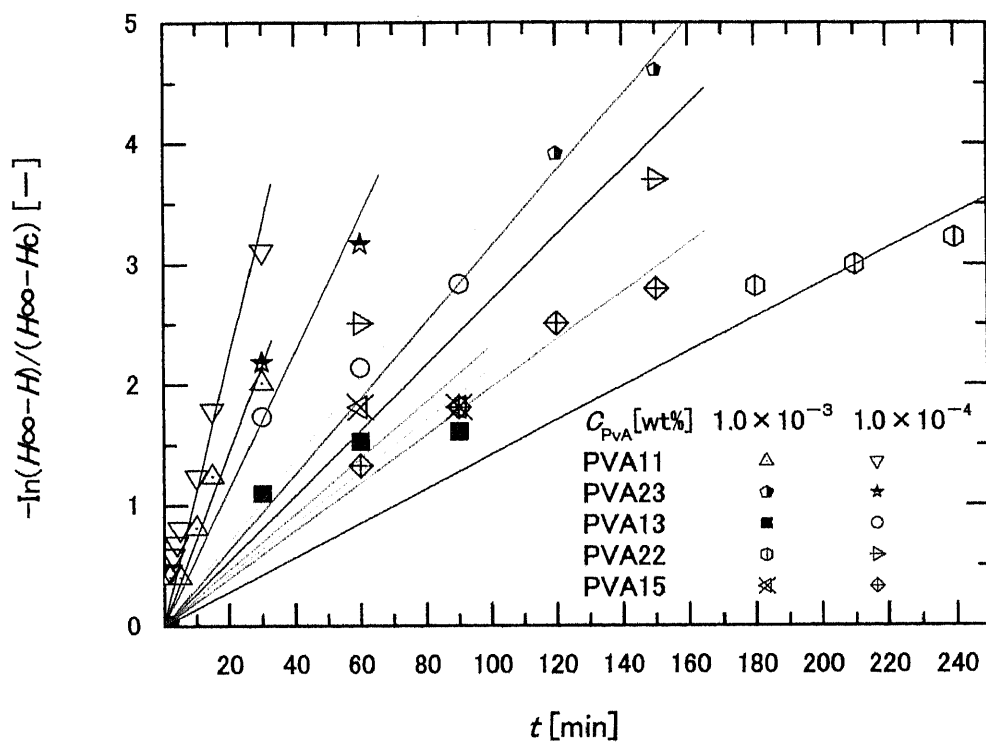Figure II -6　Transient feature of oil phase layer

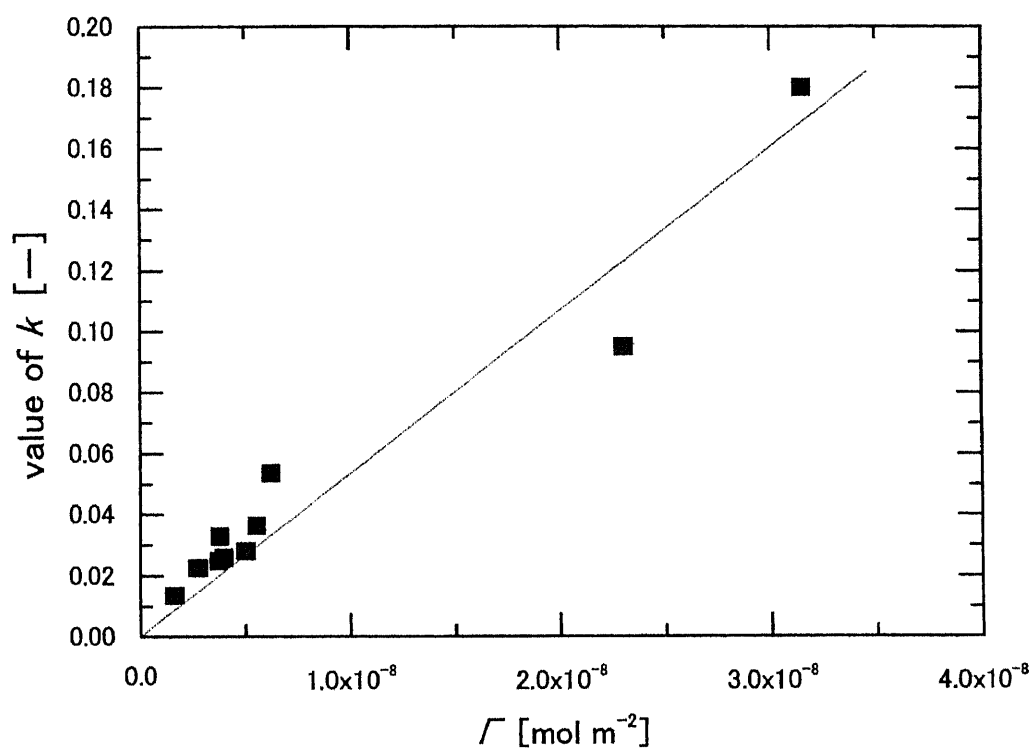Figure Ⅱ-7 Plots of height of oil phase against time according to Eq.(2)

Figure II-8   Dependence of k on interfacial excess concentration

3.5 Droplet diameter distribution and mean diameter

In the microencapsulation process by interfacial polycondensation polymerization, the diameter distribution and the mean diameter of microcapsules strongly depend on those of droplets as the oil phase. **Figure II-9** shows the microscopic photographs of the droplets taken at the constant time intervals for PVA15. It is found that, at the concentration of $C_{PVA}=1.0\times10^{-4}$ wt%, droplets coalesce rapidly to result in poor stability and, at the concentration of C_{PVA} more than 1.0×10^{-2} wt%, droplets disperse relatively stably to result in good stability. Furthermore, the droplet diameters decrease with the concentration of PVA and there are the broad droplet diameter distributions. **Figure II-10** shows the droplet diameter distributions plotted on the normal probability paper. As the plots result in the straight lines, these distributions are found to be the normal distribution. The same results are obtained for the other PVA species.

4. Conclusions

In order to obtain the fundamental information required to prepare microcapsules by interfacial polycondensation polymerization, oil-in-water emulsions were prepared by dispersing limonene oil in the aqueous solution of PVA with different degrees of polymerization and saponification.

The following results are obtained.

(1) PVA with higher degrees of polymerization and saponification shows high surface and interfacial tensions.

(2) PVA with higher surface activity shows a lower interfacial area due to the larger excess concentration.

(3) PVA which shows the smallest interfacial area occupied by one molecule gives the smallest coalescence rate

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(4) From observation by the microscopic photograph of droplets, it is found that dispersed doroplets are stable at the concentration more than 1.0×10^{-2} wt%.

(5) The diameter distributions of limonene droplets are found to be the normal distribution.

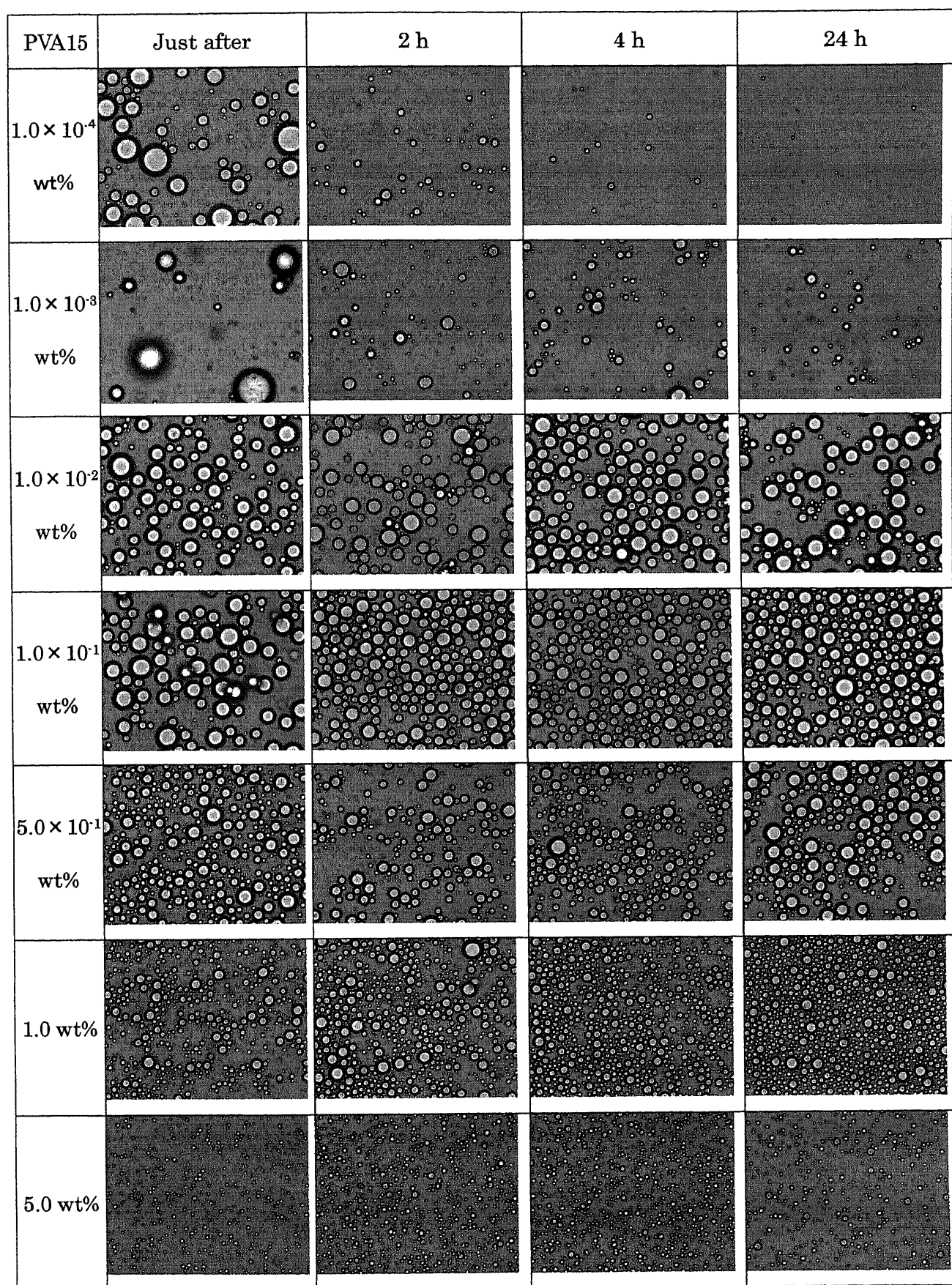| PVA15	Just after	2 h	4 h	24 h
1.0×10^{-4} wt%				
1.0×10^{-3} wt%				
1.0×10^{-2} wt%				
1.0×10^{-1} wt%				
5.0×10^{-1} wt%				
1.0 wt%				
5.0 wt%				

Figure Ⅱ-9   Photographs of transient feature of emulsion prepared by PVA15
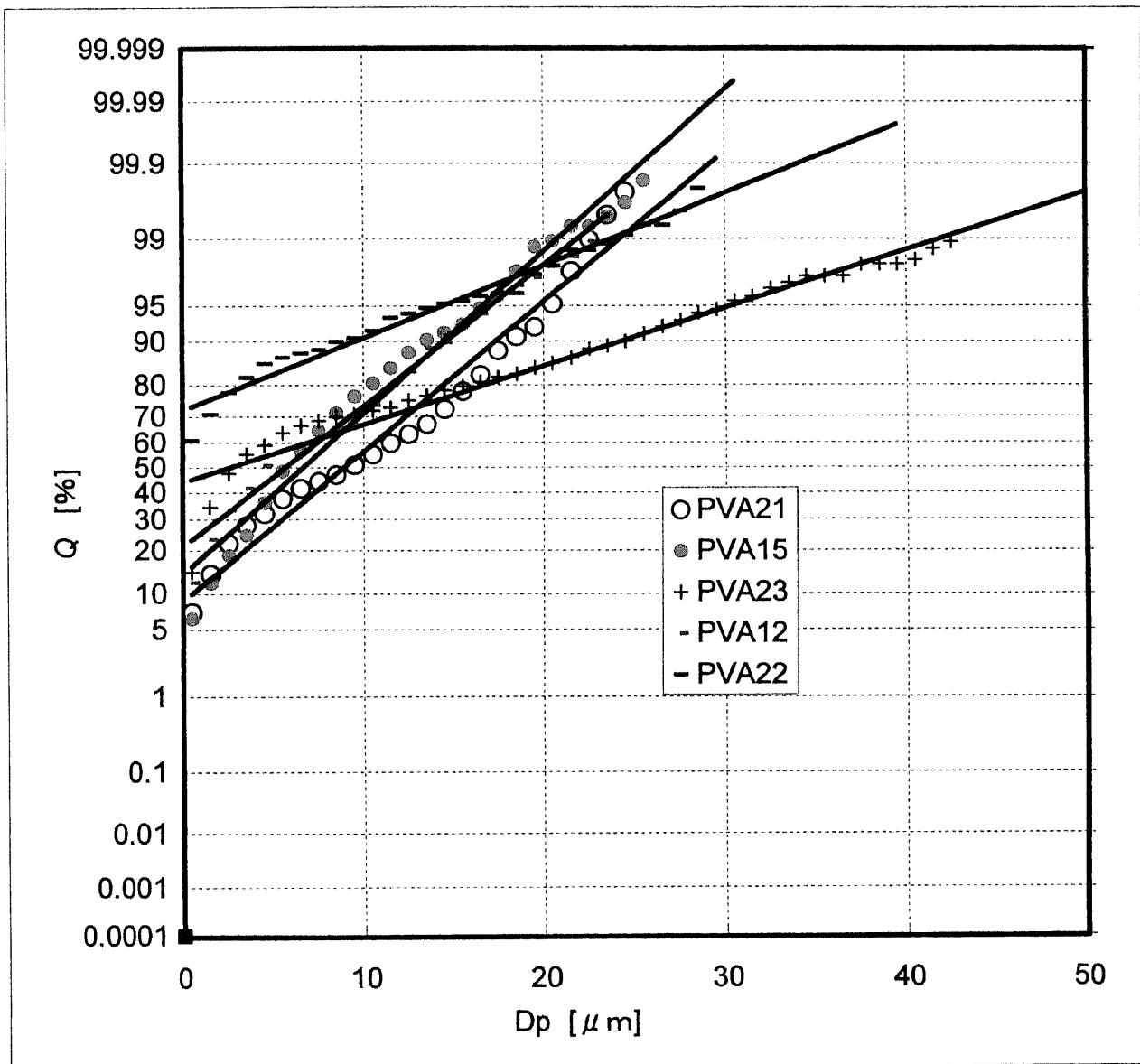
Figure Ⅱ-10 Plots of droplet diameter distribution on normal probability paper

Nomenclature

C_{PVA}	=	concentration of PVA	[wt%]
D_p	=	mean droplet diameter	[μ m]
H	=	height of oil phase layer	[m]
H_C	=	initial height of oil phase layer	[m]
H_∞	=	final height of oil phase layer	[m]
k	=	coalescence rate constant	[s^{-1}]
Q	=	cumulative fraction	[%]
t	=	time	[min]
α	=	interfacial area occupied by a PVA molecule	[μ m^2]
Γ	=	interfacial excess concentration	[mol·m^{-2}]
γ	=	interfacial tension	[mN·m^{-1}]
μ	=	viscosity of PVA solution	[mPa·s]

Reference

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Composite Particle by Semi-Chemical Recycle of EPS," *Kagaku Kogaku Ronbunshu,* 28, 569-574(2002)

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Chapter III

The Effect of the Surfactant Adsorption Layer on the Growth Rate of the Polyurea Capsule Shell

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Section III-1   The Effect of the concentration of PVA on the Growth Rate of the Polyurea Capsule Shell

1. Introduction

Interfacial polycondensation polymerization has been used as a useful method for microencapsulating the liquid phase as a core material [1-4]. The absorption layer of PVA had different interfacial area occupied by one molecule according to the kinds and the concentration of PVA in Chapter II. The surfactant is necessary for emulsion stability in microencapsulation by interfacial polycpndensation polymerization. The adsorbed surfactant forms the adsorption layer on the liquid-liquid interface. It may be supposed that polycondensation polymerization is affected by this adsorption layer more or less. Accordingly, in order to prepare the superior microcapsules and to control the shell thickness, it is necessary to investigate how the adsorption layer on the interface affects microencapsulation.

Interfacial activity such as lowering of interfacial tension, absorption amount and interfacial area occupied by an adsorbed molecule may affect the growth of microcapsule shell.

In this experiment, poly(vinyl alcohol) (PVA) which is one of water soluble macromolecules was adopted as stabilizer, because there are many homologues with various degrees of polymerization and saponification, which may show different interfacial activity and their characteristics have been investigated in detail [5,6]. The core material was (R)-(+)limonene oil which has the various functions such as a flavor,

pheromone to a species of insects and the good solvent of expanded polystyrene in recycle of plastics [7] .

The purpose of this paper is to investigate how the adsorption layer of PVA species affects polycondensation reaction, namely the shell growth of microcapsules.

2. Experimental

2.1 Materials

The degree of saponification and polymerization of Poly(vinyl alcohols) (PVA, Kuraray Co.) adopted here were 87-89 and 1700, respectively.

(R)-(+) limonene (Kanto Chemical Co.) and distilled water were used as the dispersed phase and as the continuous phase, respectively. Hexamethylene diisocianate (HMDI) as an oil soluble monomer and hexamethylenediamine (HMDA) as a water soluble monomer were used without further purification.

2.2 Preparation of emulsion and measurements of physical properties

Preparation of emulsion was performed by the same method as in the previous work [6]. Physical properties of emulsion and estimation of adsorbed amount of PVA were performed according to the same method as in the previous work [6].

2.3 Preparation of microcapsules

Microcapsules were prepared under the various concentration of each PVA. **Figure Ⅲ -1** shows a flowchart of preparing microcapsules.

At first, (O/W) emulsion was prepared prior to microencapsulation. The constant volume $(4 \times 10^{-6} \text{ m}^3)$ of limonene dissolving HMDI was poured into the continuous water phase of the volume of $10 \times 10^{-5} \text{ m}^3$, where PVA of the given concentration was dissolved. Then, this mixture was stirred for 15 min under the condition of the revolution speed of

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50 s^{-1} and 60℃ using a homogenizer (Biomixer BM-2M,Nippon Seiki Co.).

Polycondensation reaction was started under the condition of the revolution speed of 6.7s^{-1} and 60℃ after the aqueous solution $(10 \times 10^{-6} m^3)$dissolving HMDA was poured into (O/W) emulsion. From beginning of the reaction, microcapsules were sampled out by a pipet at the elapsing time designated beforehand. Microcapsules sampled were washed in distilled water twice.

2.4 Observation of microcapsule and measurement of shell thickness

The whole, the surface and the cross-section of microcapsule were observed by scanning electric microscopy (SEM). Microcapsule diameter was measured as the Sauter Diameter by a Centrifugal Particle Analyzer (SA-CP3, Shimadzu Co.). The shell thickness was measured follows. Microcapsules of each mean diameter were broken by mechanical pressure. These broken microcapsules were observed by scanning electron microscopy (SEM). The shell thickness was measured at five points per a microcapsule as shown in **Figure Ⅲ-2** and the mean shell thickness was calculated from these five values.
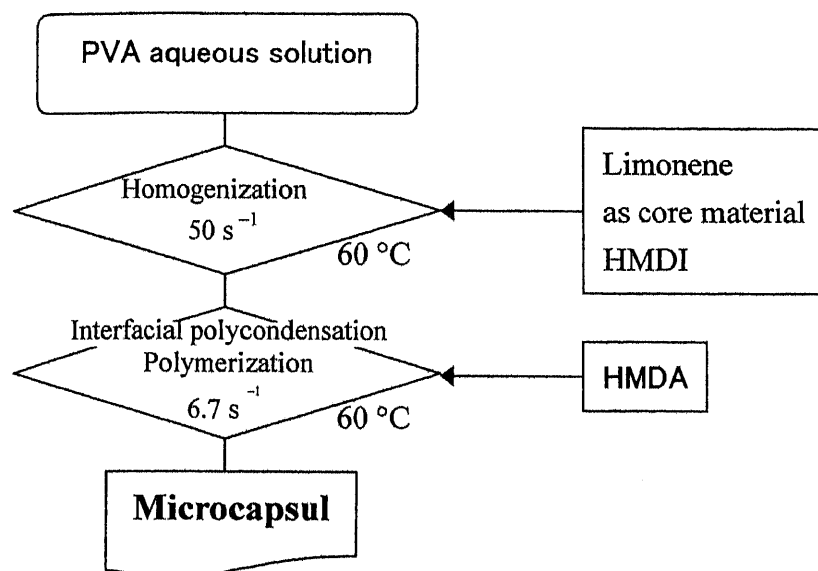
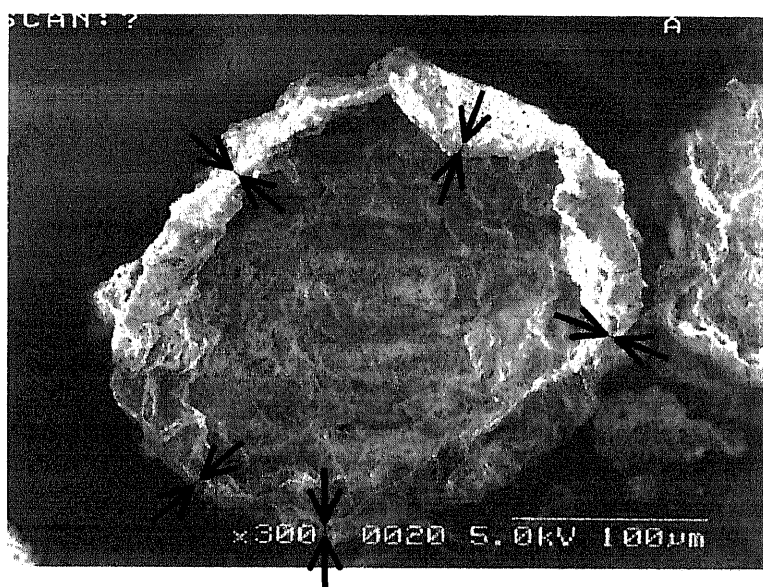Figure Ⅲ-1 Flowchart of preparing microcapsules

Figure III-2   SEM photograph of microcapsules   (1.0x10^{-2}wt%   4h)

3. Results and discussion

3.1 Interfacial excess concentration and the interfacial area occupied by one molecule

Figure III-3 shows the dependence of interfacial tension on the concentration of PVA. Interfacial tension decreases with increase in the concentration of PVA. It is well known that PVA with many acetyl groups in a molecule gives lower interfacial tension [6]. From this result, the interfacial excess concentrations and interfacial area occupied by one molecule were estimated by the same method as in the previous work [6]. Figure III-4 shows the interfacial excess concentrations calculated thus at each concentration of PVA. The interfacial excess concentrations increases from 3.5×10^{-5} $mol \cdot m^{-2}$ at $C_{PVA} = 1.0 \times 10^{-4}$ wt% to 6.5×10^{-4} $mol \cdot m^{-2}$.at $C_{PVA} = 1.0 \times 10^{-3}$

Figure III-5 shows the dependence of the interfacial area occupied by one molecule of PVA on the concentration of PVA. The interfacial areas decrease with the concentration of PVA and then, become constant. For example, the interfacial areas decrease from $5.0 \times 10^{-8} \mu m^2$ at $C_{PVA} = 1.0 \times 10^{-6}$ wt% to $2.5 \times 10^{-9} \mu m^2$ at $C_{PVA} = 1.0 \times 10^{-3}$ wt%

3.2 Dependence of the growth rate of the microcapsule shell on the microcapsule diameter and the concentration of PVA

Figure III-6 shows the effect of the microcapsule diameter on the growth of the microcapsule shell at the concentration of PVA of 1.0×10^{-2} wt%. From this result, the following important information may be able to be obtained. With the polymerization time, the thickness of the microcapsule shell increases faster in the initial region of polymerization, but increases slowly after about 0.5h. The larger the microcapsules, the thicker the microcapsule shell. These results agree well with those by Kubo *et al.*, [8]. In order to obtain the more detailed information for these results, the effects of the concentration of PVA on the growth of the microcapsule shell was investigated.

Figure III-7 shows the effect of the concentration of PVA on the growth of microcapsule shell at the same microcapsule diameter. From these results, it is found

that the shell thickness decreases with higher concentration of PVA.

3.3 Dependence of the growth rate on interfacial area occupied by one molecule of PVA

Figure III-8 shows the dependence of initial shell growth rate on interfacial area occupied by one molecule of PVA. The initial shell growth rate was estimated by measuring the slope of the T-t curve at the origin in Figure III-7. From Figure III-8, it is found that the initial shell growth rate increases with the interfacial area. In other words, the shell growth rate decreases with the adsorbed amount of PVA. Furthermore, the larger the microcapsules, the larger the initial growth rate. It may be though that the different growth rates are attributable to the transfer rate of monomer across the interface. Namely, the transfer rate of the monomer (amine) across the interface is decreased by the absorption of the PVA molecule. The different in the growth rate due to the microcapsule diameter may be attributable to the difference in the amount of HMDI in a microcapsule [8]. Namely, as the microcapsule diameter increases, the surface area of the microcapsule per microcapsule volume decreases, and the amount of HMDI per surface area increases. As the effect of the microcapsule diameter, interfacial disturbance which affects the mass transfer rate of the monomer may be considered.

In order to make this clear, more detailed investigation should be made.
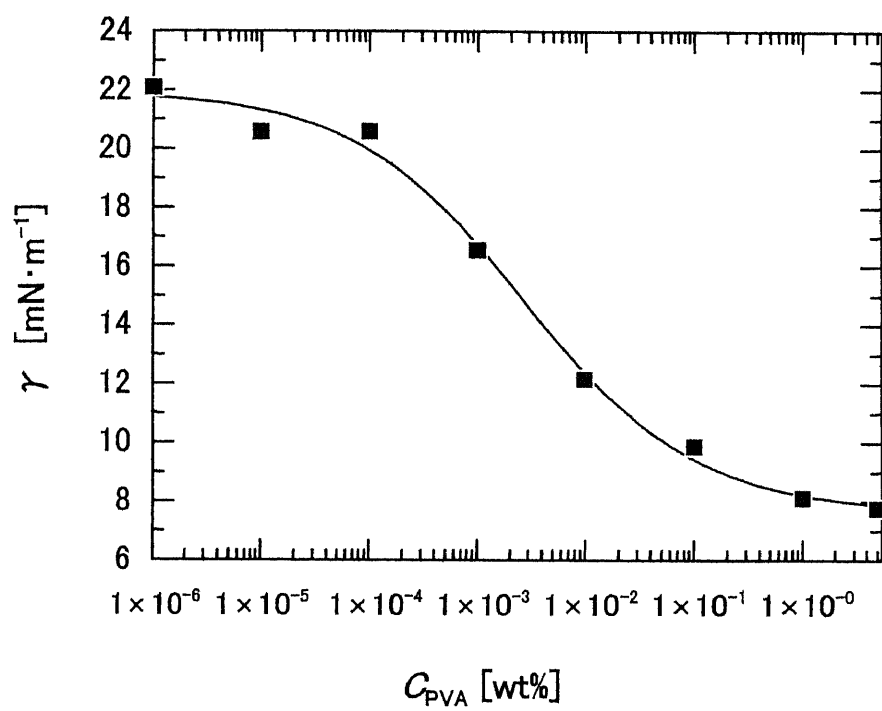
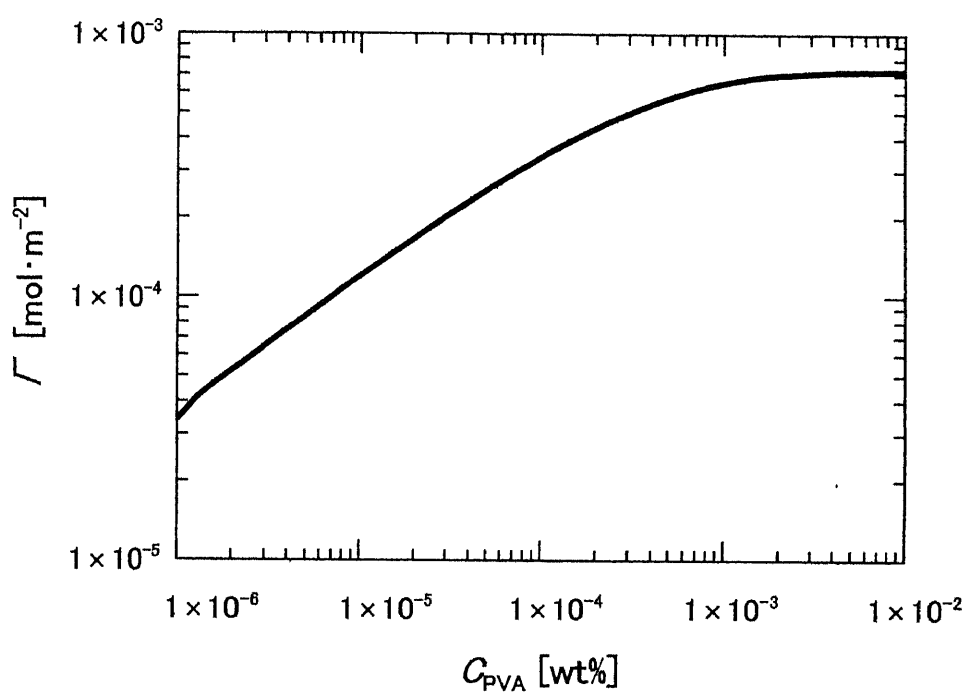Figure III-3   Dependence of interfacial tension on concentration of PVA

Figure III-4 Dependence of interfacial excess concentrations on concentration of PVA
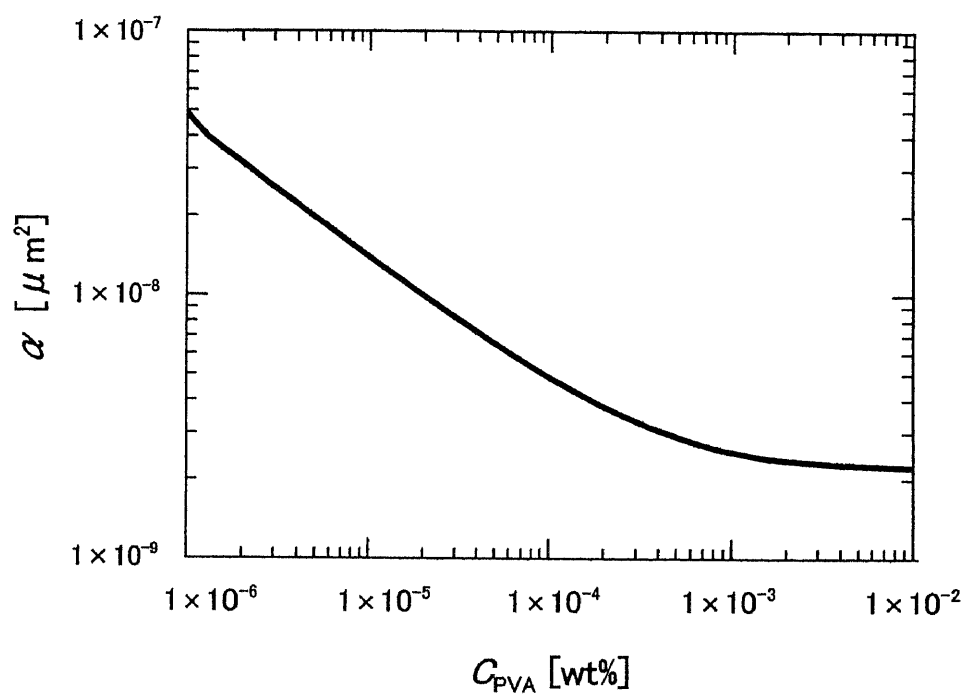
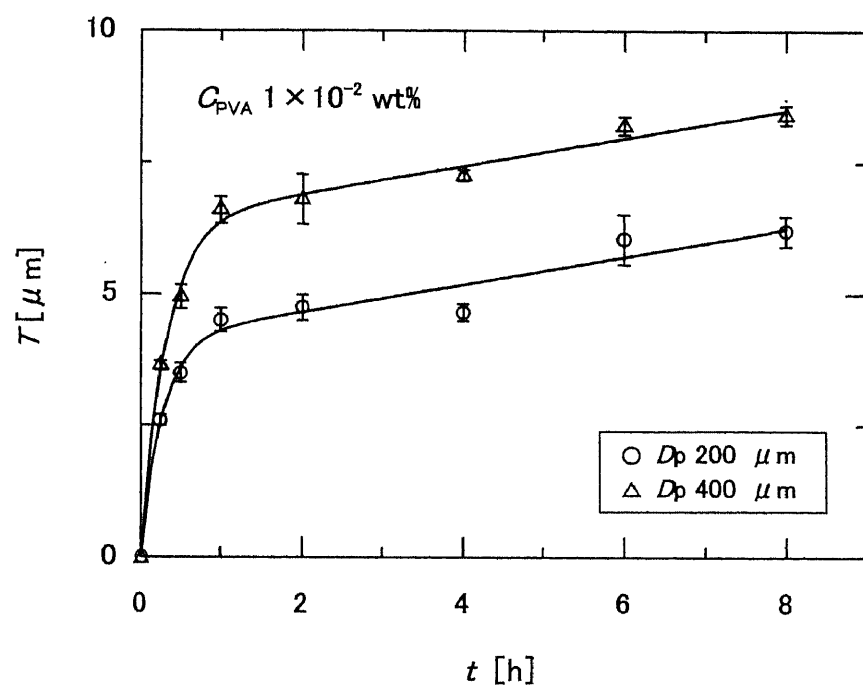Figure III-5   Interfacial area occupied by one molecule of PVA

Figure III-6 Effect of microcapsule diameter on growth of microcapsule shell
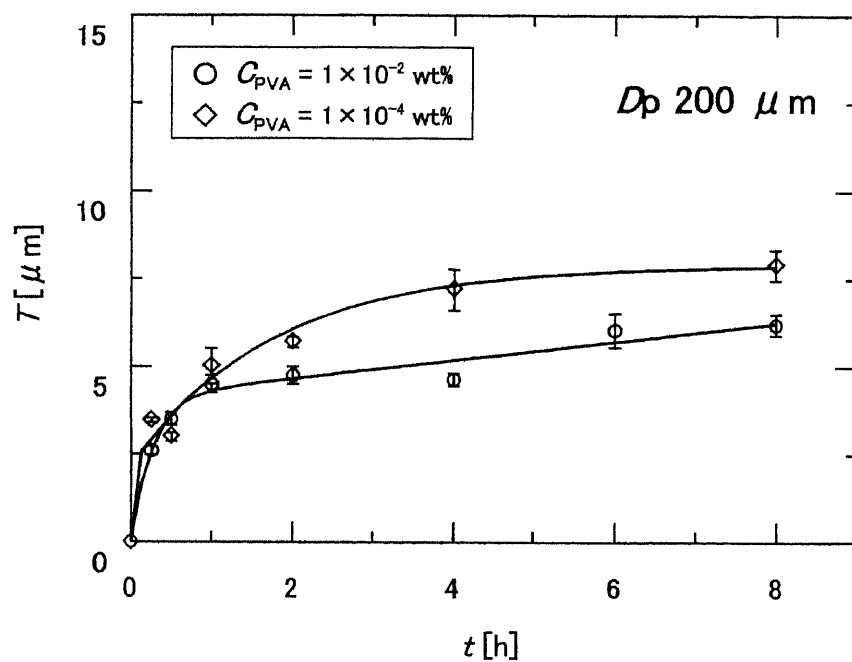
Figure III-7(a)   Effect of concentration of PVA on growth of microcapsule shell
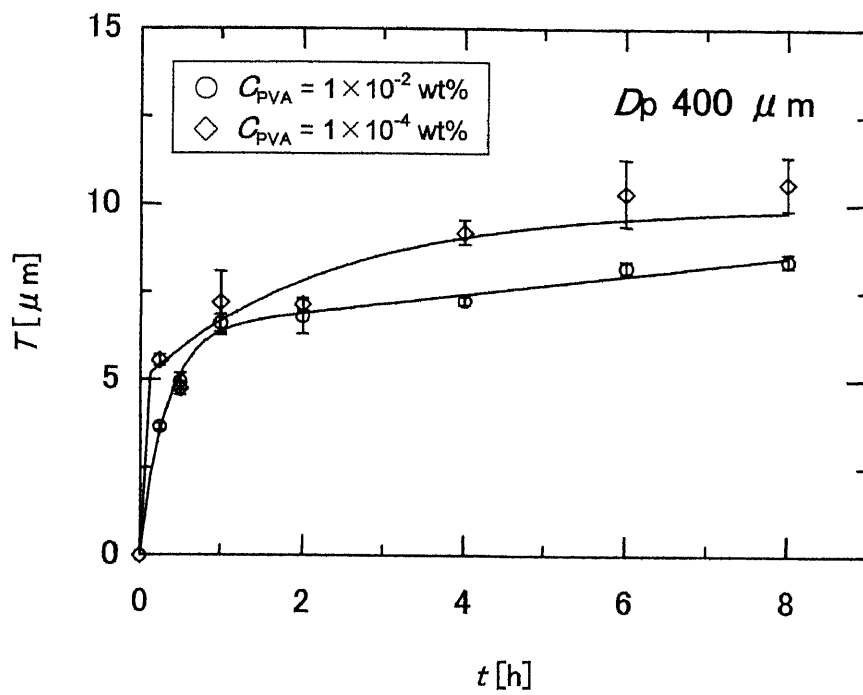at Dp = 200 μ m

Figure Ⅲ-7(b)   Effect of concentration of PVA on growth of microcapsule shell at
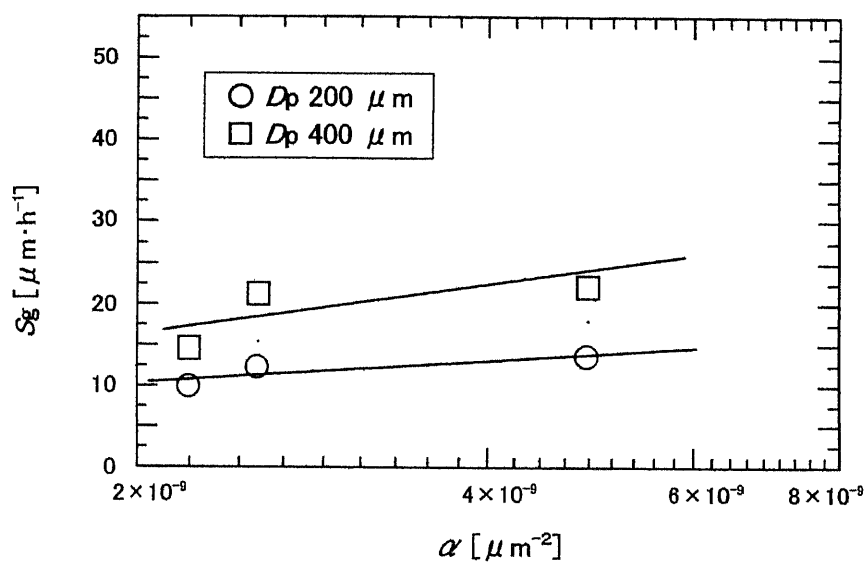Dp = 400 μ m

Figure III-8   Dependence of initial growth rate on interfacial area occupied by one
molecule of PVA

4. Conclusions

In order to obtain the fundamental information required to prepare microcapsules by interfacial polycondensation polymerization, emulsion was prepared by dispersing limonene oil in the aqueous solution of PVA and the microcapsule was prepared by polycondensation reaction between isocyanate and amine.

It was investigated how the amount of PVA adsorbed on the interface affects interfacial polycondensation polymerization. The following results were obtained.

(1)   The initial growth rate of the microcapsule shell decrease with the interfacial area occupied by one molecule of PVA, namely adsorbed amount of PVA.

(2)   The larger the microcapsules, the larger the initial growth speed.

Nomenclature

C_{PVA}	=	concentration of PVA	[wt%]
D_p	=	droplet diameter	$[\mu m]$
S_g	=	initial growth rate of the microcapsule shell	$[\mu m \cdot h^{-1}]$
T	=	thikness of the capsule shell	$[\mu m]$
t	=	time	[min]
α	=	interfacial area occupied by one molecule of PVA	$[\mu m^2]$
Γ	=	interfacial excess concentration	$[mol \cdot m^{-2}]$
γ	=	interfacial tension	$[mN \cdot m^{-1}]$

Reference

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[4] Zydowicz, N., P. Chaumont and M. L. Soto-portas; "Formation of aqueous core polyamide microcapsules obtained via interfacial polycondensation," *J. Membrane Sci.*, 189. 4-58 (2001)

[5] CHAO, D. Y; "The Role of Surfactants in Synthesizing Polyurea Microcapsule," *J. Applied Polymer Sci.*, 47, 645-651(1993)

[6] Mizuno, K., Y. Taguchi and M. Tanaka; "A Fundamental Study on Encapsulation of an Oil Phase Ingredient by Polycondensation Polymerization: The Effect of Water-Soluble Polymer on Stability of Limonene Droplets," *J. Chem. Eng. Japan*, 37, 882-888 (2004)

[7] Akutsu, Y., Y. Taguchi and M. Tanaka; "Development of Technique for Preparing Composite Particle by Semi-Chemical Recycle of EPS," *Kagakukogaku Ronbunshu*, 28, 569-574(2002)

[8] Kubo, M., Y. Harada, T. Kawakatsu and T. Yonemoto; "Modeling of the Formation Kinetics of Polyurea Microcapsules with Size Distribution by Interfacial polycondensation," *J. Chem. Eng. Japan*, 34, 1506-1515 (2001)

1. INTRODUCTION

Interfacial polycondensation polymerization is a useful method for microencapsulating

the core material of the liquid phase [1-4].

In order to obtain the fundamental informations required to prepare microcapsules by

interfacial polycondensation polymerization, emulsion was prepared by dispersing

limonene oil in the aqueous solution of PVA and the microcapsule was prepared by

polycondensation reaction between isocyanate and amine.

It was investigated how the amount of PVA adsorbed on the interface affects interfacial

polycondensation polymerization in Chapter III-1.

The following results were obtained.

(1) The initial growth rate of the microcapsule shell decreases with the interfacial area

occupied by one molecule of PVA, namely adsorbed amount of PVA.

(2) The larger the microcapsules, the larger the initial growth speed.

In this microencapsulation process, in order to prepare the superior microcapsules, it is

necessary to form the stable emulsion in advance. For this, a few surfactants or

polymers are always added to the continuous and/or the dispersed phase. As these

interfacial active additives adsorb to form the adsorption layer on the liquid-liquid

interface, it may be supposed that polycondensation polymerization and then the

growth rate of the microcapsule shell are affected by this adsorption layer more or less.

Interfacial activity which affects the interfacial tension (γ) (in $mN \cdot m^{-1}$), the

adsorption amount and the interfacial area occupied by an adsorbed molecule may

affect the growth rate of the microcapsule shell.

In this experiment, poly(vinyl alcohol) (PVA) which is one of the water soluble

macromolecules was adopted as a stabilizer, because there are many homologues with

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various degrees of polymerization and saponification, which may show different interfacial activity and their characteristics have been investigated in detail [5,6]. As the core material, we adopted (R)-(+)limonene oil which has some various functions such as flavor, pheromone to species of insects [7,8] and the good solvent of expanded polystyrene in recycle of plastics [9].

The purpose of this chapter is to investigate how PVA with the different saponification degree affects polycondensation reaction, namely the growth rate of the microcapsule shell

2. Experimental

Materials

The characteristics of Poly(vinyl alcohols) (PVA, Kuraray Co.) with the different saponification degree used as the water soluble stabilizer are shown in Table III- I .

(R)-(+) limonene (Kanto Chemical Co.) and distilled water were used as the dispersed phase and as the continuous phase, respectively.

Hexamethylene diisocianate (HMDI) as an oil soluble monomer and hexamethylenediamine (HMDA) as a water soluble monomer were used without further purification.Measurements of physical properties and Mechanical strength

Interfacial tension was measured between limonene and PVA solution with the Surface Tension Meter. The interfacial excess concentrations (Γ) (in $mol \cdot m^{-2}$) and the interfacial area occupied by one PVA molecule were estimated by the same method as in the previous one [6].

Table Ⅲ- I   Kind of PVA and their characters

Kind of PVA	Saponification degree	Polymerization degree
PVA 11	98~99	1700
PVA 13	87~89	1700

Preparation of microcapsules

Microcapsules were prepared using a few kinds of PVA. Figure III-9 shows a flowchart of preparing the microcapsules.

Microcapsules were prepared under the various concentration of each PVA. Figure III-9 shows a flowchart of preparing microcapsules.

At first, (O/W) emulsion was prepared prior to microencapsulation. The constant volume (4×10^{-6} m^3) of limonene dissolving HMDI(4×10^{-3} kg) was poured into the continuous water phase of the volume of 10×10^{-5} m^3, where PVA of the given concentration was dissolved. Then, this mixture was stirred for 15 min under the condition of the revolution speed of 50 s^{-1} and 60℃ using a homogenizer (Biomixer BM-2M,Nippon Seiki Co.).

Polycondensation reaction was started under the condition of the revolution speed of 6.7s^{-1} (by the six bladed paddle impeller with a diameter of 5.4 $\times$ 10^{-2}m) and 60℃ after the aqueous solution (10×10^{-6}m^3)dissolving HMDA(2.7 $\times 10^{-3}$kg) was poured into (O/W) emulsion. From beginning of reaction, microcapsules were sampled out by the pipet at the elapsing time designated beforehand. The microcapsules sampled were washed in distilled water twice.

Observation of the microcapsule and measurement of shell thickness

The whole, the surface and the cross-section of microcapsule were observed by scanning electron microscopy (SEM). Microcapsule diameter (d_p) (in μ m) was measured as the Sauter Diameter by a Centrifugal Particle Analyzer (SA-CP3, Shimadzu Co.). The shell thickness was measured as follows. Microcapsules of each mean diameter were broken by mechanical pressure. These broken microcapsules were observed by scanning electron microscopy (SEM). The shell thickness was measured at five points per a microcapsule as shown in Figure III-10 and the mean shell thickness was calculated from five values.
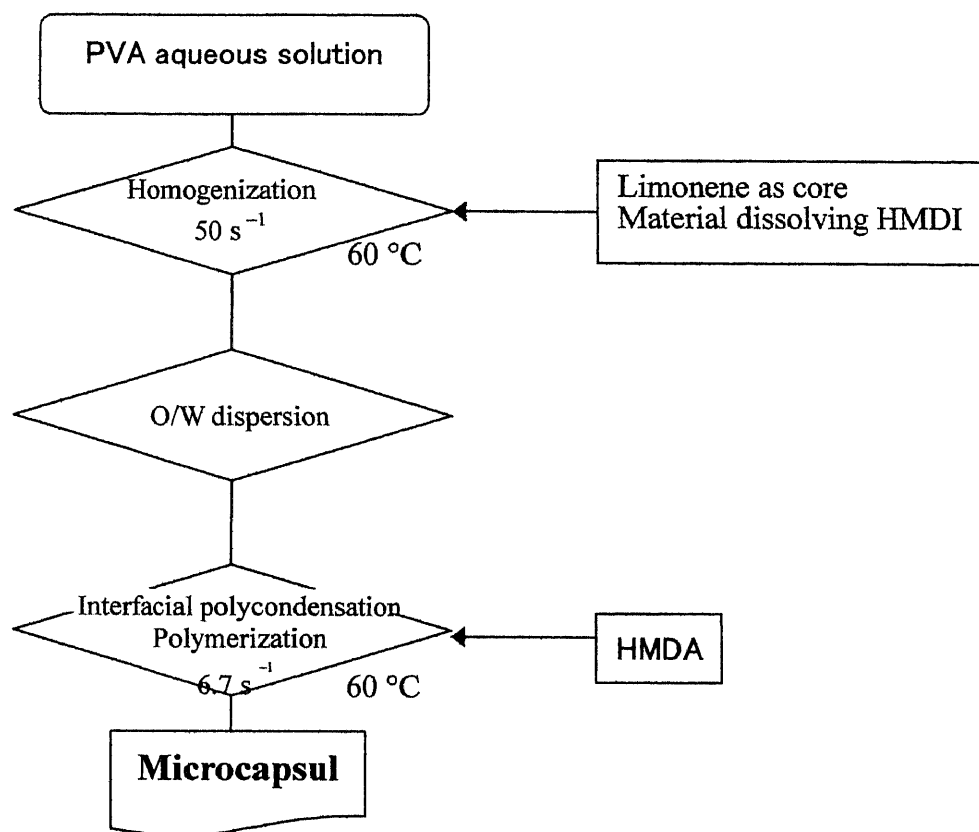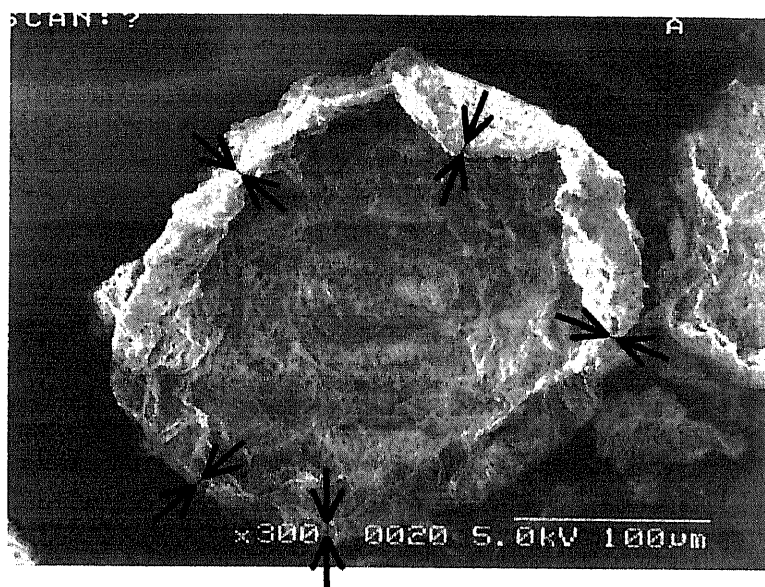
Figure Ⅲ-9   Flowchart of preparing microcapsules

Figure Ⅲ-10 SEM photograph of microcapsules (1.0x10^{-2} wt% 4h)

3. Results and Discussion

Interfacial excess concentration and the Interfacial area occupied by one molecule

Figure III-11 shows the dependence of the interfacial tension on the concentration of PVA. The interfacial tension decreases with an increase in the concentration of PVA. PVA13 results in the interfacial tension considerably lower than PVA11. For example, the interfacial tension decreases from $\gamma=22$ to 19 [mN m^{-1}] for PVA11 and from $\gamma=22$ to 7.0 [mN m^{-1}] for PVA13, respectively. This result agree with the fact that PVA with many acetyl groups in a molecule gives the lower interfacial tension [6]. The interfacial excess concentration and the interfacial area occupied by one molecule of PVA (α) (in μ m^2) were estimated by the same method as in the previous work [6]. Figure III-12 shows the interfacial excess concentrations calculated thus at each concentration of PVA. The interfacial excess concentration increases from 1.2×10^{-7} molm^{-2} at $C_{PVA}=1.0 \times 10^{-6}$ wt% to 1.6×10^{-5} molm^{-2} at $C_{PVA}=1.0 \times 10^{-3}$ wt% for PVA11 and from 5.5×10^{-5} molm^{-2} at $C_{PVA}=1.0 \times 10^{-6}$ wt% to 8.5×10^{-4} molm^{-2} at $C_{PVA}=1.0 \times 10^{-3}$ wt% for PVA13, respectively. Figure III-13 shows the dependence of the interfacial area occupied by one molecule of PVA on the concentration of PVA. The occupied interfacial areas decrease with the concentration of PVA and then, become constant. For example, these areas decrease from 1.3×10^{-5} μ m^2 at $C_{PVA}=1.0 \times 10^{-6}$ wt % to 1.0×10^{-7} μ m^2 at $C_{PVA}=1.0 \times 10^{-3}$ wt% for PVA11 and from 3.0×10^{-8} μ m^2 at $C_{PVA}=1.0 \times 10^{-6}$ wt % to 2.1×10^{-9} μ m^2 at $C_{PVA}=1.0 \times 10^{-3}$ wt% for PVA13, respectively. Their dependence on the concentration was extremely different according to the PVA species. PVA13 with higher surface activity resulted in the lower interfacial area due to the larger excess concentration. Namely, the adsorbed amount of PVA13 is larger than that of PVA11 at the same concentration.
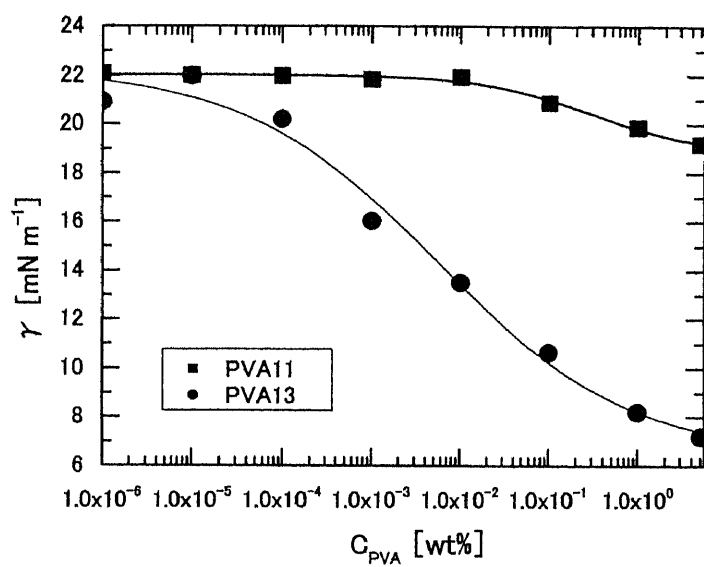
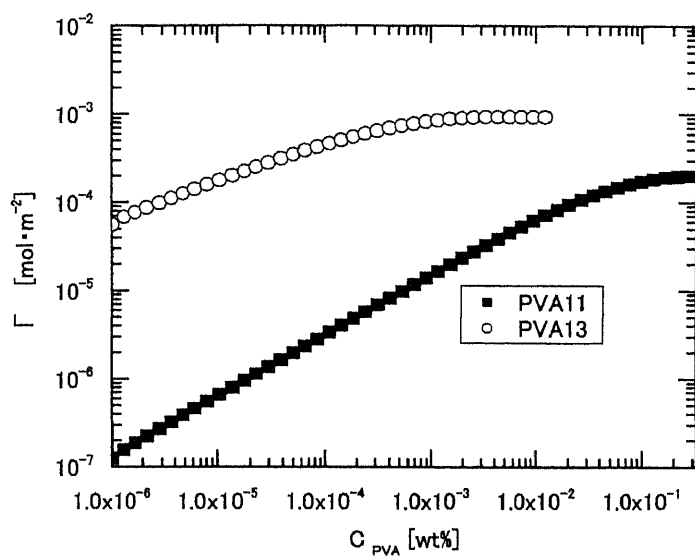Figure III-11   The dependence of interfacial tension on the concentration of PVA

Figure III-12 The dependence of the interfacial excess concentration on the concentration of PVA
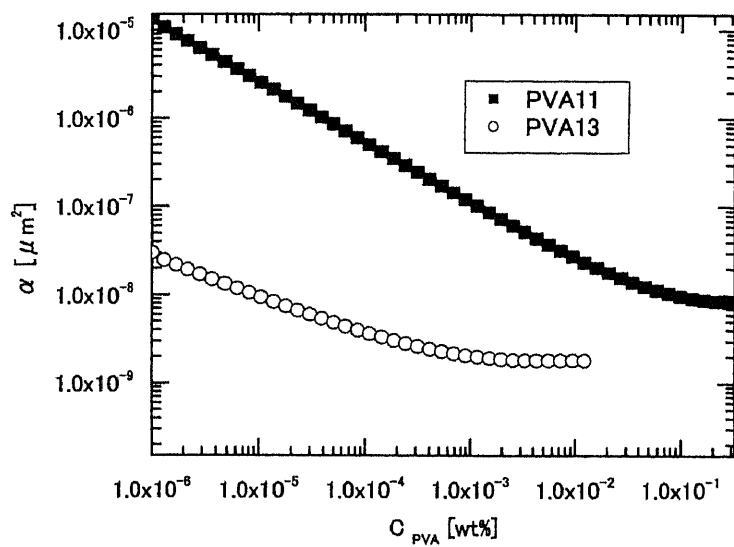
Figure III-13   The dependence of the interfacial area occupied by one molecule of PVA on the

concentration of PVA

Dependence of the growth rate of the microcapsule shell on the microcapsule diameter and the concentration of PVA

Figure III-14 shows the effect of the microcapsule diameter on the growth of the microcapsule shell at the concentration of PVA13 of 1.0×10^{-4} wt% together with the standard deviation of the shell thickness. From this result, the following important informations may be obtained. With the polymerization time, the thickness of the microcapsule shell (T) (in μ m) increases considerably faster in the initial region of polymerization, but increases slowly after about 1.0 h. The larger the microcapsule diameter, the thicker the microcapsule shell at each polymerization time [10]. The almost same results were obtained for PVA11. These results agree well with those by Kubo *et* al [11]. In order to obtain the more detailed informations for this result, the effect of the concentration of PVA on the growth of the microcapsule shell was investigated.

Figure III-15 shows how the species and the concentration of PVA affect the growth of the microcapsule shell at the different microcapsule diameter. From these results the following important results are obtained. The initial growth rate of the microcapsule shell (S_g) (in μm $\cdot$ h^{-1}) was different according to the species and the concentration of PVA. The shell thickness increases faster with the lower concentration of PVA in the initial region of polymerization.

However, the final thickness of microcapsule shell became almost the same at each microcapsule diameter irrespective to the PVA species.

This result may suggest that the adsorption layer of PVA influenced the growth rate is the diffusion rate, namely of the water soluble monomer across this layer and polymerization proceeded to the same degree depending on the amount of both monomer.
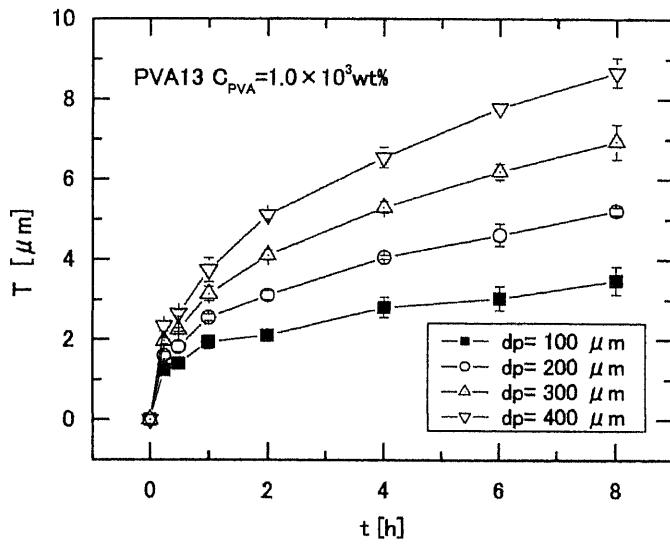
Figure III -14   The effect of the microcapsule diameter on the growth of the microcapsule shell at the concentration of PVA13 of 1.0×10^{-4} wt%
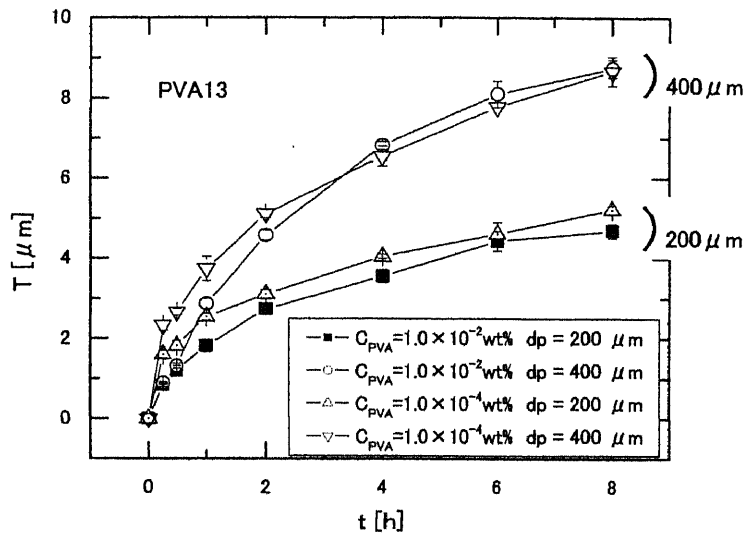
Figure III-15 (a) The effect of species and the concentration of PVA affect the growth of the microcapsule shell at the two size of microcapsule diameter (PVA13)
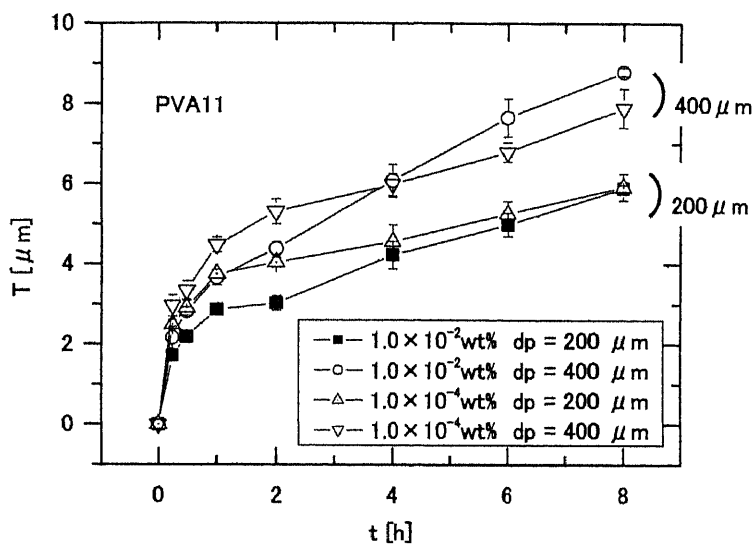
Figure III-15 (b) The effect of species and the concentration of PVA affect the growth of the microcapsule shell at the two size of microcapsule diameter (PVA11)

Dependence of the initial growth rate on the interfacial area occupied by one molecule of PVA

Figure III-16 shows the dependence of the initial growth rate on the interfacial area occupied by one molecule of PVA. It was found that the initial growth rate decreases with the decrease in the interfacial area. Here, the initial growth rate was estimated by the slope of the T-t curve at the origin in Figure III-15.

It is found that each plot in Figure III-16 was almost on a straight line and the lager, the microcapsule diameter the larger the initial growth rate regardless of a kind of PVA This means that the initial growth rate is strongly affected by the adsorbed amount of the PVA molecule.

Namely, the transfer rate of the water-soluble monomer across the interface is decreased by the adsorption of the PVA molecule. The difference in the growth rate due to the microcapsule diameter may be attributable to the difference in the amount of HMDI in a microcapsule and the concentration of the water-soluble monomer per unit interfacial area [11]. Namely, as the microcapsule diameter increases, the surface area of the microcapsule per microcapsule volume decreases, and the amounts of HMDI and HMDA per unit interfacial area increase. As the other effect of the microcapsule diameter, the interfacial disturbance which affects the mass transfer rate of the monomer may be considered. Namely, the larger the microcapsule diameter, the larger the degree of the interfacial disturbance. This may increase the mass transfer rate.
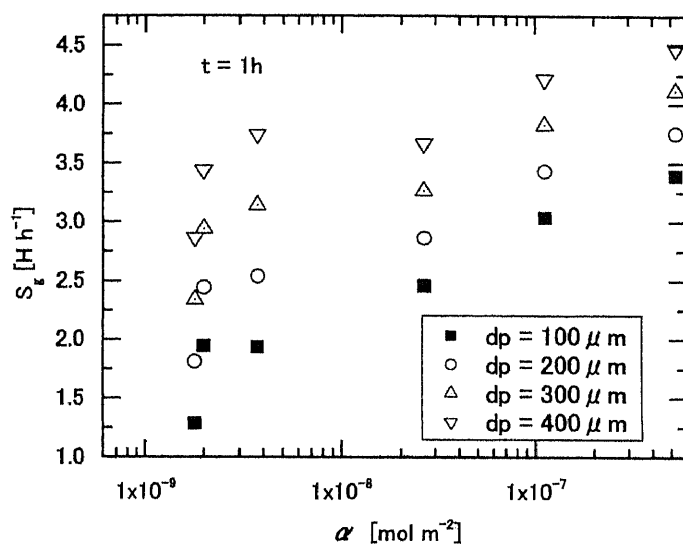
Figure III-16 Dependence of the initial growth rate on the interfacial area occupied by

one molecule of PVA

4. CONCLUSION

In order to obtain the fundamental informations required to prepare the microcapsules by interfacial polycondensation polymerization, the (O/W)emulsion was prepared by dispersing the limonene oil in the aqueous solution of PVA and the microcapsule was prepared by the polycondensation reaction between isocyanate and amine. It was investigated how the PVA species with the different degree of saponification affected interfacial polycondensation and the microencapsulation process.

The following results were obtained.

1. The initial growth rate of the microcapsule shell was different by the species and the concentration of PVA. Furthermore, the larger the microcapsules, the larger the initial growth rate.

2. The initial growth rate decreased with the decrease in the interfacial area occupied by a PVA molecule.

Nomenclature

C_{PVA}	=	concentration of PVA	[wt%]
d_p	=	microcapsule diameter	[μm]
S_g	=	initial growth rate of the microcapsule shell	[μm·h^{-1}]
T	=	thickness of the microcapsule shell	[μm]
t	=	reaction time	[h]
W	=	load imposed on the microcapsule	[N]
α	=	interfacial area occupied by one molecule of PVA	[μm^2]
Γ	=	interfacial excess concentration	[mol·m^{-2}]
γ	=	interfacial tension	[mN·m^{-1}]
σ	=	loaded pressure	[Pa]

Reference

[1] Kondo T.; Koishi M.; "Microcapsule (Shinpan Maikurokapuseru)", Sankyo Shuppan co., Tokyo, Japan(1989)

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Chapter IV

Mechanical Strength of Polyurea Capsules

---

1. Introduction

In this microencapsulation process, in order to prepare the superior microcapsules, it is necessary to form the stable emulsion in advance. In the previous study, the adsorption layer of PVA species affects polycondensation reaction, namely the shell growth of microcapsules was investigated. The initial growth rate of the microcapsule shell was different by the species and the concentration of PVA. And it became clear that absorption forms of PVA were different.

The purpose of this section is to investigate how PVA with the different saponification degree affects polycondensation reaction, namely the mechanical strength of the microcapsules. We considered whether the surfactant affects the structure of microcapsule shell

2. Experimental

Materials

The characteristics of Poly(vinyl alcohols) (PVA, Kuraray Co.) with the different saponification degree used as the water soluble stabilizer are shown in Table IV- I .

(R)-(+) limonene (Kanto Chemical Co.) and distilled water were used as the dispersed phase and as the continuous phase, respectively.

Hexamethylene diisocianate (HMDI) as an oil soluble monomer and hexamethylenediamine (HMDA) as a water soluble monomer were used without further purification.Measurements of physical properties and mechanical strength

Interfacial tension was measured between limonene and PVA solution with the Surface

Tension Meter. The interfacial excess concentrations (Γ) (in mol·m^{-2}) and the interfacial area occupied by one PVA molecule were estimated by the same method as in the previous one [1].

The microcapsule which was sample out at elapsing designated time were dried on the filter paper all day long. The mechanical strength and the diameter of Microcapsules were measured by Micro Compression Testing Machine (MCT-W 201 Shimadzu.co) one at the time.

Preparation of microcapsules

Microcapsules were prepared using a few kinds of PVA. **Figure IV-1** shows a flowchart of preparing the microcapsules.

Microcapsules were prepared under the various concentration of each PVA. Figure IV-1 shows a flowchart of preparing microcapsules.

At first, (O/W) emulsion was prepared prior to microencapsulation. The constant volume (4×10^{-6} m^3) of limonene dissolving HMDI(4×10^{-3} kg) was poured into the continuous water phase of the volume of 10×10^{-5} m^3 , where PVA of the given concentration was dissolved. Then, this mixture was stirred for 15 min under the condition of the revolution speed of 50 s^{-1} and 60℃ using a homogenizer (Biomixer BM-2M,Nippon Seiki Co.).

Polycondensation reaction was started under the condition of the revolution speed of 6.7s^{-1} (by the six bladed paddle impeller with a diameter of 5.4 × 10^{-2}m) and 60℃ after the aqueous solution (10×10^{-6} m^3)dissolving HMDA(2.7 × 10^{-3}kg) was poured into (O/W) emulsion. From beginning of reaction, microcapsules were sampled out by the pipet at the elapsing time designated beforehand. The microcapsules sampled were washed in distilled water twice.

Table IV- I   Kind of PVA and their characters

Kind of PVA	Saponification degree	Polymerization degree
PVA 11	98~99	1700
PVA 13	87~89	1700

```
┌─────────────────────────────┐
│  PVA aqueous solution       │
└─────────────────────────────┘
              │
      ◇ Homogenization ◇        ◄───  ┌──────────────────────────┐
           50 s⁻¹                      │ Limonene as core         │
               60 °C                   │ Material dissolving HMDI │
              │                        └──────────────────────────┘
      ◇ O/W dispersion ◇
              │
   ◇ Interfacial polycondensation ◇  ◄───  ┌────────┐
           Polymerization                    │ HMDA   │
           6.7 s⁻¹                            └────────┘
                  60 °C
              │
       ┌────────────────┐
       │  Microcapsul   │
       └────────────────┘
```
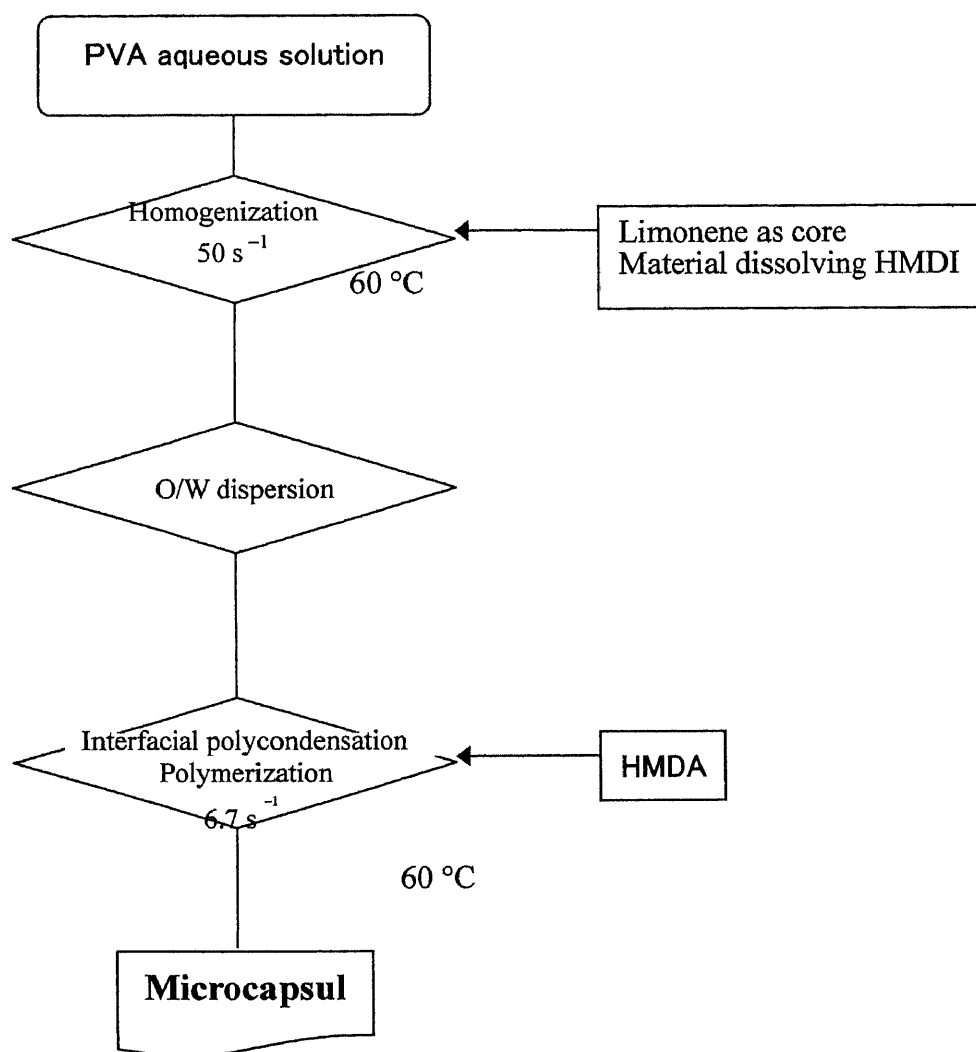
Figure IV-1   Flowchart of preparing microcapsules

3. Results and discussion

Interfacial excess concentration and the Interfacial area occupied by one molecule

Figure IV-2 shows the dependence of the interfacial tension on the concentration of PVA. The interfacial tension decreases with an increase in the concentration of PVA. PVA13 results in the interfacial tension considerably lower than PVA11. For example, the interfacial tension decreases from γ=22 to 19 [mN m^{-1}] for PVA11 and from γ=22 to 7.0 [mN m^{-1}] for PVA13, respectively. This result agree with the fact that PVA with many acetyl groups in a molecule gives the lower interfacial tension [1]. The interfacial excess concentration and the interfacial area occupied by one molecule of PVA (α) (in μ m^2) were estimated by the same method as in the previous work [1]. Figure IV-3 shows the interfacial excess concentrations calculated thus at each concentration of PVA. The interfacial excess concentration increases from 1.2×10^{-7} molm^{-2} at C_{PVA}=1.0×10^{-6} wt% to 1.6×10^{-5} molm^{-2} at C_{PVA}=1.0×10^{-3} wt% for PVA11 and from 5.5×10^{-5} molm^{-2} at C_{PVA}=1.0×10^{-6} wt% to 8.5×10^{-4} molm^{-2} at C_{PVA}=1.0×10^{-3} wt% for PVA13, respectively. Figure IV-4 shows the dependence of the interfacial area occupied by one molecule of PVA on the concentration of PVA. The occupied interfacial areas decrease with the concentration of PVA and then, become constant [2]. For example, these areas decrease from 1.3×10^{-5} μ m^2 at C_{PVA}=1.0×10^{-6} wt % to 1.0×10^{-7} μ m^2 at C_{PVA}=1.0×10^{-3} wt% for PVA11 and from 3.0×10^{-8} μ m^2 at C_{PVA}=1.0×10^{-6} wt % to 2.1×10^{-9} μ m^2 at C_{PVA}=1.0×10^{-3} wt% for PVA13, respectively. Their dependence on the concentration was extremely different according to the PVA species. PVA13 with higher surface activity resulted in the lower interfacial area due to the larger excess concentration. Namely, the adsorbed amount of PVA13 is larger than that of PVA11 at the same concentration.
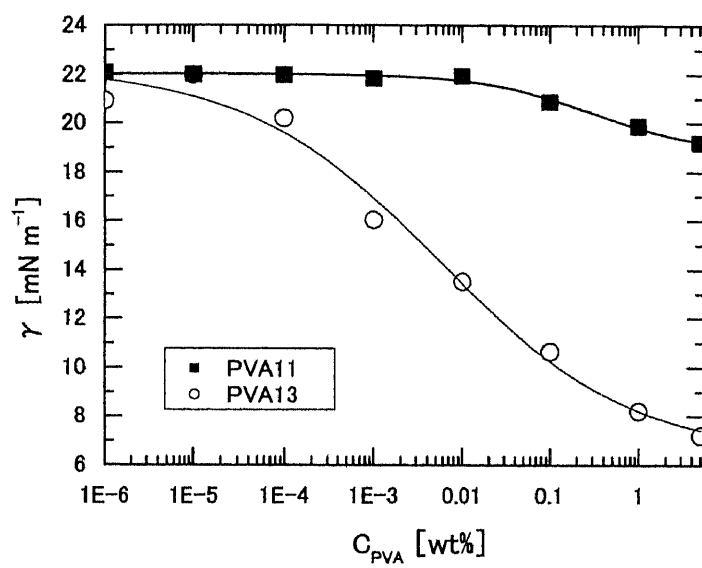
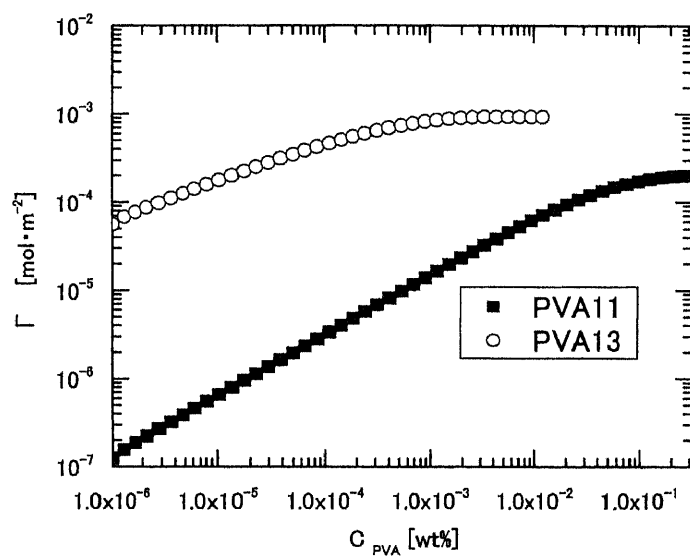**Figure IV-2** The dependence of interfacial tension on the concentration of PVA

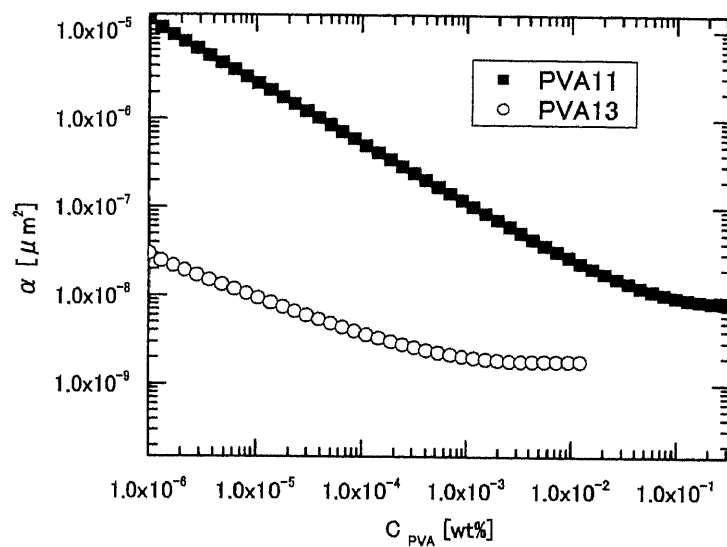**Figure IV-3**   The dependence of the interfacial excess concentration on the concentration

of PVA

Figure IV-4   The dependence of the interfacial area occupied by one molecule of PVA

on the concentration of PVA

Mechanical strength of the microcapsule

Figure IV-5 shows the effect of the concentration of PVA on the mechanical strength of the microcapsule with $d_p = 200 \mu$ m. In this figure, P is the loaded pressure (Pa) (in Pa) that can be calculated according to the following equation [3]:

$$P = W/[\pi (d_p/2)^2]$$

Where W is the load imposed on the microcapsule (W) (in N)

From Figure IV-5, it was found that the mechanical strength of the microcapsule became larger in the initial region of polymerization and them constant with the reaction time (t) (in h). Moreover, the initial mechanical strength of the microcapsule was different according to the species and the concentration of PVA.

Figure IV-6 shows the relationship between the ratio (T/d_p) of the shell thickness (T) to the microcapsule diameter(dp) and the breakdown stress (σ). Here, the values of the breakdown stress are calculated according to the Oishi's theory using the following equation [3]:

$$\sigma = P/[4(T/d_p)]$$

From this figure, it was found that the breakdown stress linearly increased with the values of (T/d_p). Namely, the microcapsules can be broken more easily with the increase in the diameter and the decrease in the shell thickness [4].

4. Conclusions

In order to obtain the fundamental informations required to prepare the microcapsules by interfacial polycondensation polymerization, the (O/W)emulsion was prepared by dispersing the limonene oil in the aqueous solution of PVA and the microcapsule was prepared by the polycondensation reaction between isocyanate and amine. It was investigated how the PVA species with the different degree of saponification affected interfacial polycondensation and the microencapsulation process. The mechanical strength and the diameter of Microcapsules were measured

The following results were obtained.

1. It was suggested that the mechanical strength of the microcapsule increased with the growth rate of microcapsule shell

2. It was suggested that the structure of the microcapsule shell was the same irrespective to the species and the concentration of PVA
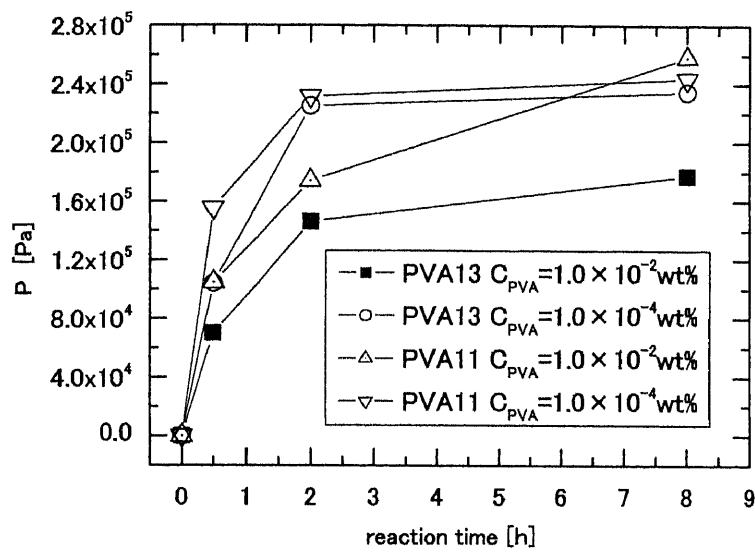
Figure IV-5 The effect of the concentration of PVA on the mechanical strength of the
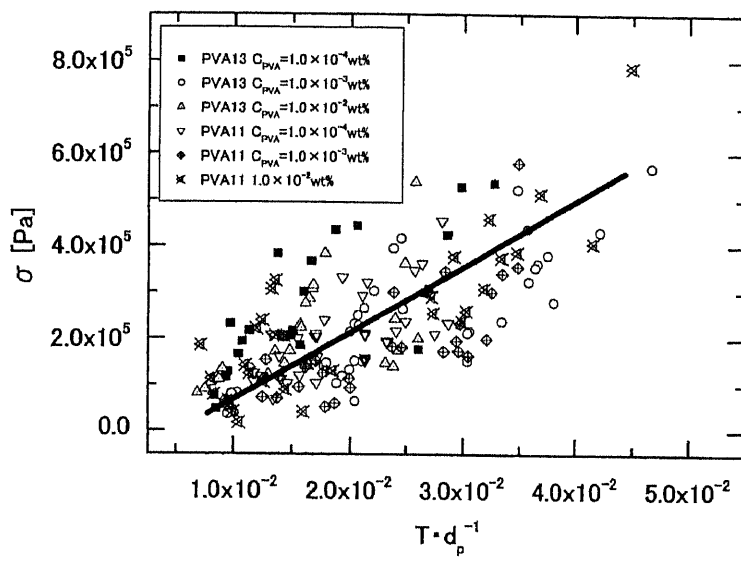
microcapsule at dp = 200 μ m

Figure IV-6   Relationship between the ratio (T/dp) of the diameter to the wall

thickness (T) (in mm) and breakdown stress (σ) (in Pa)

Nomenclature

C_{PVA} = concentration of PVA [wt%]

d_p = microcapsule diameter [μm]

S_g = initial growth rate of the microcapsule shell [μm·h^{-1}]

T = thickness of the microcapsule shell [μm]

t = reaction time [h]

W = load imposed on the microcapsule [N]

α = interfacial area occupied by one molecule of PVA [μm^2]

Γ = interfacial excess concentration [mol·m^{-2}]

γ = interfacial tension [mN·m^{-1}]

σ = loaded pressure [Pa]

Reference

[1] Mizuno, K.; Taguchi, Y.; Tanaka M.;"A fundamental study on encapsulation of an oil phase ingredient by polycondensation polymerization," *J.Chem.Eng.Japan* 2004, 37, 882

[2] Mizuno, K. Y. Taguchi, M Tanaka,; "The effect of surfactant layer on the growth rate of the polyurethane capsule shell,"*J.Chem.Eng.Japan* 2005, 38, 45

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Chapter V

Effect of monomer concentration on the growth rate of polyurea capsule shell and permeability of an oil ingredient

1. Introduction

We investigated effect of the surfactant adsorption layer on the growth of the polyurea capsule shell.

And the following results were obtained.[1-2]

1. The initial growth rate of the microcapsule shell was different according to the species and concentration of PVA. Furthermore the larger the microcapsules, the larger the initial growth rate.

2. It was suggested that the mechanical strength of microcapsule increased with the growth rate of microcapsule shell and the structure of the microcapsule shell was the same irrespective to the species and the concentration of PVA.

3. The growth rate of the microcapsule shell became slow with reaction time. And the thickness of the microcapsule shell became fixed finally.

In the interfacial polycondensation polymerization on the interface between the oil phase and the water phase, the water-soluble monomer which passed the microcapsule shell reacts with the oil-soluble monomer. [3-5]

In order to understand these phenomena easily, the formation model of the microcapsule shell is shown in Figure V-1. The microcapsule shell, which was made, obstructs diffusion of a water-soluble monomer. In other words it is suggested that diffusion resistance of a monomer increases with the thickness of the microcapsule shell. Therefore it is suggested that the rate of reaction become low. At present, we do not understand whether reaction stops owing to diffusion resistance of the monomer or not.

In this study, it is the main purpose to clarify whether the growth rate of the shell depends on the diffusion resistance of monomer through the shell or not.

Therefore we examined the effect of the monomer concentration and investigated the following things.

- To observe the microcapsule and the growth rate of the microcapsule shell thickness
- To measure the consumption of HMDA in the continuous phase
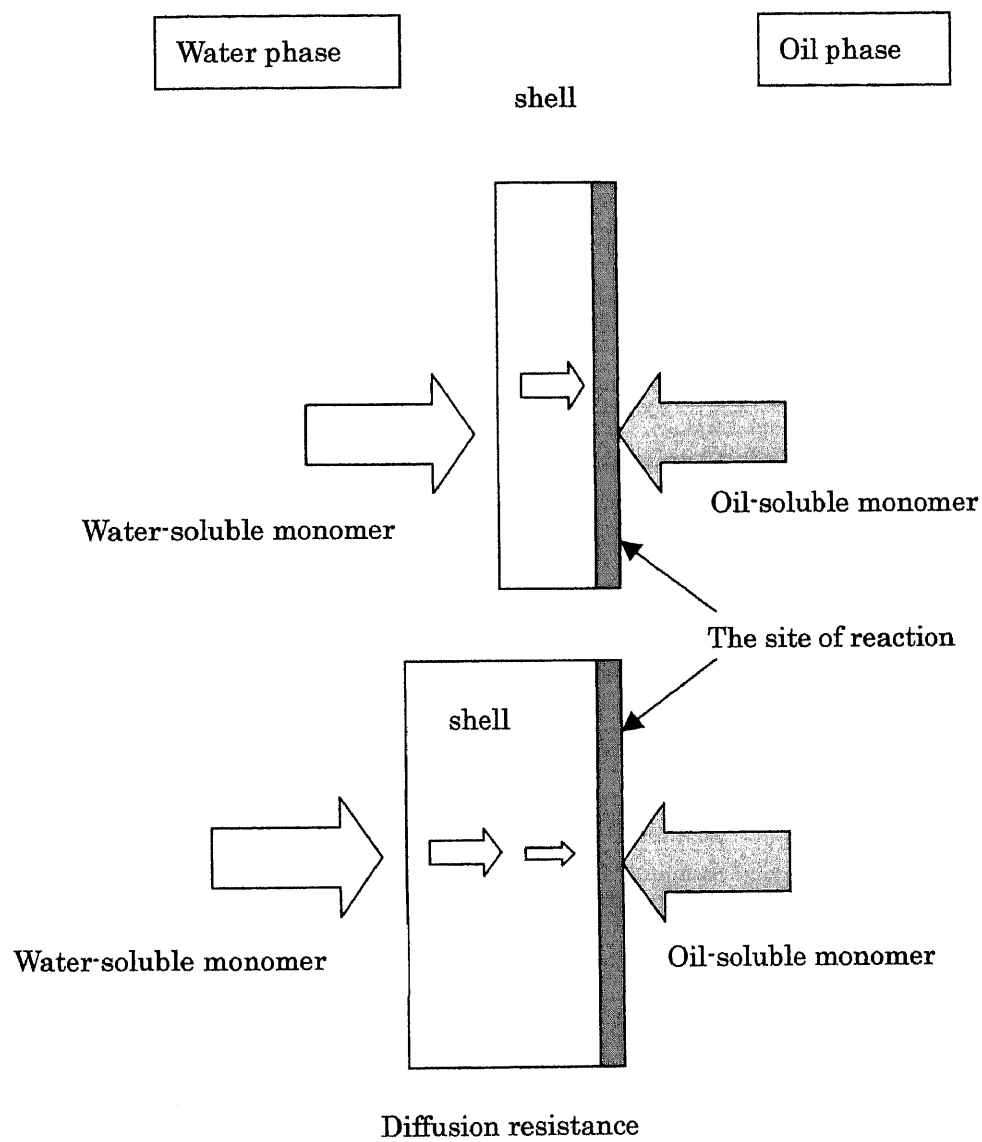- To measure the released amount of limonene ingredient as core material

Figure V-1   Forming model of the microcapsule shell

2. Experimental

Materials

The Poly(vinyl alcohols) (Saponification degree 87~89, Polymerization degree 1700) (PVA, Kuraray Co.) was used as the water soluble stabilizer.

(R)-(+) limonene (Kanto Chemical Co.) and distilled water were used as the dispersed phase and as the continuous phase, respectively.

Hexamethylene diisocianate (HMDI) as an oil soluble monomer and hexamethylenediamine (HMDA) as a water soluble monomer were used without further purification.Hydrochloric acid and Phenolphthalein solution were used to measure the amount of amine in the continuous phase.

Preparation of microcapsules

Microcapsules were prepared under the various monomer concentrations (Table V-1). Figure V-2 shows a flowchart of preparing the microcapsules.

At first, (O/W) emulsion was prepared prior to the microencapsulation process. The constant volume (4×10^{-6} m^3) of limonene dissolving HMDI of the given concentration was poured into the continuous water phase of the volume of 10×10^{-5} m^3, where PVA (0.001wt%) was dissolved. Then, this mixture was stirred for 15 min under the conditions of the revolution speed of 50 s^{-1} and 60℃ using a homogenizer (Biomixer BM-2M,Nippon Seiki Co.).

Polycondensation reaction was started under the conditions of the revolution speed of 6.7s^{-1} (by the six bladed paddle impeller with a diameter of 5.4 $\times$ 10^{-2}m) and 60℃ after the aqueous solution (10×10^{-6} m^3)dissolving HMDA(2.7 $\times 10^{-3}$kg) was poured into (O/W) emulsion. From beginning of reaction, microcapsules were sampled out by the pipet at the elapsing time designated beforehand. For neutralization titration, as for the filtered solution, the solution was measured 10ml exactly. The microcapsules sampled were washed in distilled water twice.

Table V-1 The monomer concentrations

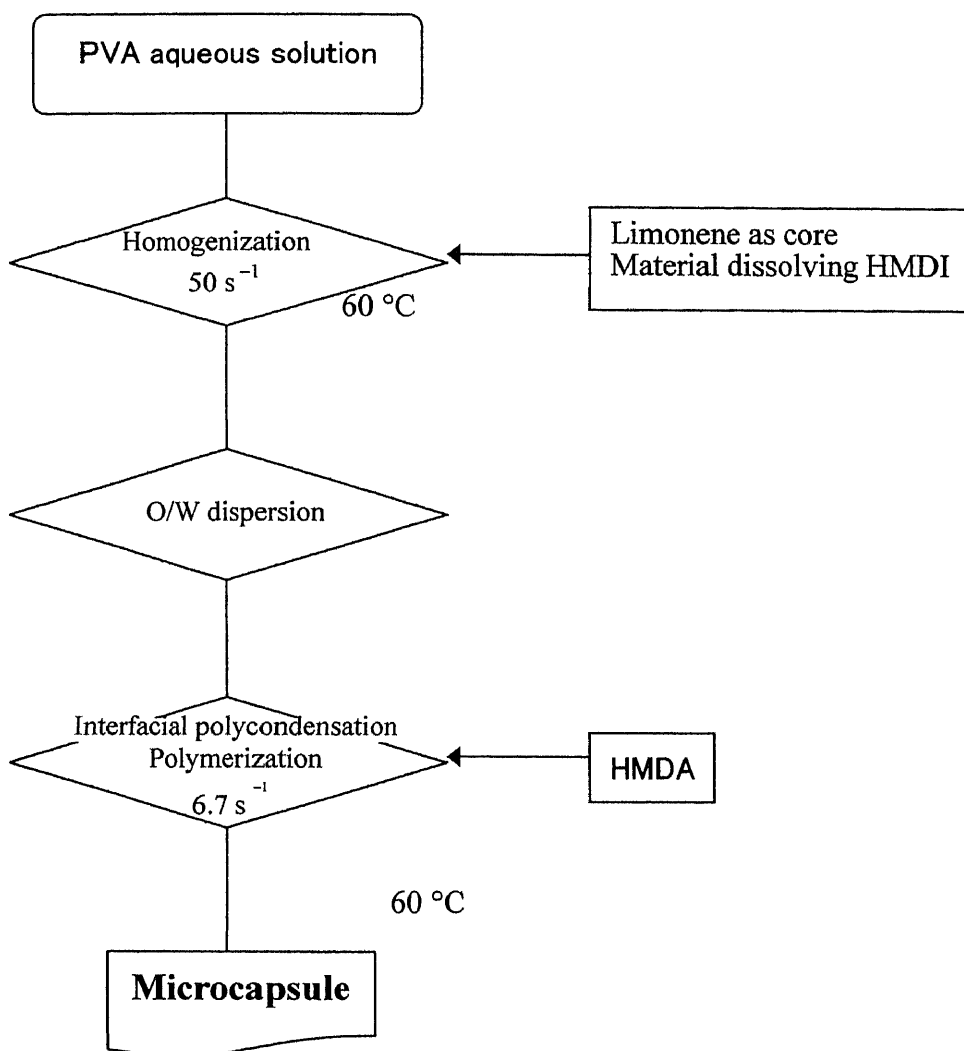| No.	①	②	③
Continuous water phase PVA (0.001wt%) was dissolved	200g	200 g	200g
Water soluble monomer HMDA	0.024M (2.79g)	0.048M(5.58g)	0.096M (11.16g)
Core Limonene	10.0g	10.0g	10.0g
Oil soluble monomer HMDI	0.024M (4.04g)	0.048M (8.08g)	0.096M (16.16g)

Figure V-2 Flowchart of preparing microcapsules

Observation of microcapsule and measurement of shell thickness

The whole, the cross-section of microcapsules were observed by scanning electron microscopy (SEM). Microcapsule diameter (d_p) (in μ m) was measured as the Sauter Diameter by Centrifugal Particle Analyzer (SA-CP3, Shimadzu Co.). The shell thickness was measured as follows. Microcapsule of each mean diameter was sliced by sharp knife. These sliced microcapsules were observed by scanning electron microscopy (SEM). The shell thickness was measured at five points per a microcapsule and the mean shell thickness was calculated from five values.

Measurement of monomer concentration

From beginning of reaction, the water phase was sampled out by the pipet at the elapsing time designated beforehand to measure the monomer concentration in the continuous phase. The solution was filtered and neutralized by hydrochloric acid (1N). The phenolphthalein solution was used as an indicator.

Measurement of the amount of limonene ingredient released

The filtered microcapsules were measured about 1g by a laboratory dish. Then, this laboratory dish was put under the condition of 60 ℃ and decrease in weight of microcapsules was measured.

3. Results and discussion

Observation of microcapsule and growth rate of the microcapsule shell thickness

Figure V-3 shows the SEM photographs of the cross-section of microcapsules. From these results, it is found that the shell thickness becomes thicker with the reaction time and with the monomer concentration. And it seems that internal structure of a capsule is different due to the monomer concentration. We thought that the difference of this morphology was made by reaction speed.

Figure V-4 shows the effect of the monomer concentration on the growth of the

microcapsule shell. From these results, it is found that the shell thickness becomes thicker with the monomer concentration. The rate of reaction decreases with reaction time and becomes constant at the elapsing time of 30hr. **Figure V-5** shows the results of the shell thickness measured after 48hr. From these results, the shell thickness is found to be proportional to the concentration of a monomer finally.

And then, the initial shell growth rate increases with the monomer concentration. **Figure V-6** shows the dependence of the initial shell growth rate on the monomer(HDMA) concentration at dp = 300μ m. The initial shell growth rate was estimated by measuring the slope of the T-t curve at the origin in Figure V-4. From Figure V-6, it is found that the initial shell growth rate increases with the monomer(HDMA)concentration. Namely, the initial shell growth rate depended on the monomer concentration.

From these results, it seems that the reaction was stopped at the elapsing time of 30hr. But it is very important to know whether reaction is stopped by increase in diffusion resistance for the monomer or not.

Then, we investigated whether the monomer was completely consumed or not.

Reactiontime[hr]	①	②	③
0.5			
1			
2			
4			
8			
48			
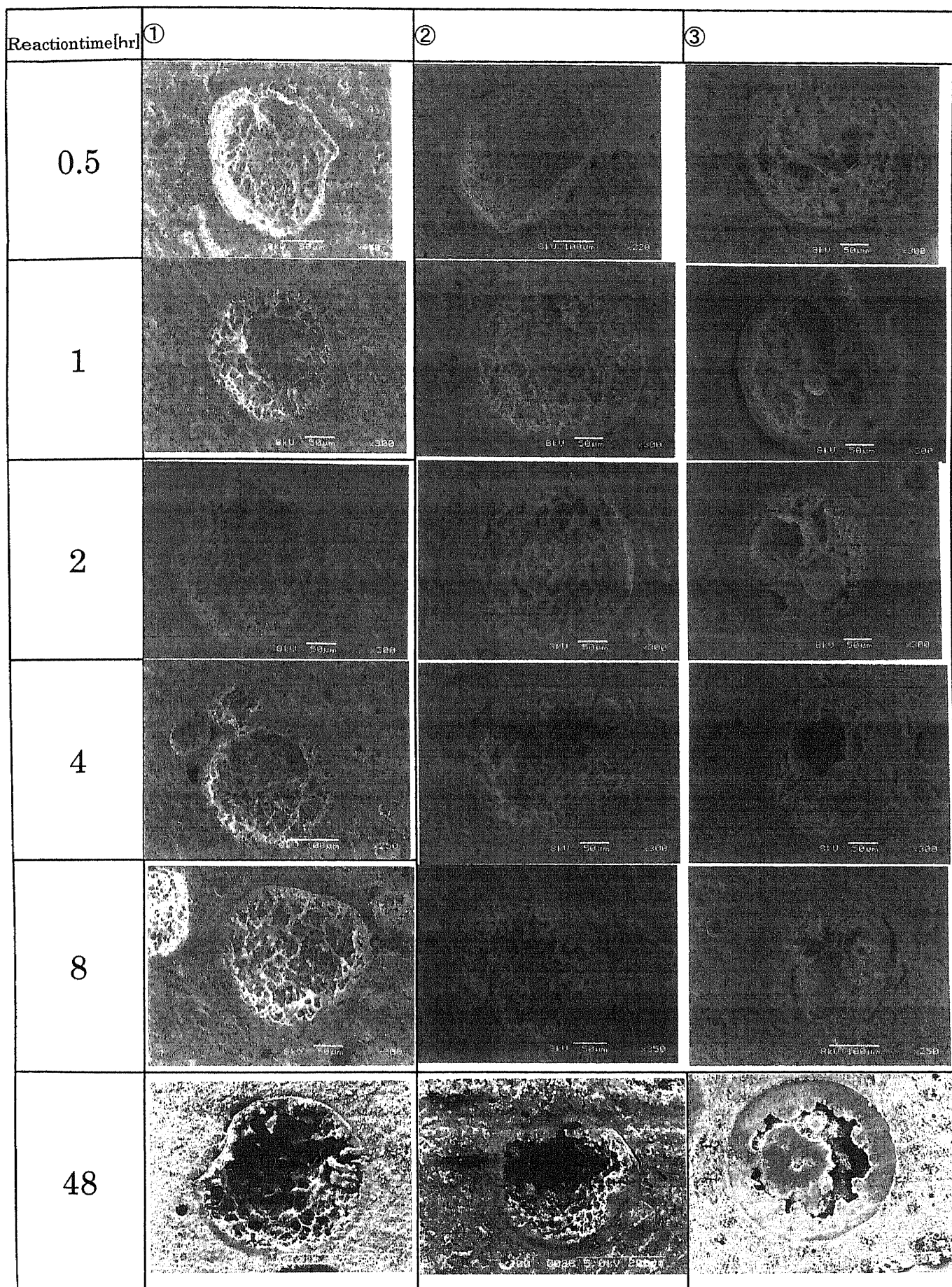
Figure V-3 SEM photographs of the cross-section of microcapsules
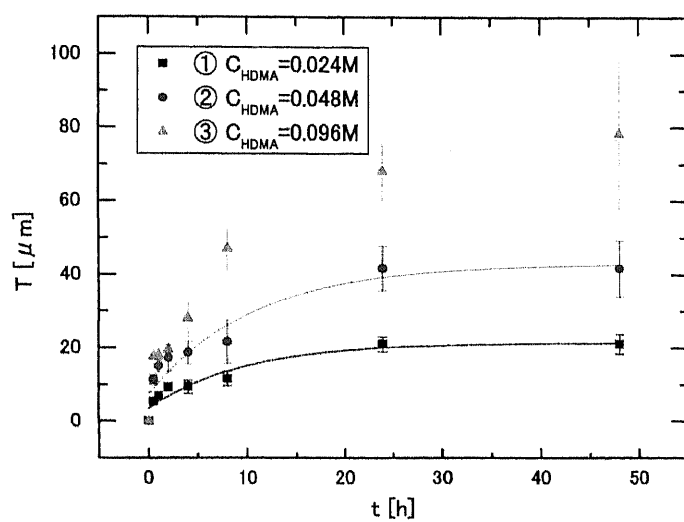
Figure V-4 The effect of the monomer concentration on the growth of the microcapsule
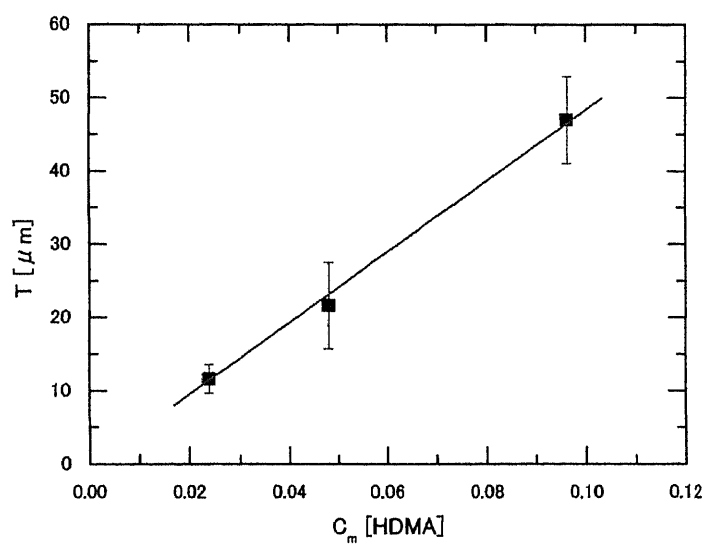
shell at dp = 300 μ m

Figure V-5   Dependence of the shell thickness on the monomer(HDMA) concentration
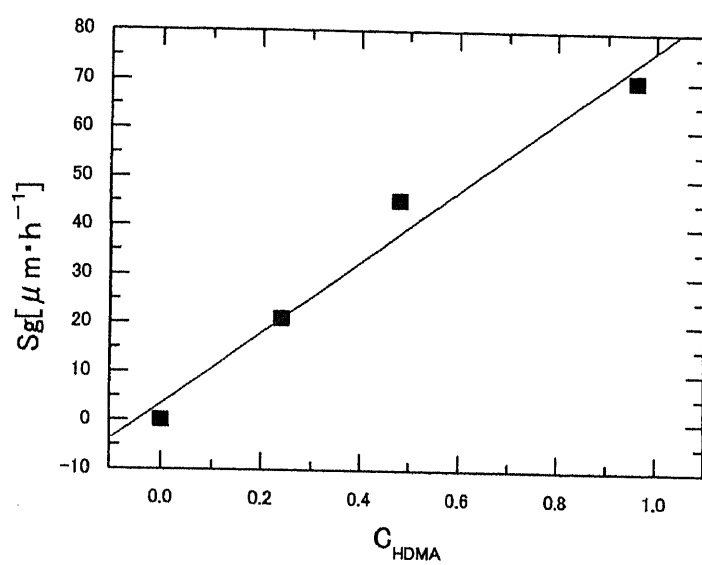
at dp=300 μ m

Figure V-6 Dependence of the initial growth rate on the monomer(HDMA)
concentration at dp = 300 μ m

The consumption of HMDA in the continuous phase

Figure V-7 shows the consumption of HMDA in the continuous phase. The monomer was consumed by the reaction in 30hr almost.

The consumption ratio of a monomer decreased slowly. It was found that growth rate of the microcapsule shelldecreased slowly, as a monomer was used more. However, monomer added was consumed in 30hr. **Figure V-8** shows the comparison with Figure V-7 and Figure V-3. The consumption of a monomer was corresponding to growth of a microcapsule shell. It was suggested that growth of the microcapsule shell was stopped by depletion of monomer. From this results, in the microencapsulation by interfacial polycondensation polymerization, a terminal of the reaction is not decided by diffusion resistance of the monomer transmitting in the shell but depends on depletion of the monomer

The released amount of limonene ingredient as core material

Figure V-9 shows the results of measuring the limonene ingredient released. From these results, it was found that the capsule had long release as a monomer is used more. **Figure V-10** shows the reciprocal number of thickness of a shell and the released amount of limonene ingredient (after 1hr). From these results, it was found that the reciprocal number of thickness of a shell has correlation with limonene ingredient released. In other words the thicker the microcapsule shell, the larger the diffusion resistance of limonene transmitting in the shell. Accordingly, it was found that the release rate of core material was strongly dependent on the shell thickness.
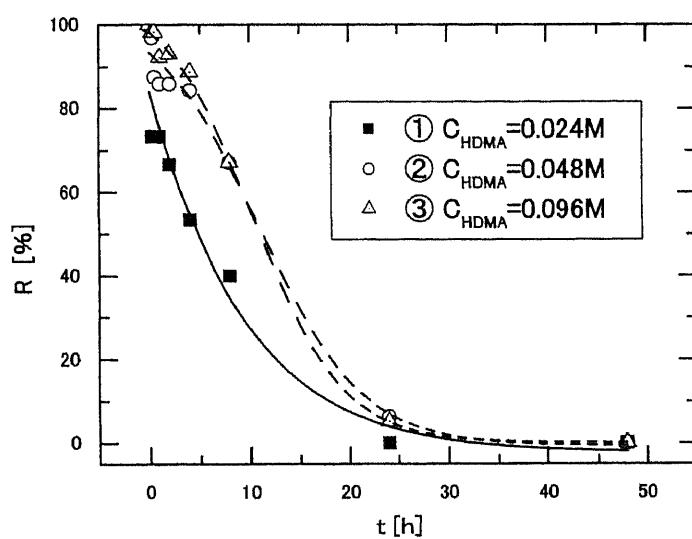
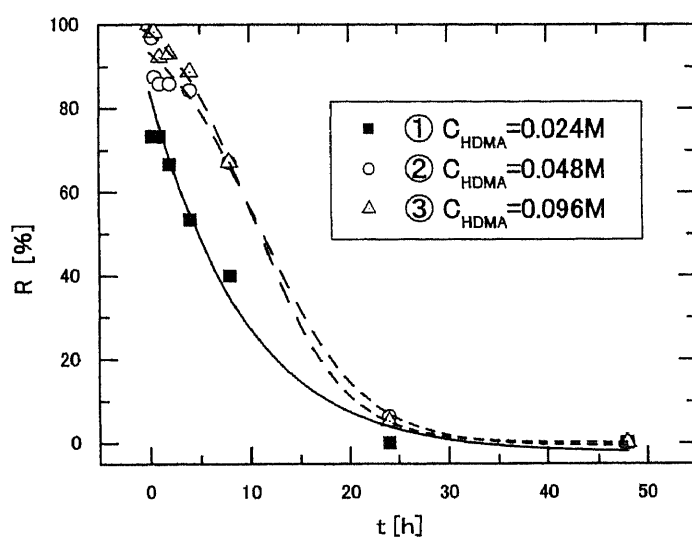Figure V-7 The consumption of HMDA in the continuous phase

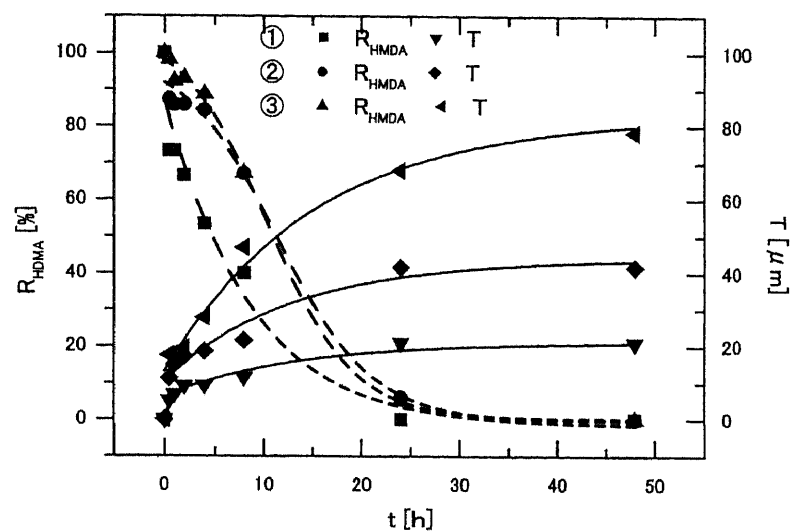Figure V-7 The consumption of HMDA in the continuous phase

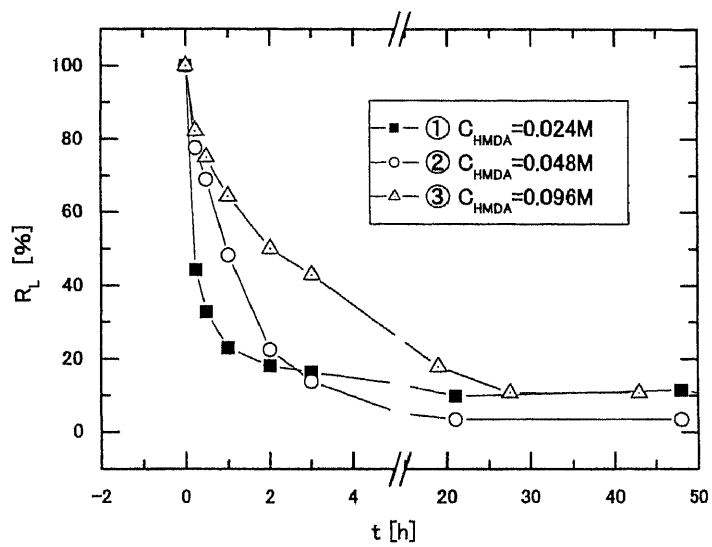Figure V-8 Comparison of the consumption of HMDA and the growth of the microcapsule shell

Figure V-9 Transient feature of released amount of limonene ingredient [8h]
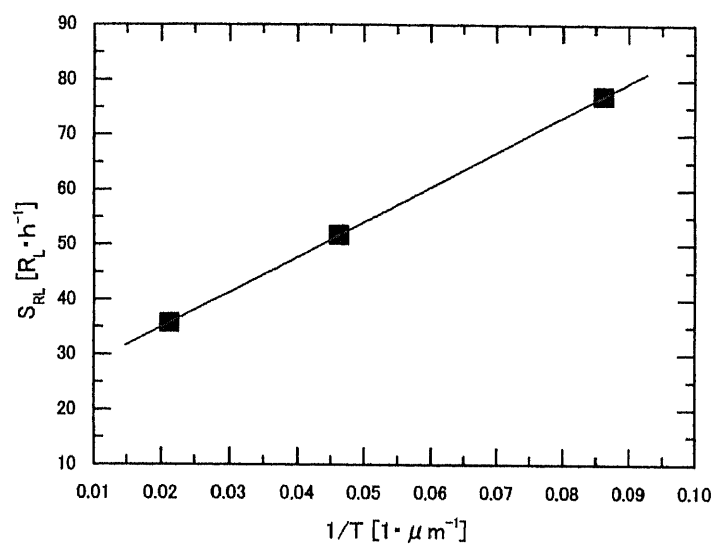
Figure V-10   The reciprocal number of thickness of a shell and the released amount of

limonene ingredient

4. Conclusions

In order to obtain the fundamental informations required to prepare the microcapsules by interfacial polycondensation polymerization, we investigated how the monomer concentration affected interfacial polycondensation and the microencapsulation process.

The following results were obtained.

1. The shell thickness was determined by the concentration of monomer finally.

2. The initial shell growth rate depended on the monomer concentration.

3. Growth of the microcapsule shell was stopped by depleting monomer

4. Release of the limonene ingredient was controlled by the shell thickness.

The microcapsule prepared by interfacial polycondensation polymerization has mono-core usually. The release from the mono-core type microcapsule, depends on the property of the shell. We knew that growth of the microcapsule shell was stopped by depleting monomer in this study. It is suggested that we can prepare the microcapsule which is able to control release of the core material, when the concentration of the monomer and size of the microcapsule are decided

Nomenclature

C_{PVA} = concentration of PVA   [wt%]

C_{HMDA} = concentration of HMDA   [wt%]

R_L = weight ratio of limonene ingredient retaining in a microcapsule [%]

d_p = microcapsule diameter   [μ m]

S_g = initial growth rate of the microcapsule shell   [μ m·h^{-1}]

S_{RL} = release rate of limonene ingredient   [R_L·h^{-1}]

T = thickness of the microcapsule shell   [μ m]

t = reaction time   [h]

Reference

[1] Mizuno, K.; Taguchi, Y.; Tanaka M.;"A fundamental study on encapsulation of an oil phase ingredient by polycondensation polymerization," *J. Chem.Eng.Japan* 2004, 37, 882

[2] Mizuno, K. Y. Taguchi, M Tanaka,; "The effect of surfactant layer on the growth rate of the polyurethane capsule shell,"*J. Chem.Eng.Japan* 2005, 38, 45

[3] Kondo T.; Koishi M.; "Microcapsule (Shinpan Maikurokapuseru)", Sankyo Shuppan co., Tokyo, Japan(1989)

[4] Janssen, L.J.J.M. and K. te Nijenhuis; "Encapsulation by interfacial polycondensation. I . The capsule production and a model for wall growth," *Journal of Membrance Science*, (1992) 65 59-68

[5] Janssen, L.J.J.M. and K. te Nijenhuis; "Encapsulation by interfacial polycondensation. II . The capsule production and a model for wall growth," *Journal of Membrance Science*, (1992) 65 69-75

Chapter VI

Conclusion

This thesis deals with the microencapsulation by interfacial polycondensation polymerization

In order to obtain the fundamental information required to prepare microcapsules by interfacial polycondensation polymerization, oil-in-water emulsions were prepared by dispersing limonene oil in the aqueous solution of PVA with different degrees of polymerization and saponification and the microcapsule was prepared by polycondensation reaction between isocyanate and amine. It was investigated how the amount of PVA adsorbed on the interface effects interfacial polycondensation polymerization and mechanical property. And then it was investigated how the monomer concentration effected interfacial polycondensation and the microencapsulation process.

The following results were obtained:

In Chapter I, the background of the thesis as well as a review of the previous work was given.

In Chapter II, the effects of adsorption behavior and the adsorption layer of PVA on stability of limonene droplets in the continuous water phase were investigated.

PVA with higher degrees of polymerization and saponification shows high surface and interfacial tensions. PVA with higher surface activity shows a lower interfacial area due to the larger excess concentration. From these results, the interfacial excess concentrations(Γ) for each PVA were evaluated according to the Gibbs equation; $\Gamma = -(d/RT)(d\gamma/dc)$. PVA which shows the smallest interfacial area occupied by one molecule gives the smallest coalescence rate.

And the fundamental information required for encapsulating the fine oil droplets was

obtained. From observation by the microscopic photograph of droplets, it is found that dispersed droplets are stable at the PVA concentration more than 1.0×10^{-2} wt%. And the diameter distributions of limonene droplets are found to be the normal distribution.

In Chapter III-1, the effects of the adsorption layer of the concentration of PVA on polycondensation was investigated. The initial growth rate of the microcapsule shell was different by the species and the concentration of PVA. Furthermore, the larger the microcapsules, the larger the initial growth rate.

From interfacial tension results, the interfacial excess concentrations(Γ) for each PVA were evaluated according to the Gibbs equation. And these results were compared with growth rate of microcapsule shell. The initial growth rate decreased with the decrease in the interfacial area occupied by a PVA molecule.

In Chapter III -2, the effects of the adsorption layer of PVA species on polycondensation reaction was investigated. The initial growth rate of the microcapsule shell was different by the species and the concentration of PVA. Furthermore, the larger the microcapsules, the larger the initial growth rate.

And the initial growth rate decreased with the decrease in the interfacial area occupied by a PVA molecule.

From these results, PVA species effects polycondensation reaction. Especially, the interfacial area occupied by a PVA molecule effects initial growth rate. It seems that the Surfactant adsorption layer obstructs monomer diffusion.

In Chapter IV, the mechanical strength and the diameter of microcapsules were measured. It was suggested that the mechanical strength of the microcapsule increased with the growth rate of microcapsule shell. It was investigated that relationship between the ratio (T/d_p) of the shell thickness (T) to the microcapsule diameter(dp) and the breakdown stress (σ). Here, the values of the breakdown stress are calculated according to the Oishi's theory using the following equation : $\sigma = P/[4(T/d_p)]$

From this equation, it was found that the breakdown stress linearly increased with the

values of (T/d_p). It was suggested that the structure of the microcapsule shell was the same irrespective to the species and the concentration of PVA

In Chapter V, it is the main purpose to clarify whether the growth rate of the shell depends on the diffusion resistance of monomer through the shell or not.

Therefore we examined the effect of the monomer concentration and observed the microcapsule and the growth rate of the microcapsule shell thickness

And it was suggested that the shell thickness relate to the concentration of monomer finally. And the initial shell growth rate depended on the monomer concentration.

Next the consumption of HMDA in the continuous phase was measured. And it was suggested that growth of the microcapsule shell was stopped by depleting monomer.

Next the released amount of limonene ingredient as core material was measured. And it was suggested that release of the limonene ingredient was controlled by the shell thickness.

From these results, the mechanism of microcapsule shell growth by interfacial polycondensation polymerization was clarified by a serial study.

Knowledge obtained in this study is shown as follows

- The factors of initial growth rate are the interfacial area occupied by one molecule, size of the microcapsule and concentration of the monomer. The interfacial area occupied by a PVA molecule affected initial growth rate irrespective of PVA species. It seems that the surfactant adsorption layer obstructs monomer diffusion.

- The shell thickness depends on the concentration of monomer. Growth of the microcapsule shell was stopped by depleting monomer.Release of the limonene ingredient was controlled by the shell thickness.

The microcapsule prepared by interfacial polycondensation polymerization has mono -core usually. The release from the mono-core type microcapsule depends on the property of the shell. We knew that growth of the microcapsule shell was stopped by depleting monomer in this study. It is suggested that we can prepare the microcapsule

which is able to control release of the core material, when the concentration of the

monomer and size of the microcapsule are decided

Acknowledgment