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SHORT COMMUNICATION

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Preparation of colored latex with polyurea shell by miniemulsion polymerization

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Abstract Colored latexes with polyurea shell were prepared by applying interfacial polycondensation reaction to the miniemulsion polymerization process. These colored latexes were composed of polystyrene core and polyurea shell, and their particle size was adjusted to <100 nm. Diisocyanate was used as a hydrophobic monomer, and the equivalent mole of diamine was used as a hydrophilic monomer for interfacial polymerization. It was important to control the rate of interfacial polycondensation reaction in order to prepare small particles. Dye preservation property of colored latex loaded with oil-soluble dye was investigated. Polyurea shell formed at the surface of latex particles could restrain the migration of dyes from the latex particles and improve the dye preservation property. The ability to prevent dye migration depended on the composition of the polyurea shell.

Keywords Miniemulsion polymerization · Core-shell particle · Polyurea · Colored latex · Interfacial polycondensation · Dye migration

Introduction

Miniemulsion polymerization is carried out by polymerizing the monomer droplets prepared by miniemulsification [1]. The polymerization of miniemulsion globules provides advantages with respect to incorporation of various hydrophobic compounds, because the compounds do not have to diffuse into the polymerizing loci through the aqueous phase during the particle growth. The miniemulsion process was applied not only to incorporate water-insoluble compounds in polymer particles, but also to synthesize polyurethane dispersions [2].

In our previous work [3], we prepared “colored latex” with high dye content by miniemulsion polymerization for the purpose of the development of the third colorant, that is, next to dye and pigment. “Colored latex” is the latex loaded with oil-soluble dye. Colored latex with strong color depth was prepared using some kinds of dyes. Then, we studied the improvement of storage stability and photostability of colored latex [4]. Colored latex must keep dye molecules inside the latex particles for practical usage. But, in some cases, the migration of dyes from the latex particles becomes a severe issue, especially with increasing dye concentration in particles. The dye migration property depends on the diffusion rate of dye molecules in latex particles. We suggested that bulky dye molecules should be selected for the preparation of colored latex in order to obtain good dye preservation property.

A microcapsule is a micro-order container that involves active reagents. A characteristic function of a microcapsule is to protect the reagents from the environment and to control the release of the reagents. Microcapsules are widely used in industrial applications such as recording materials, drugs, foods, perfumery, and cosmetics [5]. Interfacial polycondensation is one of the techniques to make microcapsules [6–8]. A polycondensation reaction occurs at the interface of two immiscible phases such as water and oil, and a polymer membrane is produced. Each phase contains one of the monomers participating in the reaction to form the polymer membrane. In a typical method, an emulsion is first prepared and a polycondensation reaction is forced to proceed at the surface of the emulsion.

In this study, we applied interfacial polycondensation reaction to the miniemulsion polymerization process to improve storage stability of colored latexes. Polyurea membrane is completely insoluble in water and other common solvents. We prepared colored latex consisting of polystyrene core and polyurea shell so that polyurea membrane formed at the surface of the latex particles would restrain the migration of dyes from the latex particles. The effect of the chemical structure of the shell on dye migration properties of colored latex was investigated.

Experimental

Materials

An oil-soluble dye, the molecular structure of which is shown in Fig. 1, was used. Isophorone diisocyanate (IPDI, Mw = 222.3), hexamethylene diisocyanate (HMDI, Mw = 168.2), and isophorone diamine (IPDA, Mw = 170.3) were purchased from Wako Pure Chemical Industries. Other chemicals used in this work include tolylene-2, 4-diisocyanate (TDI, Mw = 174.16) from Tokyo Kasei Co., styrene, hexadecane (HD), and tetrahydrofuran (THF) from Junsei Chemical Co., hexamethylenediamine (HMDA) and sodium dodecyl sulfate (SDS) from Kishida Chemical Co., and ethylenediamine (EDA, Mw = 60.1), and azobisisobutyronitrile (AIBN) from Wako Pure Chemical Industries. All chemicals were used as received. Water was deionized before use.

Preparation of miniemulsions

The dyes, HD, AIBN, and diisocyanate monomer were dissolved in styrene. This nonaqueous solution was added to the aqueous solution of SDS and stirred at room temperature (r.t.) for several minutes. The resultant emulsion was then homogenized by an ultrasonicator, ULTRASONIC HOMOGENIZER UH-600 (SMT Co.) operated at 80% amplitude for 15 min under ice cooling.

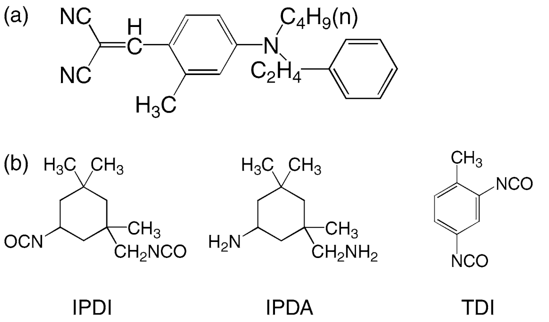

Fig. 1 Molecular structures of **a** dye, and **b** monomers for interfacial polycondensation reaction

Polymerization process

The miniemulsion was transferred to a flask equipped with an agitator, a thermometer, a nitrogen tube, and a reflux condenser. The system was purged with nitrogen for several minutes and then heated to 20–50°C under nitrogen flowing. The aqueous solution of diamine was added to the miniemulsion and the reaction mixture was stirred at 200–300 rpm for 1–1.5 h, so that polyurea shell would be formed first. In some cases, diamine solution was slowly added by using a dropping funnel to control the interfacial polycondensation reaction rate. Then, the system was heated to 80°C, in order to polymerize styrene by AIBN and stirred for 3 h. Colored latex without polyurea shell was prepared as a reference standard by polymerizing miniemulsion that contained neither diisocyanate nor diamine at 70 or 80°C for 3 h. The solid content and conversion of monomer were determined by the gravimetric method.

Droplet and particle size

The average size and size distribution of monomer droplets were obtained from dynamic light scattering (DLS), using Microtrac UPA (Honeywell Co.). The sample was diluted with water to adjust the intensity of the scattering light. The diluted water was a monomer-saturated solution of 8 mM SDS. In the case of the measurement of polymer particle size, latex was diluted with deionized water.

TEM analysis

Transmission electron microscopy (TEM) was performed with a HITACHI H-9000NA operating at 100 kV. Colored latex was filtered through 200 nm microfilters and diluted with deionized water. The diluted colloidal solution was applied to a 200 mesh carbon-coated collodion substrate and left to dry.

FTIR measurement of polyurea shell

Polyurea shell was analyzed by using an Abatar360 FT-IR (Nicolet Japan Co.). Colored latex with core-shell structure was dried on a hotplate. THF was added to the dried polymer particles. The dye and polystyrene are soluble in THF, but polyurea shell is insoluble. Particles were washed in THF several times to remove dye and polystyrene from polyurea and then dried. IR spectra of polyurea were measured using KBr pellet method.

Absorbance preservation properties

Dye content in colored latex particles at t_0 (storage time $(t)=0$) was measured immediately after the latex preparation. Then, the latex products were maintained in a thermostat at 25°C for 4 weeks, and dye contents in the particles were measured at storage time t. The measurement by absorptiometry was carried out as follows:

Colored latex was filtered through 200 nm microfilters to remove the unfilterable solids such as the aggregates of dye molecules, and the aggregates of particles. Then, the filtered latex was dried on a hotplate. Dried polymer particles were dissolved in THF and the solid content was adjusted to the fixed value. Polyurea is insoluble in THF, but dye molecules inside polyurea shell gradually elute in THF. Therefore, THF solutions were left for 1 day before measurements. The visible absorption spectra of the THF solution of the colored latex were measured using an absorptiometer (HITACHI Spectrophotometer U-3500). If the dye concentration is low enough, the relation of absorbance with concentration obeys Beer's law. The absorbance at absorption maximum ($\lambda_{\max}$) of colored latex immediately after the preparation was regarded as the value of absorbance 100%. The value of residual absorbance of colored latex at t were calculated by Eq. 1,

$$\text{Residual absorbance }(\%) = \frac{A_t}{A_0} \times 100 \qquad (1)$$

where A_t is absorbance at $\lambda_{\max}$ of colored latex (THF solution) at storage time t, A_0 is absorbance at $\lambda_{\max}$ of colored latex (THF solution) at storage time t_0.

Dye content analysis

The latex products were maintained in a thermostat at 25°C for 4 weeks. The colored latex was filtered through 200 nm microfilters to remove the unfilterable solids. Then, the filtered latex was dried on a hotplate. Nitrogen (N) content in dried polymer particles was determined by elemental analysis. As the dye molecule contains nitrogen, dye content of polymer particles was calculated from nitrogen content in particles. Polymer particles contained not only dye, but also AIBN and polyurea as N source, and N content determined by elemental analysis was assigned to dye, AIBN, and polyurea. Assuming that the decrease of N content in polymer particles wholly resulted from dye migration, residual dye in polymer particles was calculated after 4 weeks. The dye content in polymer particles immediately after the preparation was regarded as the value of dye content 100%. The value of residual dye after 4 weeks was calculated by Eq. 2,

$$\text{Residual dye }(\%) = \frac{N_t}{N_0} \times 100 \qquad (2)$$

where N_t is nitrogen content attributed to dye in polymer particles at storage time t (4 weeks), N_0 is nitrogen content attributed to dye in polymer particles at storage time t_0.

Results and discussion

Colored latexes with core-shell structure were prepared by the applied miniemulsion polymerization. The recipes and analytical characteristics of the resulting latexes were summarized in Table 1. Colored latex must provide brilliant color. If the particle size is too large, colored latex will show a dull color due to the scattering of light. It is known that the influence of the scattering of light to the color development can be neglected in case the diameter of colored latex particles is smaller than a quarter of the shortest wavelength of visible ray. Therefore, we adjusted the particle size to < 100 nm, much shorter than the wavelength of visible lights, in order to achieve high color brilliance.

Some kinds of water-insoluble dyes work as a hydrophobe in miniemulsion system and offers resistance

Table 1 Recipes and characteristics of colored latexes with core-shell structure

Colored latex	Monomer(g)		Conversion (%)	Diameter (nm)
	Diisocyanate	Diamine		
C1	–	–	74	42.9
C2	–	–	93	77.5
C/S1	0.400[a]	0.306[d]	91	58.6
C/S2	0.464[a]	0.243[e]	92	51.7
C/S3	0.556[a]	0.150[f]	92	42.6
C/S4	0.355[b]	0.355[d]	84	53.3
C/S5	0.418[b]	0.289[e]	84	Aggregate
C/S6	0.520[b]	0.186[f]	93	Aggregate
C/S7	0.357[c]	0.349[d]	49	Aggregate
C/S8	0.424[c]	0.283[e]	66	Aggregate

Dye/Styrene/HD/AIBN/SDS/H_2O = 0.34/3.06/0.2/0.1/0.416/36 (g)

[a] IPDI

[b] HMDI

[c] TDI

[d] IPDA

[e] HMDA

[f] EDA, diisocyanate + diamine = 0.706 (g)

to diffusional degradation of the monomer droplets (Ostwald ripening) [9, 10]; but the dye hardly stabilized the miniemulsion. So, HD was used as a hydrophobe to stabilize the miniemulsion.

IPDI, HMDI, and TDI were used as oil-soluble monomers, and the equivalent mole of diamine was added to the aqueous phase for interfacial polycondensation reaction (Table 1). IPDA, HMDA, and EDA were used as hydrophilic monomers, and polyurea shells, which had a different composition, were formed by the combination of diisocyanate and diamine. Molecular structures of some monomers were shown in Fig. 1. After polyurea shells were formed by interfacial polymerization first, cores mainly composed of dye and polystyrene were formed by polymerization of styrene inside miniemulsion globules. If cores were polymerized first, hydrophobic monomers would diffuse slowly inside polystyrene cores and the interfacial polymerization rate would be low.

In some cases, aggregates were formed after diamine solutions were dropped to the reaction mixtures (Table 1). When the reactivity of interfacial polymerization was too high, aggregates were formed by cohesion between the particles. The reactivity of hydrophobic monomers is IPDI < HMDI < TDI, and that of hydrophilic monomers is IPDA < HMDA < EDA. The combination of monomers with relatively high reactivity resulted in aggregation. As we adjust droplet size to < 100 nm, the total interfacial area is so large that the reactivity is likely to be too high. The rate of interfacial polycondensation reaction must be properly controlled so that the latex product will be monodisperse without aggregates. Therefore, the reaction temperature should be moderately controlled. When we used IPDI and/or IPDA, which had mild reactivity, we were able to gain a stable dispersion without aggregates. However, when TDI having relatively high reactivity was used, we could not avoid aggregation (Table 1).

It is desirable that the size distribution of colored latex be narrow, because aggregates affect the color brilliance. If the monomer concentration in the reaction system is too high, the resulting latex will be polydisperse due to cohesion between the particles. Diamine solutions must be added dropwise to the reaction mixture in order to control the rate of interfacial polymerization. The average size and size distribution of latex particles was measured by DLS. The size distribution of particles was compared with that of latex products prepared by adding IPDA in a lump (Fig. 2). We could prevent particles from aggregating during the interfacial polycondensation reaction, and make the size distribution narrow, by adding IPDA little by little. When excess IPDA, which was four times as much as the equivalent mole of IPDI, was added to the aqueous phase little by little, aggregates formed and dye fading was obviously observed. When the concentration of diamine in reaction mixture was too high, the control of reaction velocity was difficult. Then, pH of the latex product was chosen to be 11, at which the electronic state of the dye molecule and the color of the dye might be influenced by pH.

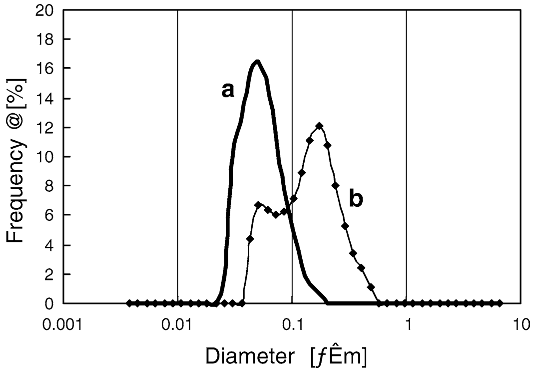

Fig. 2 Size distribution of colored latex: Dye/Styrene/IPDI/HD/AIBN/IPDA/SDS/H_2O = 0.34/3.06/1.019/0.2/0.1/0. 781/0.624/36 (g). **a** IPDA was dropped little by little. **b** IPDA was added in a lump

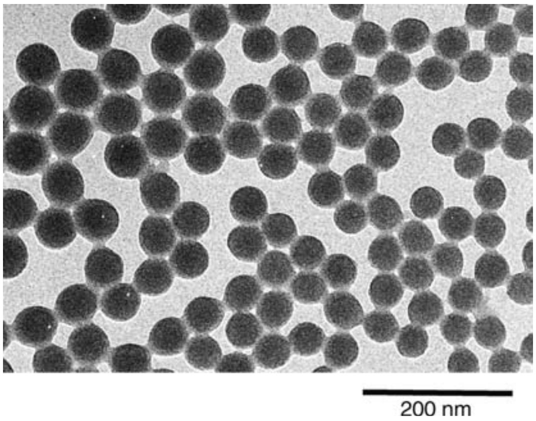

Fig. 3 TEM photograph of colored latex with core-shell structure: Dye/Styrene/HMDI^{tri}/HD/AIBN/IPDA/SDS/H_2O = 1.6/6.4/1.135/0.4/0.2/0.513/0.736/32 (g)

The TEM image of colored latex shown in Fig. 3 revealed that spherical particles with a relatively narrow size distribution were formed. Colored latex was filtered through 200 nm microfilters before TEM analysis. The aggregates of dye molecules that had existed outside the particles, the aggregate of particles, and extremely large size particles, although their amount was almost negligible, were not observed in TEM photographs.

FTIR spectra of polyurea shell consisting of IPDI and IPDA are shown in Fig. 4. The sample had strong bands known for a N–H stretching vibration at about 3400 cm^{-1}. C–H stretching vibrations were observed at both 2950 and 2860 cm^{-1}. The peaks at around 1560 cm^{-1} were probably attributed to CN. The NCO

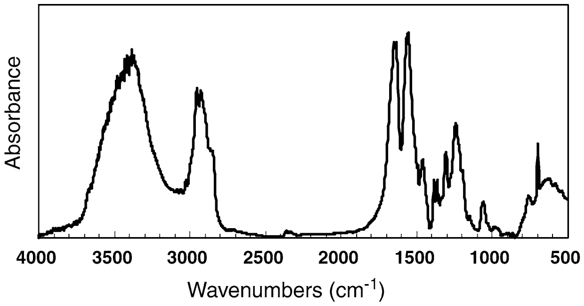

Fig. 4 IR spectra of polyurea shell (C/S1)

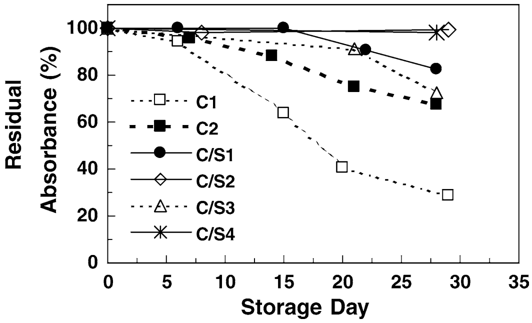

Fig. 5 Dye migration property of colored latex

peak in IPDI at 2270–2240 cm^{-1} disappeared and carbonyl stretching bands were observed at 1700–1650 cm^{-1}. These characteristic peaks indicated that polyurea shell was formed successfully [11–13].

Colored latex is required to exhibit good dye preservation property for a long storage time. But, in some cases, dyes inside latex particles migrate to aqueous phase and precipitate as dyestuff aggregates. Dye migration from the colored latex particles must be minimized as possible. To evaluate the dye migration from the particle to the medium, dye contents inside the particles were measured as a function of storage time *t* at 25°C.

In our previous work, we investigated the correlation between the size of dye molecule and dye migration property. The radius of dye molecule affects the migration of dye, as supposed from Eq. 3,

$$D = \frac{kT}{r\eta} \tag{3}$$

where D is the diffusion constant, k a constant, T absolute temperature, r the radius of solute, and η the viscosity of matrix. In fact, colored latex containing bulkier dye molecules exhibited better dye preservation property than colored latex containing smaller dye molecules. Therefore, in order to obtain good dye preservation property, it was suggested that bulky dye molecules be selected for preparation of colored latex.

The dye used in this study shows a brilliant yellow color and has relatively high solubility in styrene. Colored latex containing this dye exhibited the most inferior dye preservation property among the dyes that we had investigated in the previous work, due to the small radius of dye molecule. In this study, we used the dye for preparation of colored latex to make the evaluation of dye preservation property easier. The purpose of this study was to develop another technique that improves the dye migration property of colored latex.

Colored latexes without polyurea shell, **C1** and **C2** were prepared as reference standards (Table 1). Each conversion of styrene in **C1** and **C2** was controlled to 74% and 93% by adjusting reaction temperature and reaction time during polymerization. The dye migration properties depended on the residual monomer inside particles (Fig. 5). In the case of **C1**, half of the dye escaped from the particles, formed dye molecule clusters and precipitated in aqueous phase within 3 weeks after preparation. With decreasing residual monomer in latex, the viscosity of the particle increased and the colored latex exhibited more resistance against migration of dye molecules as supposed from Eq. 3.

Colored latexes with core-shell structure were prepared by the interfacial polycondensation reaction, using various combinations of monomers.

The absorbance at $\lambda_{\max}$ of colored latex was measured immediately after the latex preparation. Colored latex was filtered, dried, and dissolved in THF. Although, the solid content of THF solution was adjusted to the fixed value, the absorbance of the dye in some core-shell particles was smaller than that in the reference standard without shell (Table 2). It had already been confirmed that core-shell particles at t_0 had contained most of the dye added initially. It appeared that the absorption coefficient of the dye in latex products decreased during interfacial polymerization. In other words, some of the dye molecules lost their color. The dye is probably damaged in the course of interfacial polymerization process. After polymerization, absorption coefficient of the dye decreased and $\lambda_{\max}$ shifted (Table 2).

The degree of damage was not the same among the particles prepared under different conditions; it depended on the sorts of monomers for interfacial polymerization. As monomers with higher reactivity were used, absorbance at $\lambda_{\max}$ was likely to become smaller. Monomers dissolved in styrene probably had greater implications for the absorption coefficient of the dye than monomers dissolved in water, because the former had more chance to interact with dye. That is, diisocyanate caused more severe damage to dye. When IPDI, which had mild reactivity, seemed to cause little damage to dye as shown with a large absorbance in Table2 (**C/S1** and**C/S2**), which exhibited little decrease of absorbance and shift of $\lambda_{\max}$. When HMDI, the reactivity of which is

Table 2 Characteristics of colored latexes with core-shell structure

Colored latex	Monomer		Absorbance	λ_{max} (nm)	Residual absorbance (%)	Residual dye (%)
	Diisocyanate	Diamine				
C2	–	–	(1.3546)	443	67.3	78.6
C/S1	IPDI	IPDA	1.1703	443	82.4	90.2
C/S2	IPDI	HMDA	1.1813	444	99.2	98.6
C/S3	IPDI	EDA	0.4182	413	72.4	80.7
C/S4	HMDI	IPDA	0.5305	438	98.4	103.0

Absorbance at λ_{max} of THF solution of dried particles (0.2 mg/ml)
Residual absorbance (%) at storage time $t=4$ weeks
Residual dye (%) at storage time $t=4$ weeks

higher than that of IPDI, was used (**C/S4**), decrease of absorbance and shift of λ_{max} were obviously recognized (Table 2). The dye molecule might contain a functional group that reacts with the isocyanate group. If the electronic state of the chromophore changes, the color of the dye may slightly change or fade.

While **C/S3** consisting of IPDI and EDA exhibited considerable shift in the absorption maximum and the smallest absorption intensity (Table 2), it indicated that not only diisocyanate, but also diamine had implications on absorption coefficient of the dye. The reactivity of EDA is the highest among those of IPDA, HMDA, and EDA. Besides, EDA has the smallest molar mass among them. In the case of **C/S3**, the molar quantity of diamine added in the reaction mixture was the highest because of the smallest molar mass of EDA. As more diamine is added, the pH of reaction mixture is likely to be higher temporarily. The pH of latex products may influence the electronic state of the chromophore, and the color of the dye may change or fade. These factors might cause the dye fading in **C/S3**.

The latex products were maintained in a thermostat at 25°C. After 4 weeks, colored latex was filtered, dried and the dissolved in THF. The absorbance at λ_{max} of colored latex was measured in the same way and the absorbance was compared with that of colored latex immediately after the preparation. The value of residual absorbance after 4 weeks was calculated by Eq. 1, Residual absorbance (%) at storage time $t=4$ weeks of colored latex with a core-shell structure was larger than that of colored latex without shell (Fig. 5 and Table 2). As a particular example, the decrease of absorbance resulted from dye migration during storage period. The residual styrene in particles and diameters of latex particles also exert influences on dye migration property. The total surface area of latex particles increases as diameters decrease. Dye molecules will diffuse inside particles and migrate into aqueous phase easier, if the particles are smaller. It indicated that the polyurea shell could prevent dye molecules from migrating into aqueous phase to a degree, even though those influences were considered. The reference standard without shell exhibited the smallest residual absorbance (%), although the average diameter was the largest and residual styrene was least. The ability to prevent dye migration depended on compositions of polyurea shells. Residual absorbance (%) of **C/S2** and **C/S4** was approximately 100%, and these shell's ability to prevent dye migration was relatively high. The polyurea shell of **C/S2** consisted of IPDI and HMDA, and that of **C/S4** consisted of IPDA and HMDI. After all, these shells had similar polyurea composition. Both **C/S2** and **C/S4** could keep the initial absorbance for 4 weeks, even though **C/S4** contained more residual styrene monomer than **C/S2**. It indicated that polyurea composition closely correlated with the ability to prevent dye migration. Polyurea shells with hexamethylene units resulted in better dye migration property.

Perhaps, it might be difficult that dye molecules pass through polyurea shell and migrate to aqueous phase, because the miscibility between dye molecules and polyurea is low. It was supposed that polyurea shell having lower miscibility with the dye molecule was more effective against dye migration.

As another cause of the decrease of absorbance, we thought that dye molecules were gradually fading during the storage period. In order to confirm whether the decrease of absorbance was attributed to dye migration or dye fading, the dye content of colored latex was examined by elemental analysis. Colored latex immediately after preparation was filtered and dried, and the nitrogen content in dried polymer particles was determined by elemental analysis. As to colored latex after 4 weeks, the nitrogen content was determined in the same way. Polymer particles contained not only dye but also AIBN and polyurea as *N* source and *N* content determined by elemental analysis was assigned to dye, AIBN, and polyurea. Assuming that the decrease of *N* content in polymer particles wholly resulted from dye migration, residual dye in polymer particles after 4 weeks was calculated. Residual dye (%) of **C/S2** and **C/S4** was approximately 100% (Table 2), and these consequences were in accordance with their residual absorbances. As to the other samples, changes of dye content were less than changes of absorbance. The gap between changes of dye content and changes of absorbance would be attributed to dye fading.

C/S2 and **C/S4** exhibited the best dye preservation property, and the absorbance of **C/S2** was relatively high without dye fading during interfacial polymerization. Therefore, **C/S2** synthetically showed the highest quality among these samples.

Conclusions

Dye migration properties of colored latexes with polyurea shell were investigated. Core-shell particles were prepared by applied miniemulsion polymerization. Polyurea shells were formed by interfacial polymerization first, and cores mainly composed of dye and polystyrene were formed by polymerization of styrene inside miniemulsion globules afterward. IPDI, HMDI, and TDI were used as hydrophobic monomers, respectively, and IPDA, HMDA, and EDA were used as hydrophilic monomers for interfacial polycondensation reaction. It was important to control the rate of interfacial polymerization reaction in order to avoid aggregation of particles. When we used monomers with mild reactivities, we could gain stable dispersion without aggregates.

Core-shell particles exhibited better dye preservation properties than reference standards. It indicated that polyurea shell could prevent dye molecules from migrating into aqueous phase, to a degree. The ability to prevent dye migration depended on the compositions of polyurea shells.

We suggested another technique that improves the dye migration property of colored latex. To achieve the best dye migration property, it is effective to select bulky dye molecules that are not damaged during the polymerization, for preparation of colored latex.

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