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Studies on Microcapsules. XVII.[1] Effect of Chemical Structure of Acid Dichlorides and Bisphenols on the Formation of Polyphenyl Ester Microcapsules

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Polyphenyl ester microcapsules were prepared by the interfacial polycondensation reactions between each of 2,2-bis(4-hydroxyphenyl)propane and 4,4′-dihydroxydiphenyl sulfone and each of *p*-phthaloyl dichloride and sebacoyl dichloride in the presence of alkali under various conditions.

The percentage of reacted bisphenols, and the size distribution and mean diameters of the microcapsules formed were determined and factors affecting them were studied.

The size distribution of the microcapsules was found to depend strongly on chemical structure of the reactants used. This was plausibly explained by taking account of the percentage of reacted bisphenols with the acid dichlorides. The mean diameters varied with the percentage of reacted bisphenols in a way similar to that for the size distribution.

In the preparation of microcapsules by the interfacial polycondensation method the size of microcapsules obtained was found to depend not only on the conditions for emulsification[3,4] but also on those for polycondensation.[5] However, no investigation has yet been carried out on the way in which the size distribution is affected by chemical structure of the reactants to be used for the preparation of microcapsules.

In this paper, therefore, an attempt was made to investigate the effect of chemical structure of acid dichlorides and bisphenols on the size of polyphenol ester microcapsules prepared from them.

Experimental

Materials——The bisphenols used as water soluble monomers in this work were 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) (Tokyo Kasei Ind. Co., Ltd., Tokyo) and 4,4′-dihydroxydiphenyl sulfone (bisphenol S) (Nika Kagaku Ind. Co., Ltd., Fukui). These were recrystallized before use.

p-Phthaloyl dichloride and sebacoyl dichloride, both of which are of reagent grade, were used as oil soluble monomers without further purification.

Preparation of Microcapsules——A) Preparation of Polyphenyl Ester Microcapsules: Preparation of polyphenyl ester microcapsules was made by utilizing the interfacial polycondensation reaction between bisphenols and acid dichlorides studied by Eareckson.[6]

In Table I are given the combinations of the bisphenols and the acid dichlorides adopted in this experiment.

The procedure consisted of the following three steps: 1. To 20 ml of 0.4M solution of bisphenol A or bisphenol S in aqueous 1.5M sodium hydroxide solution in a reaction vessel, as shown in Fig. 1, surrounded by ice was added an equal volume of distilled water. To this solution was added 200 ml of mixed organic solvent (chloroform–cyclohexane 1 : 3, v/v), containing 0—10% (v/v) Span 85 as emulsifier. Span 85 is a nonionic surfactant with chemical description of sorbitan trioleate (Atlas Power Co., Ltd., U.S.A.). The mixed solution was then mechanically emulsified with a Chemistirrer (Tokyo Rika Kikai Co., Ltd., Tokyo,

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Table I. Combinations of Bisphenols and Acid Dichlorides for Preparing Polyphenyl Ester Microcapsules

Bisphenol	Acid dichloride
2,2-Bis(4-hydroxyphenyl)propane	*p*-phthaloyl dichloride
2,2-Bis(4-hydroxyphenyl)propane	sebacoyl dichloride
4,4′-Dihydroxydiphenyl sulfone	*p*-phthaloyl dichloride
4,4′-Dihydroxydiphenyl sulfone	sebacoyl dichloride

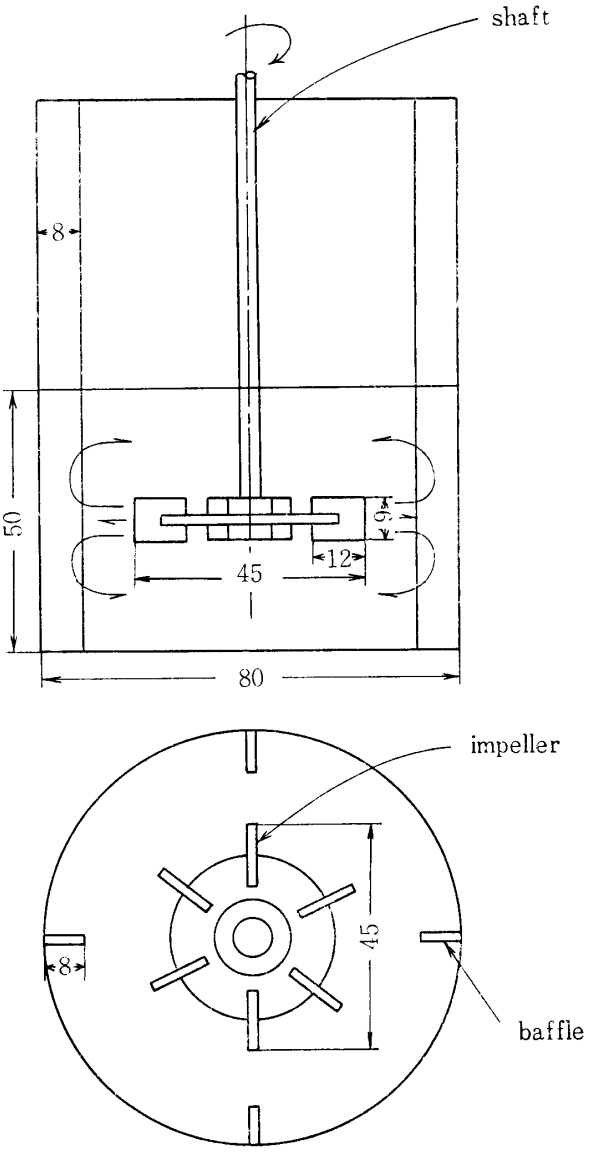

Fig. 1. Reaction Vessel
unit: mm

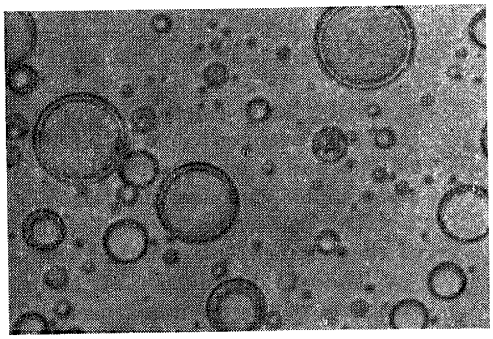

Fig. 2. Photomicrograph of Polyphenylsebacate Microcapsules prepared from Bisphenol S and Sebacoyl Dichloride in Chloroform–Cyclohexane (1:3) Containing 4% (v/v) Span 85 at a Speed Setting of 200 rpm (×600)

Model B-100) at a speed setting of 200 rpm for 10 min to yield a water-in-oil emulsion. 2. Without stopping the stirring, 1.7 ml of sebacoyl dichloride or 20 ml of 0.4 M *p*-phthaloyl dichloride solution in the mixed organic solvent was quickly added to the emulsion, and stirring was further continued for 20 min. 3. The dispersion was centrifuged for 10 min at 350—2000 ***g*** to separate the newly formed microcapsules. Finally, the microcapsules thus obtained were completely dispersed in 40 ml of aqueous 50% (v/v) Tween 20 (polyoxyethylene sorbitan monolaurate) solution. After stirring for 30 min, the dispersion was diluted with an appropriate amount of distilled water for photographing microcapsules.

B) Determination of Apparent Partition Coefficient of Bisphenols: Since the transfer of water soluble monomers from aqueous phase to organic phase is very important in the formation of microcapsules,[3,4] the determination of the apparent partition coefficient of the bisphenols is desirable. The apparent partition coefficient of bisphenol A or bisphenol S was determined as follows. An emulsion obtained by mechanically emulsifying a mixture of aqueous bisphenol solution and the mixed organic solvent under the same conditions as those in the preparation of microcapsules was centrifuged at 2000***g*** for 10 min to separate it completely into two liquid layers. Then, the concentration of bisphenol A or bisphenol S in the aqueous phase was determined by measuring the absorption at 245 mμ (bisphenol A) or 297 mμ (bisphenol S) with a Hitachi 323-type Recording Spectrophotometer. The transferred amount of the bisphenols was calculated from their initial and final concentrations in the aqueous phase, and the bisphenol partition coefficient between the aqueous and organic phases was estimated.

Determination of Percentage of Reacted Bisphenols——The determination was carried out as follows. Microcapsule dispersions prepared in the same way as above were centrifuged at 48000 ***g*** for 15 min. The

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centrifugation caused the breakdown of microcapsules and a clear aqueous phase was obtained. The concentration of the bisphenols remaining unreacted in the aqueous phase was determined spectrophotometrically as in the determination of the partition coefficient. The percentage of reacted bisphenols with *p*-phthaloyl dichloride or sebacoyl dichloride was calculated from their initial and final concentrations in the aqueous phase.

Determination of Size and Size Distribution of Microcapsules——Each of polyphenyl ester microcapsule samples was placed on a hemocytometer and photographed under an optical microscope. Then, 200—800 microcapsule diameters were measured on photomicrographs. The scales in the hemocytometer and standard scales cut in a glass plate were photographed and used for calibration.

The length mean diameter, standard deviation, mean surface diameter, mean volume diameter, and size distribution were calculated by using a SEIKO-S-301 electric calculator.

In the case of double microcapsules as seen in Fig. 2, only the diameters of outside capsules were measured.

Measurement of Interfacial Tension——A modification of the ring method using a chemical balance was used to measure the interfacial tension between the aqueous and the organic phases. The interface was formed between aqueous 1.5M sodium hydroxide solution containing 0.4M bisphenol A or bisphenol S and the mixed organic solvent containing 10^{-7}—10^{-1}% (v/v) Span 85.

The interfacial tension between the two liquids was calculated by the following equation:

$$T = Mg/4\pi r$$

where T is the interfacial tension, Mg the weight of the wire ring at the point of detachment, and r the radius of the ring.

Result and Discussion

Apparent Partition Coefficient

The dependence of the apparent partition coefficients of the bisphenols on the Span 85 concentration in the organic phase and the time of emulsification at a constant speed setting of 200 rpm is shown in Table II.

Table II. Effect of the Concentration of Span 85 on the Partition Coefficient of Bisphenols at a Speed Setting of 200 rpm

Span 85 conc. % (v/v)	Agitation time (min)	Bisphenol A partition coefficient $K(C_{aq}/C_{org})$	Bisphenol S partition coefficient $K(C_{aq}/C_{org})$
0	2	—a)	—a)
0	6	—a)	—a)
0	10	—a)	—a)
0.5	2	2.4	2.0
0.5	6	1.6	2.0
0.5	10	1.6	2.1
5.0	2	2.0	2.3
5.0	6	2.9	2.3
5.0	10	2.4	3.4
10.0	2	1.7	2.8
10.0	6	1.5	2.3
10.0	10	1.4	2.4

a) Transfer of bisphenol was not detectable.

In the absence of Span 85, the transfer of the bisphenols from the aqueous to the organic phase was not detected. The presence of Span 85, however, caused a drastic increase in the transfer of the bisphenols. The apparent partition coefficient was virtually constant irrespective of the time of emulsification at all concentrations of Span 85 studied in this work. Furthermore, we see from Table II that the transferred amount did not increase if the Span 85 concentration increased. These results may be interpreted as showing that the time necessary for the interface between the aqueous and the organic phases to be stabilized by the adsorption

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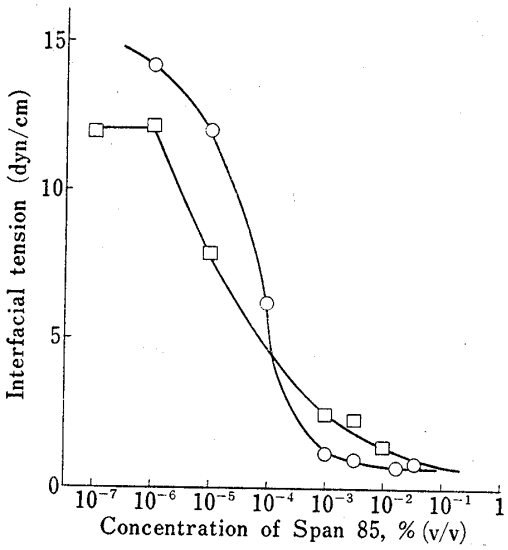

Fig. 3. Effect of the Concentration of Span 85 on the Interfacial Tension between Aqueous Solution of Bisphenol A or Bisphenol S and Mixture of Chloroform–Cyclohexane (1:3)

bisphenol A: ○, bisphenol S: □

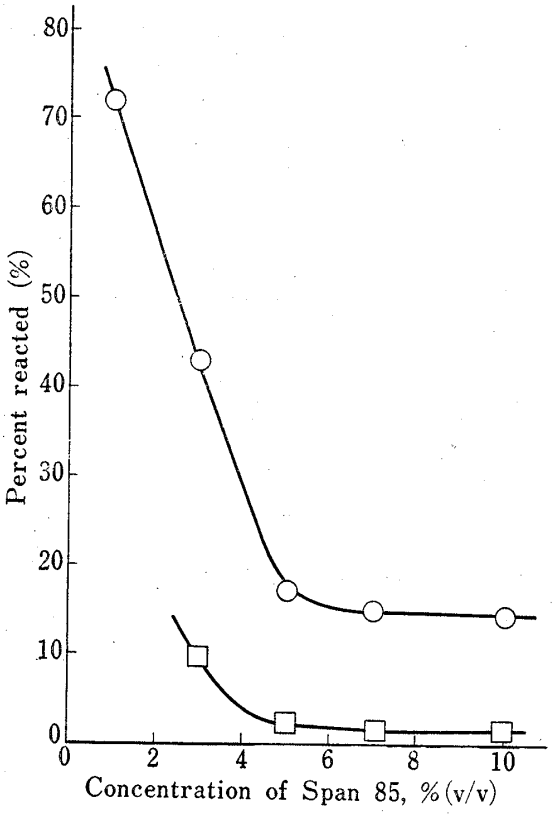

Fig. 4. Effect of the Concentration of Span 85 on the Percentage of Bisphenols reacted with *p*-Phthaloyl Dichloride at a Speed Setting of 200 rpm

bisphenol A: ○, bispherol S: □

of Span 85 molecules is very short, the transferred amount of the bisphenols approaches quickly to a saturation value at all concentrations of Span 85, and the increase in the Span 85 concentration prevents the transfer of the bisphenols from proceeding unlimitedly. Although the exact role of Span 85 in facilitating the transfer of the bisphenols is not yet fully understood, a portion of the bisphenols transferred should exist in the solubilized form in Span 85 micelles since the concentrations of Span 85 we used lie beyond its CMC (9.3×10^{-2} %).[7] This consideration may be supported from the result of interfacial tension measurements as seen in Fig. 3. That is, in the presence of Span 85, the interfacial tension decreased first and then levelled off as the concentration of Span 85 increased. The levelling-off was observed at a concentration of about 10^{-1}% (v/v) Span 85.

Percentage of Reacted Bisphenols

The percentages of the reacted bisphenol A and bisphenol S with *p*-phthaloyl dichloride and sebacoyl dichloride at various Span 85 concentrations are given in Fig. 4—5.

The percentage was greatly affected by both chemical structure of the acid dichlorides and the Span 85 concentration in the organic phase. In Fig. 4, the percentage of reacted bisphenols in the formation of polyphenylphthalates shows a tendency to diminish with increasing concentration of Span 85. In contrast, there is a reverse tendency when polyphenylsebacates are formed as shown in Fig. 5. Although the reason why the apparent partition coefficient is virtually constant at any Span 85 concentrations is not yet fully understood as mentioned already, the relations between the percent reacted of the bisphenols and the Span

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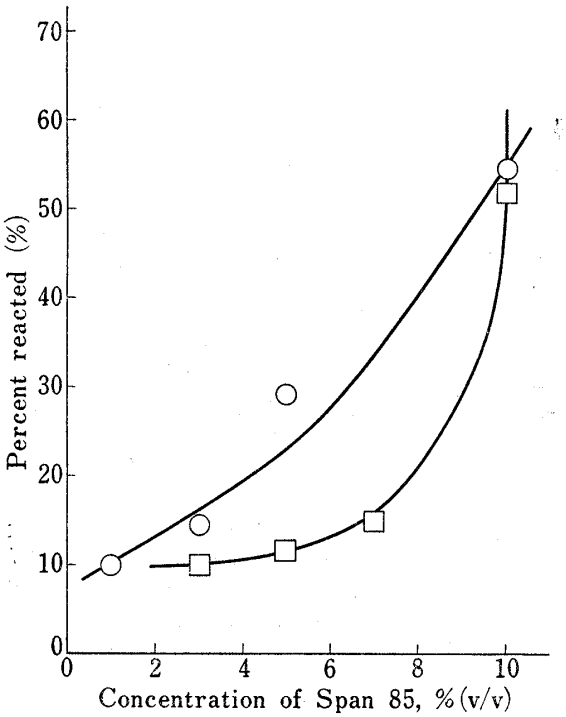

Fig. 5. Effect of the Concentration of Span 85 on the Percentage of Bisphenols reacted with Sebacoyl Dichloride at a Speed Setting of 200 rpm

bisphenol A: ○, bisphenol S: □

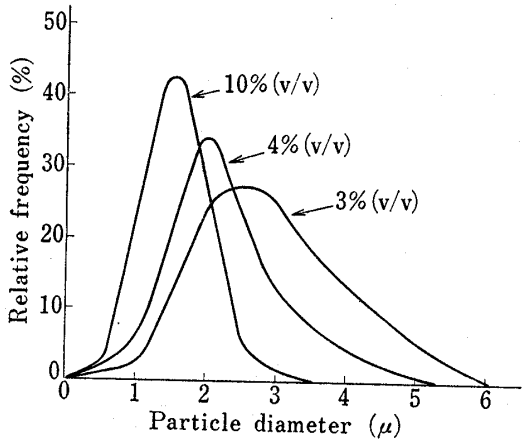

Fig. 6. Effect of the Concentration of Span 85 on the Size Distribution of Microcapsules prepared from Bisphenol A and Sebacoyl Dichloride in Chloroform–Cyclohexane (1: 3) at a Speed Setting of 200 rpm

85 concentration in Fig. 4 and 5 may be explained in terms of the difference in chemical structure between sebacoyl dichloride molecules in which two reactive chlorine atoms are attached to the ends of a linear, flexible methylene chain and *p*-phthaloyl dichloride molecules with two reactive chlorine atoms at the *para*-positions of a rigid aromatic ring and the role of Span 85 molecules in the polycondensation reactions.

It is quite likely that the space available to acid dichloride molecules to react with bisphenol molecules in the organic phase decreases with increasing Span 85 concentration, provided that molecules of the emulsifier do not participate in the polycondensation but reduce the number of free solvent molecules through solvation. Then, the effective concentrations of acid dichloride and bisphenol molecules would increase as the emulsifier concentration increases, thereby raising the percentage of reacted bisphenols. This argument seems to be aptly applicable to the polycondensation reaction between sebacoyl dichloride and the bisphenols. However, the percentage of reacted bisphenols lowers when the emulsifier concentration increases in the formation of polyphenylphthalates. The discrepancy between these two cases would arise from the difference in the molecular flexibility between sebacoyl dichloride and *p*-phthaloyl dichloride. As sebacoyl dichloride molecules are flexible owing to their linear methylene chain, it would be easy for them to take favorable conformations to react with bisphenol molecules in the organic phase even in the presence of high concentrations of Span 85. In contrast, the presence of a rigid aromatic ring in its molecules would make *p*-phthaloyl dichloride difficult to assume advantageous orientations to the reactions with bisphenol A or bisphenol S. This trend should go upwards with increasing emulsifier concentration. Accordingly, we may expect a decrease in the percentage of reacted bisphenols if the emulsifier concentration rises. In the foregoing discussion, we have assumed that the reactivity of chlorine atoms is the same for both sebacoyl and *p*-phthaloyl dichlorides. In view of the high reactivity of acid dichlorides, this assumption would not be unreasonable.

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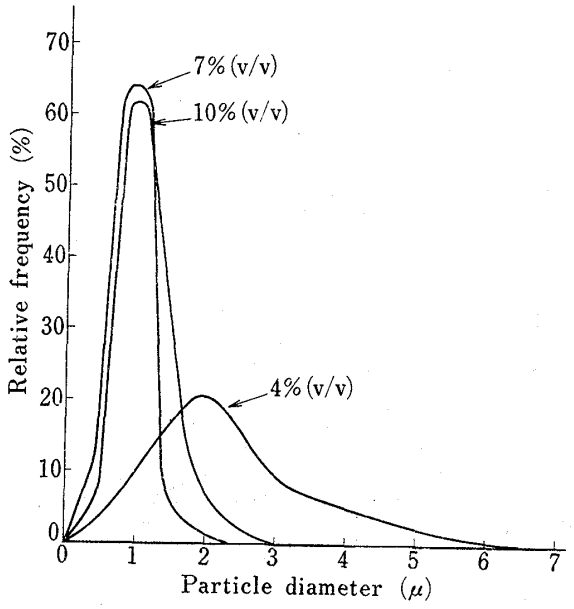

Fig. 7. Effect of the Concentration of Span 85 on the Size Distribution of Microcapsules prepared from Bisphenol S and Sebacoyl Dichloride in Chloroform–Cyclohexane (1 : 3) at a Speed Setting of 200 rpm

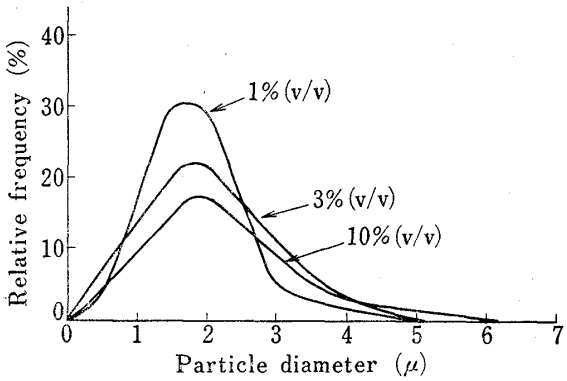

Fig. 8. Effect of the Concentration of Span 85 on the Size Distribution of Microcapsules prepared from Bisphenol A and *p*-Phthaloyl Dichloride in Chloroform–Cyclohexane (1 : 3) at a Speed Setting of 200 rpm

As is seen from Fig. 4—5, the percent reacted of bisphenol S is always lower than that of bisphenol A. This may be interpreted as follows. Bisphenol S which contains a sulfonyl group, a negative substituent, does not enter into the polycondensation as readily as does the positively substituted bisphenol A. This would mean that the electron-withdrawing sulfonyl group increases the acidity of the phenol and thereby decrease the basic strength of the phenoxide ion prepared from the phenol as a reactive species.[6] Thus, the lower percentage of reacted bisphenol S may be understood.

Size Distribution and Mean Size

The size distribution of microcapsules was strongly affected by the concentration of Span 85 and chemical structure of the acid dichlorides and the bisphenols. Fig. 6 and 7 show the size distributions of microcapsules prepared from sebacoyl dichloride and bisphenol A and bisphenol S in the presence of Span 85 at a speed setting of 200 rpm, respectively. The size distribution curves became narrower and sharper with increase in the Span 85 concentration. Moreover, the modal diameter shifted downwards as the emulsifier concentration increased. No significant effect of the difference in chemical structure of the bisphenols was found on the size distribution curve.

On the other hand, an unusual tendency of the size distribution curve to broaden was noted with increase in the Span 85 concentration for microcapsules prepared from bisphenol A and *p*-phthaloyl dichloride at a speed setting of 200 rpm as seen in Fig. 8. A close relation is clearly observed between the broadening tendency of the size distribution curve and the percentage of reacted bisphenol A when Fig. 8 is compared with Fig. 4. Namely, a decrease in the percentage of reacted bisphenols results in a broader and easier size distribution curve. On the contrary, the size distribution curve becomes narrower and steeper as the percentage of reacted bisphenols rises. It may be concluded, therefore, that the percentage of reacted bisphenols is closely related to the shape of the size distribution curve of polyphenyl ester microcapsules. The increase in the percentage of reacted bisphenols should raise the amount of polymer formed on the surface of emulsion droplets. Accordingly, the probability that the coalescence of emulsion droplets during the polymerization would be lower when the

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amount of polymer formed increases.[5] This may account for the change in the shape of the size distribution curve of polyphenyl ester microcapsules.

In Tables III and IV are summarized the results on the calculations of mean diameters of polyphenyl ester microcapsules. The variation of the mean diameters with the Span 85 concentration had a strong resemblance to that of the size distribution curve.

Table III. Effect of the Concentration of Span 85 on the Length Mean Diameter (d_1), Standard Deviation (δ), Mean Surface Diameter (d_2) and Mean Volume Diameter (d_3) of Microcapsules prepared from Sebacoyl Dichloride and Bisphenol A and Bisphenol S in Chloroform–Cyclohexane (1:3) at a Speed Setting of 200 rpm

Span 85 conc. % (v/v)	Sebacoyl dichloride			
	d_1 (μ)	d_2 (μ)	d_3 (μ)	δ
Bisphenol A				
3.0	3.21	3.41	3.61	1.15
4.0	2.59	3.01	3.62	1.53
10.0	1.73	1.79	1.84	0.43
Bisphenol S				
4.0	3.94	5.38	6.79	3.65
7.0	1.24	1.56	2.15	0.95
10.0	1.37	1.47	1.58	0.51

Table IV. Effect of the Concentration of Span 85 on the Length Mean Diameter (d_1), Standard Deviation (δ), Mean Surface Diameter (d_2) and Mean Volume Diameter (d_3) of Microcapsules prepared from Bisphenol A and *p*-Phthaloyl Dichloride in Chloroform–Cyclohexane (1:3) at a Speed Setting of 200 rpm

Span 85 conc. % (v/v)	*p*-Phthaloyl dichloride			
	d_1 (μ)	d_2 (μ)	d_3 (μ)	δ
Bisphenol A				
1.0	2.42	2.62	2.85	0.99
3.0	2.73	3.05	3.40	1.32
10.0	3.15	3.66	4.01	1.72
Bisphenol S				
Stable microcapsules were not formed				

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