The Role of Surfactants in Synthesizing Polyurea Microcapsule

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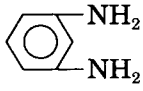
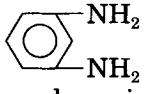
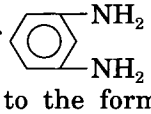
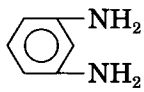
SYNOPSIS

Our lab has successfully synthesized microcapsules using interfacial polymerization technique. The core material and the wall of these microcapsules have been illustrated to be crystal violet lactone and polyurea, respectively, by both infrared and ultraviolet spectra. To make unique microcapsules, the presence of ethylene diamine in toluene diisocyanate system is important. Use of methyl cellulose with longer ethylene oxide chain length of nonylphenyl polyoxyethylene ether in a toluene diisocyanate system containing ethylene diamine will form small particles of polyurea microcapsules. Furthermore, in the presence of a fixed amount of sodium lauryl benzene sulfonate as an emulsifier, sodium carboxy methyl cellulose is better than methyl cellulose for use in making polyurea microcapsules in terms of their particle sizes. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The reaction of toluene diisocyanate (TDI) with water yields CO and  . Large amounts of  formed will substantially prevent the polymerization of toluene diisocyanate,[1,2] in the presence of di-*n*-butylphthalate (DBP) and crystal violet lactone (CVL),[3] with aqueous ethylene diamine at the oil–water interface to form polyurea microcapsule. On the other hand, small amounts of  formed, is believed to be beneficial to the formation of polyurea microcapsule.[4–6] In aqueous system, surfactants, having both hydrophobic and hydrophilic properties, are able to form hydrogen bonding with water and capable of reducing considerable amounts of unbound water reacting rapidly with toluene diisocyanate to yield large amount of  . Since the particle size and the wall thickness of microcapsules are highly affected by the surfactants, therefore, the type and amount of surfactant chosen becomes important in constructing a unique microcapsule. But very few work-related effects of surfactants on particle size of microcapsule has been published so far. Therefore, we attempt to study the effect of surfactants on the particle size of polyurea microcapsule prepared by interfacial polymerization[7–10] technique.

EXPERIMENTAL

Material

Toluene diisocyanate (TDI), ethylene diamine (EDA), dibutyltin dilaurat (DBZDL), crystal violet lactone (CVL), and xylene were purchased from Merck Co. Triethylamine and sodium lauryl benzene sulfonate (NaLAS) were received from Ferk, Germany and Hayashi Pure Chemical Co., respectively. Nonylphenylpolyoxy ethylene ether with different moles of ethylene oxide (termed NP_8, NP_{10}, NP_{12};

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8, 10 and 12 represent the moles of ethylene oxide, respectively) was supplied by Sino-Japan Chemical Co. Methyl cellulose (MC) and sodium carboxy methyl cellulose (CMC) were obtained from Kan Chemical Co. and Wako Pure Chemical Co., respectively. Di-*n*-butylphthalate (DBP), reagent grade, was purchased from Nihon Shiyaku Ind., Ltd. All the chemicals were used without further purification.

Preparation

A small amount of NP with different ethylene oxide chain length or NaLAS as an emulsifier was charged into a four-necked 1000 mL pyrex glass flask containing 4 g MC or 4 g CMC as a protective colloid in the presence of 150 g water. The PH of this aqueous solution was adjusted to around 7 by NaOH solution. Ten grams of TDI was added to a 250 mL beaker containing 30 g Di-*n*-butylphthalate nonaqueous solvent and 0.2 g crystal violet lactone, followed by adding 0.1 g DBZDL as a catalyst.[11,12] This nonaqueous solution consisting of toluene diisocyanate, di-*n*-butylphthalate and crystal violet lactone was gradually poured into the above aqueous solution in the presence of 3.5 g ethylene diamine under agitation with a speed at 800 rpm for 3 h reaction at 70°C.

Samples of polyurea microcapsules were analyzed by IR (Report-100 Infrared spectrometer), UV spectrophotometer (UV-240 shinadzu), and polarized microscope (Olympus Optical Co. Ltd.). The mean diameters of the volume distribution of polyurea microcapsules in liquids were also measured by Microtrac analyzer (Leeds & Northrup Instrument, model 7995-10). This Microtrac Particle Size Analyzers can be used to measure particle size distribution both from 0.7 to 125 μm and from 1.6 to 300 μm.

RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) show the infrared spectra of crystal violet lactone and microcapsule, respectively. The reaction of TDI with EDA at the oil-water interface forms the urea linkage illustrated by the absorbance peaks at 3300 cm^{-1} (NH) and 1720 cm^{-1} (c=0), as shown in Figure 1(b). A comparison of Figure 1(a) and (b), indicates that the absorbance

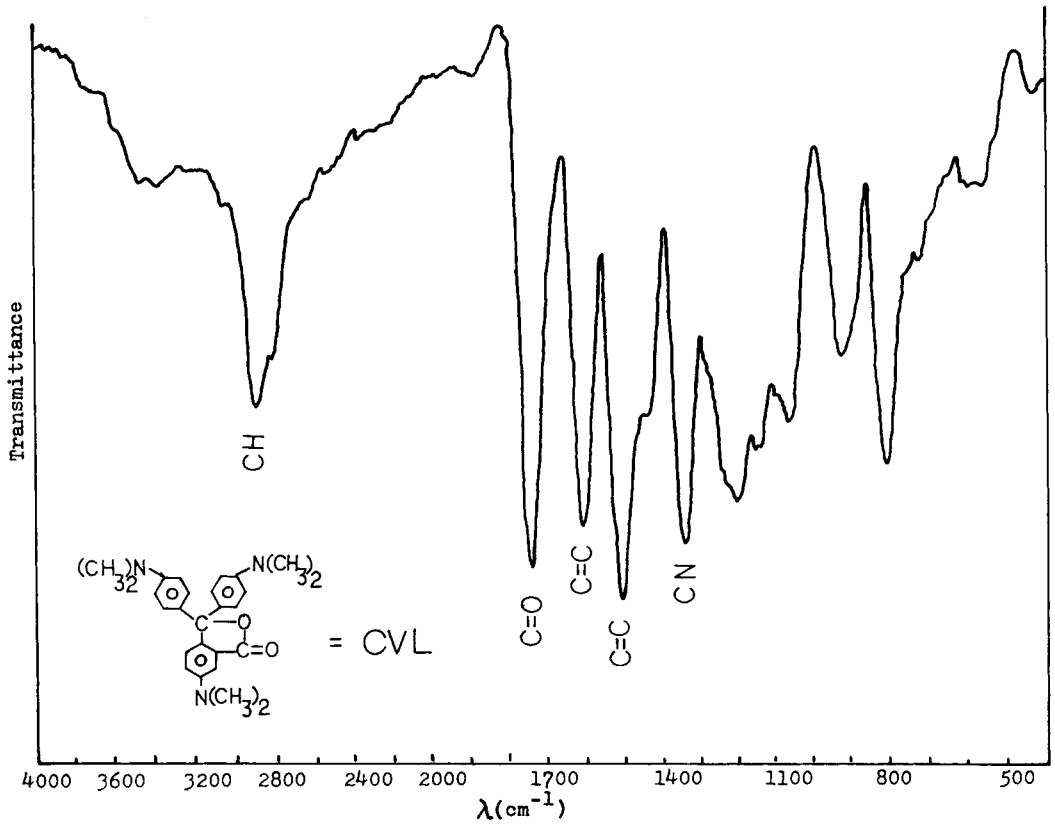

Figure 1(a) Spectra of CVL at 25 ± 0.05°C.

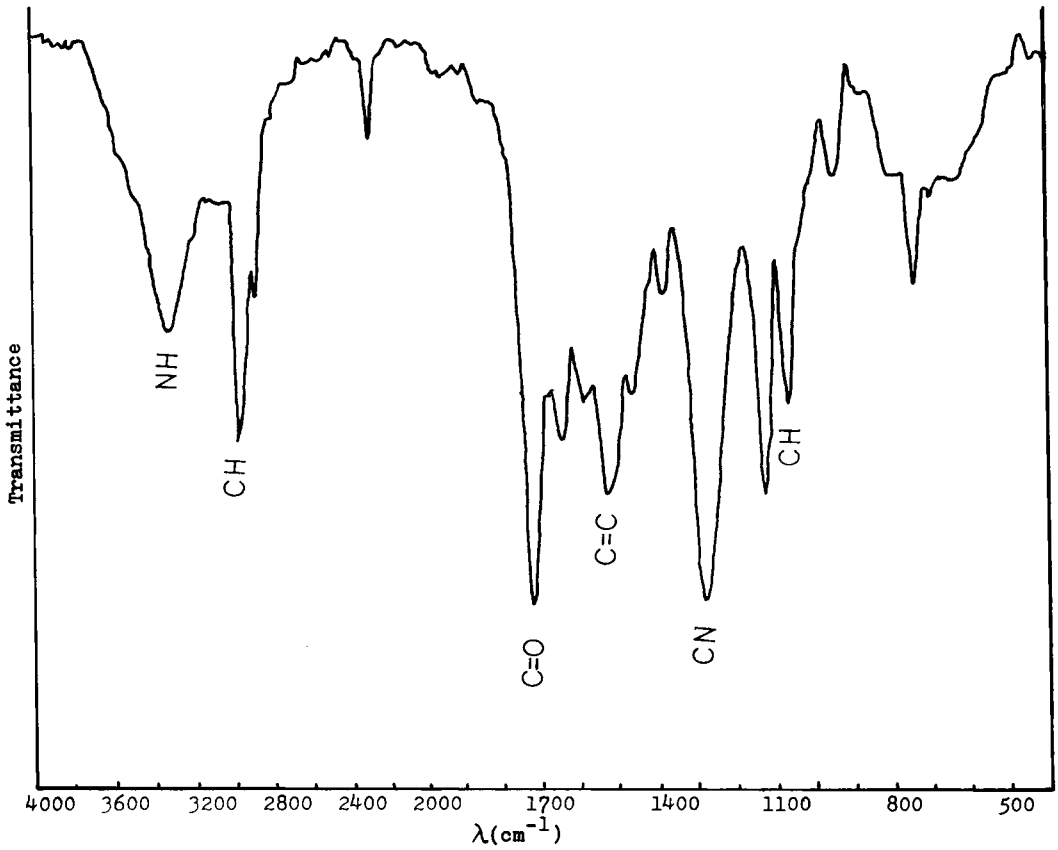

Figure 1(b) Spectra of polyurea microcapsule at 25 ± 0.05°C.

peaks at 2940 cm^{-1} (CH), 1720 cm^{-1} (c=0), 1620 cm^{-1} (NH) and 1360 cm^{-1} (CN) presented in Figure 1(a) are more or less the same as the corresponding peaks given in Figure 1(b). Furthermore, by an analysis of UV spectra of pure crystal violet lactone and the core material of polyurea microcapsule in Di-*n*-butylphthalater solvent shown in Figure 2, their shape and peak position are seen to be almost identical. These results suggest that the core and the shell of microcapsules are likely to be crystal violet lactone and polyurea, respectively. Microscopic examination of samples under polarized light at 25 ± 0.05°C exhibited the presence of microcapsules with spherical shape (Fig. 3).

ASTM D2572-70 method used to analyze the content of NCO present in oil-water mixture is briefly described as follows:

$$\text{NCO \%} = \{[(B - V) \times N \times 0.042]/\text{w}\} \times 100$$

where B is the amount of HCl used for the system with no toluene diisocyanate samples; V the amount of HCl used for the system with toluene diisocyanate samples; N the equivalent weight of HCl and W the weights of the samples.

$$X = \frac{\text{NCO \% (at t = 0, no reaction)} - \text{NCO \% (at t = t)}}{\text{NCO \% (at t = 0, no reaction)}}$$

where X represents the degree of conversion of NCO. In the presence and absence of ethylene diamine, the plots of the conversion of NCO versus the reaction time at 25, 45, and 60°C for toluene diisocyanate systems with and without DBZDL as a catalyst are given in Figure 4. Figure 4 shows that the conversion of NCO is higher for toluene diisocyanate systems with ethylene diamine than for toluene diisocyanate systems without ethylene diamine at high temperature (i.e., 60°C) in the presence of dibutyltin dilaurate as a catalyst. This is because dibutyltin dilaurate as a catalyst can accelerate the polymerization of toluene diisocyanate with ethylene diamine to take place at the oil–water interface. Similarly, as the reaction temperature is elevated to 60°C, the thermal energy imparted to the system

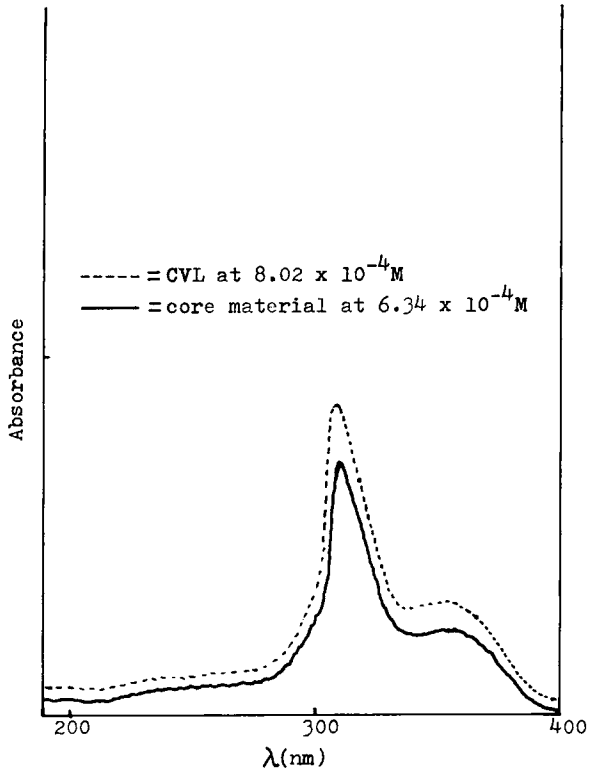

Figure 2 Spectra of CVL (dashed line) and core (solid line) of polyurea microcapsule at 309.9 nm and at 25 ± 0.05°C.

can speed up both toluene diisocyanate and ethylene diamine to polymerize at the interface as well.

The number-average diameter of polyurea microcapsule, prepared by polymerization of toluene diisocyanate with ethylene diamine in the presence of methyl cellulose, methyl cellulose with NP_{12} and methyl cellulose with sodium lauryl benzene sulfonate, respectively, at the oil-water interface, decreases with increasing the concentration of methyl cellulose (Fig. 5). Methyl cellulose, having hydrophilic and hydrophobic properties, at higher concentration greater than the critical micelle concentration, can form large aggregates called micelles. Therefore, methyl cellulose can be treated as a polymer-like nonionic surfactant. Increased concentration of methyl celluloses (0.5 g $\gg$ critical micelle concentration), due to the formation of large aggregates themselves and of lots of hydrogen bonding with water, will substantially reduce the amount of unbound water reacting with toluene diisocyanate monomers to form urea at the interface. In addition, the interaction between large aggregates may become stronger as the concentration of methyl cellulose increases. Judged from this point of view, the average particle size of microcapsule decreasing with increasing methyl cellulose concentration may be the result of micelle–micelle interaction in addition

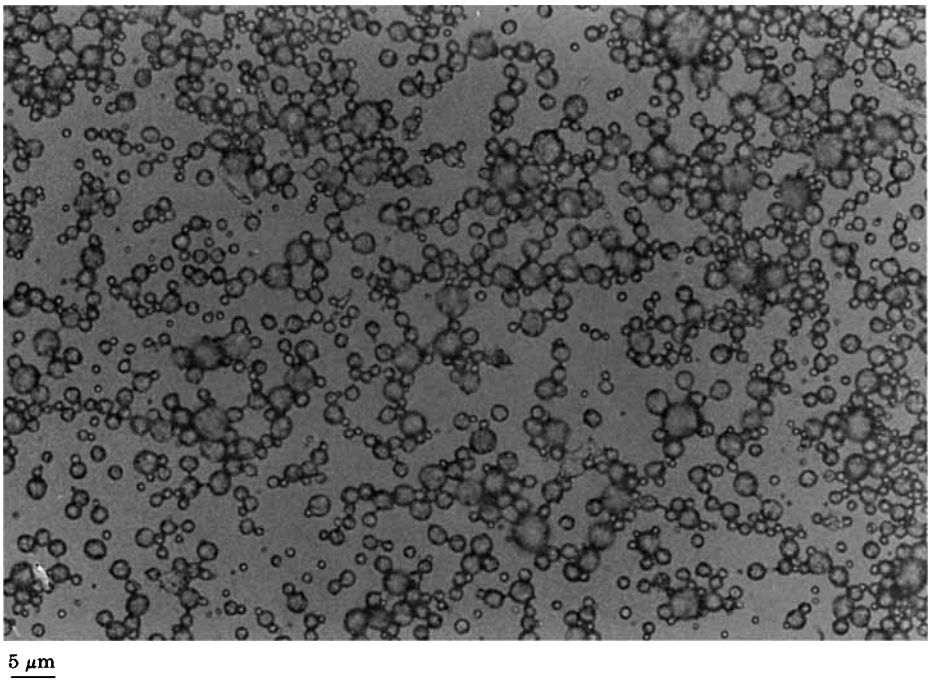

Figure 3 Optical microscopy of crossed polarizers for the sample of polyurea microcapsule prepared in the presence of MC containing a fixed amount of NP_{12}, at 25 ± 0.05°C (×200).

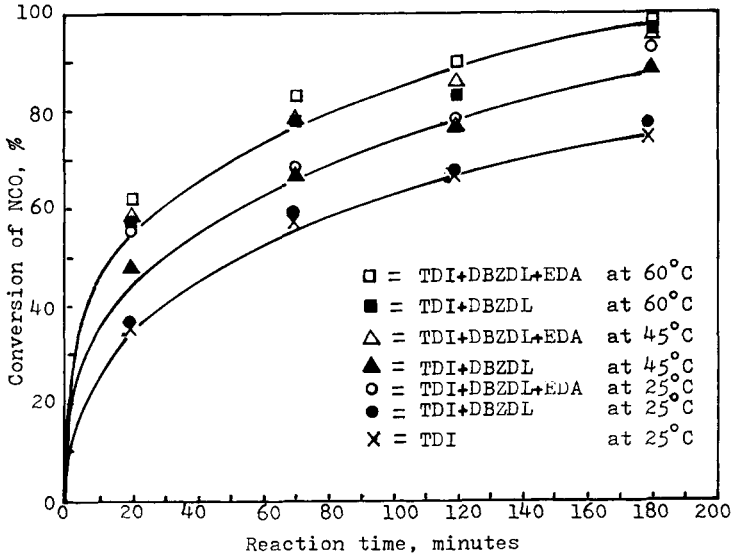

Figure 4 Plot of the conversion of NCO for TDI with and without dibutyltin dilaurant versus the reaction time of interfacial polymerization at 25, 45, and 60°C, respectively.

to the effect of hydrogen bonding formation. The presence of a fixed amount of NP_{12} (3.2 g ≫ critical micelle concentration) nonionic surfactant in methyl cellulose aqueous system not only forms large aggregates themselves and hydrogen bonding with water but, on the other hand, may help more ethylene diamine molecules diffusing into the interface to rapidly react with toluene diisocyanate monomers as well. Therefore, under the same experimental condition as described above, the presence of a fixed

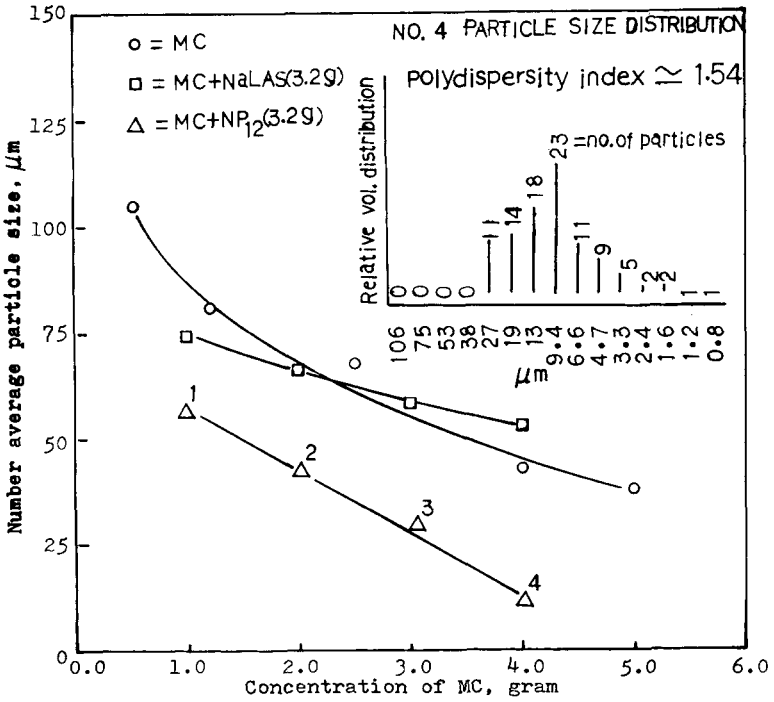

Figure 5 Plot of the particle size of polyurea microcapsule formed versus the concentration of MC with and without a fixed amount of NP_{12} and NaLAS, respectively, for use in making microcapsule, at room temperature.

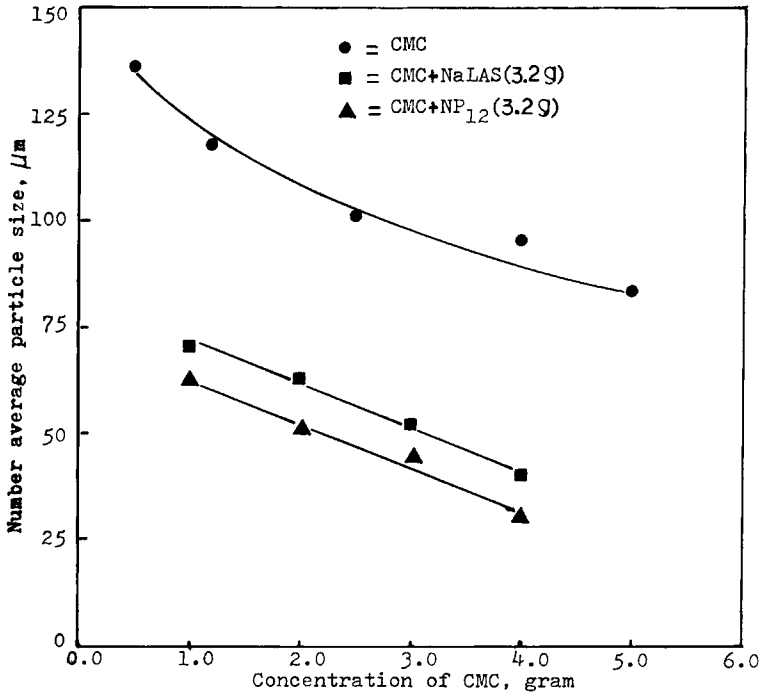

Figure 6 Plot of the particle size of polyurea microcapsule formed versus the concentration of CMC with and without a fixed amount of NP_{12} and NaLAS, respectively, for use in making microcapsule, at room temperature.

amount of NP_{12} (3.2 g) may make the average particle size of microcapsule become smaller, as a result of micelle-micelle (i.e., NP_{12}-NP_{12} and NP_{12}-MC) interactions, coupled with the hydrogen-bonding effect. An interesting note is that the average particle size of polyurea microcapsules formed is seen to be smaller for the system with a fixed amount of NP_{12} (3.2 g) than for the system with a fixed amount of NaLAS (3.2 g) for use in making this microcapsule (Fig. 5). In the system, the presence of NaLAS molecules at high concentration will form large aggregates called micelles. These micelles with high charge densities on their surface may slightly retard the polymerization of TDI monomers with ethylene diamine, as a result of strong electrostatic interaction between micelles. This may be the reason why the average particle size of polyurea microcapsule decreases slightly with increasing the concentration of methyl cellulose in the presence of a fixed concentration of NaLAS (3.2 g).

With the exception of the substitution of methyl cellulose by sodium carboxy methyl cellulose (CMC) as a protective colloid, the experimental conditions are the same as above. Their results shown in Figure 6 indicate that the average particle size of polyurea microcapsule decreases with increasing the concentration of CMC in the presence and absence of a fixed amount of NP_{12} (3.2 g by weight). Unlike methyl cellulose, CMC, a surface active agent, is not an anionic surfactant. However, decreased average particle size of microcapsule with an increase in the concentration of CMC is obviously related to strong electrostatic interaction generating from CMC molecules. In comparison of Figures 5 and 6, it appears that the average particle sizes of polyurea microcapsules formed are smaller for the system with methyl cellulose than for the system with sodium CMC. This is because charged CMC molecules strongly repelling each other may prevent some of ethylene diamine molecules diffusing into the interface to react with TDI monomers. For this reason, the interfacial polymerization of TDI monomers with ethylene diamine in the presence of other additives may need longer time to be completed. Therefore, the average particle size of polyurea microcapsule decreases slowly for the system with CMC in the presence and absence of a fixed concentration of NP_{12} (3.2 g). More interestingly, in the presence of a fixed concentration of NaLAS (3.2 g), the average particle size of polyurea microcapsule is seen to be slightly smaller for the system with sodium CMC than for the system with methyl cellulose. This may be attributed to both charged CMC and NaLAS molecules generating very strong elec-

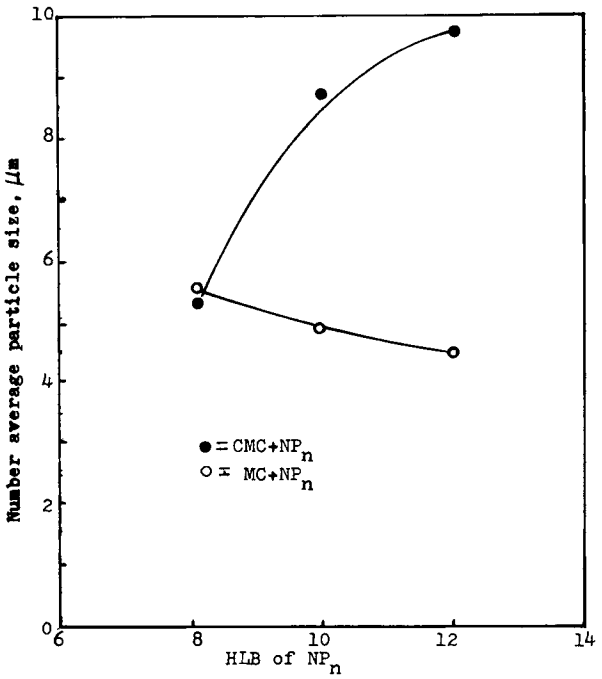

Figure 7 Plot of the particle size of polyurea microcapsule formed versus the fixed amount of NP with different EO chain length in the presence of 4 g MC and CMC, respectively, for use in making microcapsule, at room temperature.

trostatic repulsion among them. This strong repulsion may not allow CMC and NaLAS molecules to adsorb ethylene diamine molecules. On the other hand, more ethylene diamine molecules may be pushed to the interface, rapidly reacting with TDI monomers to form polyurea microcapsule. Therefore, the average particle size of this microcapsule becomes smaller.

Figure 7 illustrates that the average particle size of polyurea microcapsule slightly decreases with increasing ethylene oxide chain length of nonylphenyl polyoxy ethylene ether in the presence of 4 g MC for use in preparing this microcapsule. Under the same experimental condition, but substituting CMC for MC, the opposite results on the average particle size of polyurea microcapsule are observed. This may be the result of strong electrostatic repulsion.

CONCLUSION

It has been found that the conversion of NCO is higher for toluene diisocyanate systems with ethylene diamine than for toluene diisocyanate systems with no ethylene diamine at high temperature in the presence of dibutyltin dilaurate. Formation of a unique microcapsule, definitely requires the presence of ethylene diamine in a toluene diisocyanate system. The core and the wall of microcapsules prepared at our lab have been shown to be crystal violet lactone and polyurea, respectively, by both IR and UV spectra.

The average particle size of polyurea microcapsules is significantly affected by the type and concentration of protective colloid and surfactants chosen for use in making microcapsules. Our experimental results suggest that use of methyl cellulose with longer ethylene oxide chain length of nonylphenyl polyoxy ethylene ether in toluene diisocyanate system in the presence of ethylene diamine forms particles of smaller size of polyurea microcapsule. In addition, in the presence of a fixed amount of sodium lauryl benzene sulfonate as an emulsifier, use of sodium carboxy methyl cellulose in a toluene diisocyanate system is better than that of methyl cellulose in a toluene diisocyanate system for preparing polyurea microcapsules in terms of their average particle sizes.

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