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Preparation of colored latex containing oil-soluble dyes with high dye content by mini-emulsion polymerization

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Abstract Polymer particles containing oil-soluble dyes (colored latex particles) were prepared by mini-emulsion polymerization. Copper phthalocyanine dyes and styryl dyes were used as oil-soluble dyes. Highly hydrophobic dyes played the role of hydrophobe by themselves and enabled the full incorporation of dyes in the latex without additional hydrophobes. Two phthalocyanine dyes having similar color were blended in a mini-emulsion polymerization so that the resulting colored latex showed enough strong color depth as a colorant. Colored latexes with high dye content (more than 30 wt% for phthalocyanine dye system and 40 wt% for styryl one) and with particle size less than 100 nm were obtained.

Keywords Mini-emulsion polymerization · Hydrophobe · Dye polymer composite · Colored latex · Oil-soluble dye

Introduction

Mini-emulsions are relatively stable and small (20–500 nm) oil droplets dispersed in an aqueous medium [1, 2, 3, 4, 5]. Such droplets are prepared by using high force dispersion devices such as an ultrasonicator and high-pressure homogenizers. The droplet size can be adjusted by the volume fraction and solubility of disperse phase, and the type and amount of surfactant. The stability of small droplets in mini-emulsions arises from the use of highly water-insoluble molecule (hydrophobe) and surfactant. The hydrophobes depress molecular diffusion degradation, so called "Ostwald ripening", and surfactants depress coalescence by collisions.

Mini-emulsion polymerization is carried out by polymerizing the monomer droplets in mini-emulsions. The polymerization of mini-emulsions provides advantages with respect to incorporation of various hydrophobic compounds, because molecules do not have to diffuse into the polymerizing loci through the aqueous phase during particle growth.

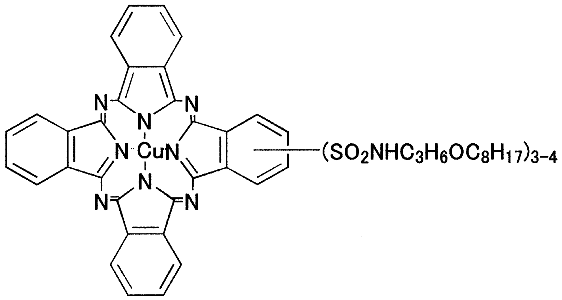
These days, in the field of colorants such as ink and paint, organic volatiles are undesirable because of safety, health, and environmental reasons, and use of an aqueous system is generally required.

While colorants consisting of water-soluble dyes have a variety of colors and provide brilliant colors, the light fastness and the waterproofness of them are not sufficient. On the other hand, colorants consisting of pigments provide excellent light fastness but the color brilliance is not satisfactory.

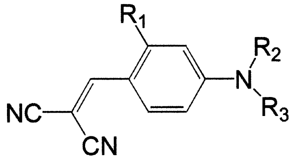
We aimed to prepare "colored latex" with high dye content by mini-emulsion polymerization for the purpose of the development of a third colorant next to dye and pigment. "Colored latex" is the oil-soluble dye-loaded latex with particle size of less than 500 nm. Up to now, many other groups have tried to prepare colored latex but the dye-loading in the latex has not been enough for use as a colorant. In the process of conventional emulsion polymerization, oil-soluble dye molecules must diffuse from oil droplets as monomer reservoirs to monomer-swollen polymerizing particles through the aqueous phase. This process often results in dye aggregates and the dye content in the particle is not high enough for practical use.

In this paper, we report that colored latex that contains more than 40 wt% of dye could be prepared by mini-emulsion polymerization. We selected dyes having high solubility in monomer and mixed some of them to increase the concentration of dyes in monomer, so that the colored latex showed enough strong color depth.

Colored latex must also 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 where the diameter of colored latex particles is smaller than a quarter of the shortest wavelength of visible ray. Therefore, we tried to adjust the particle size to 30–100 nm in order to achieve high color brilliance.



a) Dye I



b) DyeⅢ (R_1:CH_3, Mw.343.47)
DyeⅣ (R_1:H, Mw.399.54)

Fig. 1a, b Molecular structure of **a** phthalocyardne dye **b** styryl dyes

Experimental

Materials

Copper phthalocyanine dyes Dye I (Fig. 1), Dye II (the chemical structure of which has not been disclosed)) were supplied by Chiba Specialty Chemicals as Orasol Blue GL, and Orasol Blue GN, respectively. Styryl dye (Dye III, Fig. 1) was supplied by Mitsubishi Chemical Co. as HSY-2068. Another styryl dye (Dye IV, Fig. 1) was supplied by Dai Nippon Printing Co. as Disperse Yellow 201. Other chemicals used in this work include styrene (Junsei), sodium dodecyl sulfate (SDS) (Nacalai Tesque), potassium persulfate (KPS) (Kishida), sodium hydrocarbonate ($NaHCO_3$), azo-bis-isobutyronitrile (AIBN) (Wako), hexadecane (Junsei), tetrahydrofuran (THF) (Junsei). All chemicals were used as received. Water was deionized before use.

Preparation of mini-emulsions

The monomer solution of dyes (containing hexadecane and AIBN in some cases) was added to the aqueous SDS solution and stirred at room temperature for several minutes. The resultant emulsion was then homogenized by an ultrasonicator, Ultrasonic Homogenizer UH-600 (SMT) operated at 80% intensity for 15 min under ice cooling.

Polymerization process

The monomer mini-emulsion 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 heated to 80 °C under nitrogen flowing. Stirring at 300 rpm was provided by a paddle stirrer. The reaction was initiated by injection of a KPS solution at 60–80 °C. When AIBN was present in the monomer mixture, the reaction started during the heating period. The solid content and conversion of monomer were determined by the gravimetric method. For conventional emulsion polymerization, the emulsion that had not been ultrasonicated was polymerized in the same way.

Droplet and particle size

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

Self stability of mini-emulsions

The stability of mini-emulsions was evaluated by the change of monomer droplet size during storage at room temperature. After storage at room temperature, the mini-emulsion was diluted with a monomer-saturated aqueous solution of 8 mM SDS, and the average size of monomer droplets was measured by DLS.

Dye content analysis

The colored latex was filtered through 200 nm or 450 nm microfilters to remove the unfilterable solids such as the dye molecule clusters that had not been incorporated into particles, the aggregate of particles, and extremely large size particles. Then the filtered latex was dried on a hot plate.

Phthalocyanine dye content analysis

Dried polymer particles were dissolved in THF and the concentration of the THF solution was adjusted to 0.1 mg/mL. The visible absorption spectra of the THF solution of the colored latex (0.1 mg/mL) were measured with an absorptiometer (Hitachi spectrophotometer U-3500). If the dye concentration is low enough, the absorbance of solution obeys Beer's law. Then, the dye content in colored latex was determined from the absorbance at absorption maximum (λ_{max}) using the calibration curve of the absorbance at λ_{max} (669 nm) versus dye concentration (in THF) (Fig. 2). Absorption spectra of phthalocyanine dyes are shown in Fig. 3.

Styryl dye content analysis

Nitrogen content in dried polymer particles was determined by elemental analysis. As molecules of two styryl dyes (Dye III, Dye IV) contain nitrogen of 12.23 wt% and 10.52 wt%, dye content of polymer particles was calculated from nitrogen content of particles.

Size of dye aggregates in latex particles

The state of phthalocyanine dye molecules in latex particles were investigated by using the small-angle X-ray scattering method (SAXS). SAXS measurement was performed with Confocal Maxflux Mirror installed on Rotaflex RU-200B (Rigaku), operated at 50 kV, 200 mA. The confocal beam at the wavelength $\lambda = 1.54$ Å (Cu Kα) was obtained by this mirror. The sample solution was kept at room temperature during the measurement.

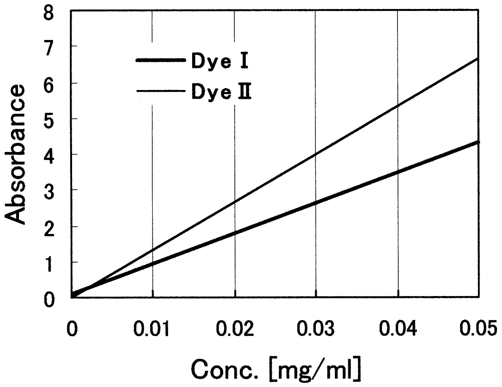


Fig. 2 Calibration curve of the absorbance at 669 nm versus dye concentration data (in THF)

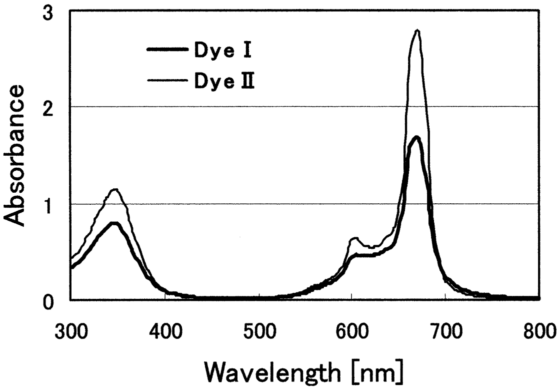


Fig. 3 Absorption spectra of THF solutions of phthalocyanine dyes (0.02 mg/ml)

Results and discussion

Comparison between mini-emulsion polymerization and conventional emulsion polymerization

Colored latexes containing copper phthalocyanine dye (Dye I) were prepared by conventional emulsion polymerization and mini-emulsion polymerization. The same recipe was used in both cases except for the ultrasonication process, which was applied only to the latter system. It is known that some kinds of water-insoluble dyes work as a hydrophobe in a mini-emulsion system and offer resistance to diffusional degradation of the monomer droplets (Ostwald ripening) [6, 7]. It was difficult to obtain small latex particles (< 100 nm) whose dye content was more than 10% by conventional methods. We tried to prepare colored particles containing much more dye. First, we examined the stability of mini-emulsion containing Dye I. The stability of mini-emulsion containing Dye I of 15 wt% (in oil phase) was evaluated by the change of the average monomer droplet size two days after mini emulsification. No change in size indicated that the Dye I can stabilize the mini-emulsion. Therefore, we did not add any hydrophobes other than Dye II to the monomer phase.

In case of emulsion polymerization, the dye clusters were formed during the polymerization, and the color of latex became relatively faint and dull. The data of DLS measurement indicated that the dye molecule clusters of the size over 1 micron was suspended in the latex B2 (Fig. 4). The dark blue precipitate was found on standing.

On the other hand, the colored latex B1 prepared by mini-emulsion polymerization showed uniform deep blue color on the whole, and no dye clusters suspended in the latex. It indicated that all of the dye charged in monomer droplets was successfully encapsulated in the polymer particles. The hydrodynamic diameter of the droplet was not measured exactly but it was certain that the size decreased during polymerization more than expected, referring to the difference in the density between monomer and polymer. Therefore, the possibility of new particle formation in the aqueous medium during polymerization was undeniable. The size dispersity (the ratio of weight average diameter to number average diameter) of latex particles of B1 was 1.36.

The amount of dye incorporated into the latex particles was determined by using the calibration curve (Fig. 2) as follows. The latex products B2 and B1 were

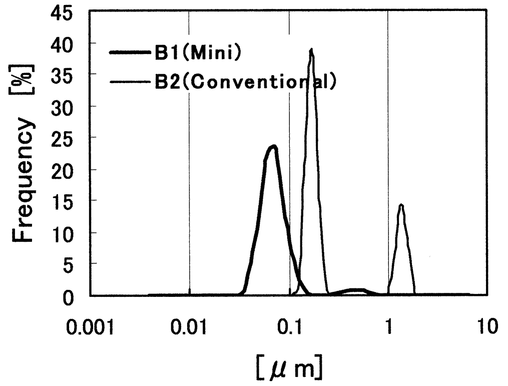


Fig. 4 Size distribution of colored latex. *B1* colored latex prepared by minlemulsion polymerization, *B2* colored latex prepared by conventional emulsion polymerization. Dye I/St/SDS/KPS/$NaHCO_3$/H_2O = 1.6/6.4/0.184/0.021/0.007/32 g

filtered through 450 nm and 200 nm micro-filters, respectively, to remove the dye molecule clusters. Then, each sample was dried, and the dried particles were dissolved in THF. The absorbance at 669 nm of the THF solution was measured (Fig. 5) and the dye content of the latex particles was calculated from the calibration curve. The latex particles B2 contained dye of only 4.4 wt%. Because the Dye I is more hydrophobic than styrene monomer, all the dye molecules cannot diffuse into polymerization sites in micelles across aqueous phase and, as a result, most of dye remained out of the particles. On the other hand, the latex particles B1 contained dye of 20.1 wt% in accordance with the theoretical value. This is a reasonable result, reflecting the advantage of mini-emulsion polymerization.

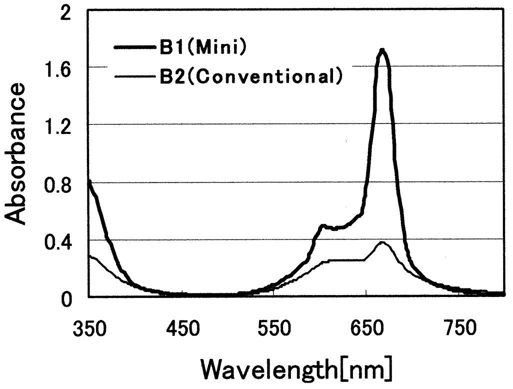


Fig. 5 Absorption spectra of THF solutions of dried particles (0.1 mg/ml)

Synthesis of colored latex with high dye content

Dye-loading styrene mini-emulsions were prepared with different contents of dye ([dye] = 20, 25, and 30 wt% based on total oil phase) (Table 1). In the range of dye content examined, the dye was soluble in styrene monomer, on the whole. During the polymerization, no bulk dye became suspended in the aqueous phase, and the resulting latexes produced homogeneous dark blue color. The higher the content of dye in the oil phase, the larger the diameter of the latex particle (Table 1). The latex of colored particles with a diameter larger than 100 nm shows relatively dull color due to the scattering of light. The particle size is expected to become smaller if we use more surfactants. Table 1 shows that the dye content of the latex particle increased with the content of dye in the oil phase. It indicates that most of the dye can be incorporated into latex particles. In case of [dye] = 25 and 30 wt%, dye content was higher than the theoretical value, because the conversion of styrene monomer was less than 100%.

Color strength of the latex product was evaluated by absorptiometric method. The latex products were diluted with deionized water and adjusted to 1.0 mg/mL. Then the absorbance of the diluted latex was measured. The absorption spectra of the diluted latex (Fig. 6) were different from those of the THF solutions of dyes. Phthalocyanine dye has a planar molecular structure and it is likely that dye molecules become stacked and form dyestuff aggregates [8, 9]. The spectrum of copper phthalocyanine dye in THF solution is characterized by some absorption bands. The first of them appears at around 340 nm (Fig. 3) and has been used as a "marker" band since it obeys Beer's law over a wide range of dye concentrations and experimental conditions. In the case of latex particles, on the other hand, the absorption band at 340 nm is not suitable for a marker band of dye content, because polystyrene particles themselves have absorbance at around 340 nm (Fig. 6). When the concentration of dye solution in THF is low, another band appears in the visible region at around 670 nm (Fig. 3), and is attributed to the dye monomers. The monomeric species also contribute to the absorption at shorter wavelengths (around 600 nm). The absorption spectra of

Table 1 Characteristics of colored latex containing Dye I

Colored latex	Dye I (g)	Styrene (g)	Conversion (%)	Diameter (nm)	Absorbance[a]	Dye content (%)
B1	1.6	6.4	95	63.5	1.714	20.1
B3	2.0	6.0	93	75.7	2.368	26.2
B4	2.4	5.6	85	102.9	2.707	32.0

SDS/KPS/$NaHCO_3$/H_2O = 0.184/0.021/0.007/32 g

[a] THF solution of dried particles (0.1 mg/ml), λ_{max} 669 nm

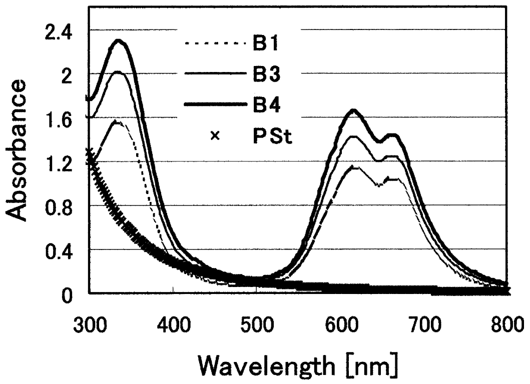


Fig. 6 *B1*, *B3*, *B4* Absorption spectra of colored latex containing phthalocyanine dye (1.0 mg/ml). *PSt* Absorption spectrum of polystyrene latex without dye (1.0 mg/ml), diameter 42 nm

the diluted colored latex show two absorption bands in the visible region at λ_{max} 616–618 nm and λ_{max} 665–666 nm (Fig. 6). The shorter wavelength band (λ_{max} 616–618 nm) is attributed to the dimeric dye molecules and the longer one (λ_{max} 665–666 nm) to the dye monomers [10]. As there is an appreciable overlap between these two bands, it is difficult to make quantitative assessment of aggregate and monomer concentrations. Nevertheless, qualitatively useful information can be obtained from the relative intensities of these two bands. The absorption spectra of the diluted latex indicate that dyestuff aggregates have been formed inside the latex particle by π-π interaction. In the range of 20–30% dye content of the latex particle, the absorption peak derived from the dyestuff aggregates is higher than that of the dye monomers, but the dependence of the relative intensities of these two bands on the dye content is not observed clearly. However, for the colored latex of 5 wt% dye content, the absorption peak derived from the dye monomers is as high as that of the dyestuff aggregates (data not shown). It indicates that the degree of aggregation is less when dye content in colored latex is low.

The size of phthalocyanine dye aggregates in latex particles was evaluated by SAXS. The SAXS profile of B3 is shown in Fig. 7. The magnitude of the scattering vector Q and long spacing L are provided by Eq. 1 and Eq. 2

$$Q = (4\pi/\lambda)\ \sin\,(\theta/2) \tag{1}$$

$$L = 2\pi/Q \tag{2}$$

Here λ and θ are the wavelength of the incident beam and the scattering angle, respectively. The peak was observed at $Q = 0.24$ Å^{-1}, which was equivalent to $L = 2.6$ nm. The SAXS peak can be attributed to the phthalocyanine dye aggregates in latex particles and indicate that Dye I formed aggregates with a size of 2.6 nm. But the peak might be attributed to the lamellar structure formed by surfactant molecules.

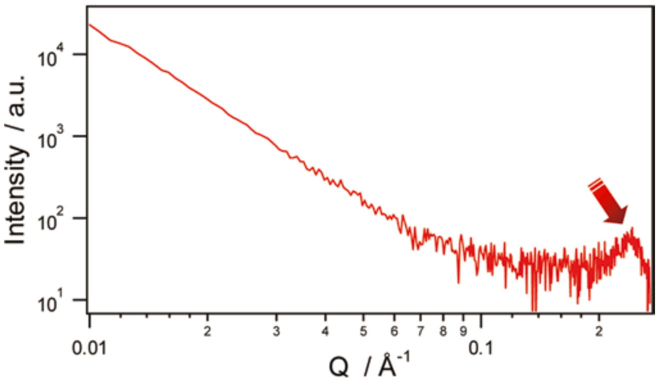


Fig. 7 SAXS data of colored latex B3

The stability of the latex product during storage was good. The latex particles keep dyes inside themselves and the dye content is unchanged for more than 1 year.

Combination of phthalocyanine dyes

The color of phthalocyanine dyes arises from the ring structure of hetero-polyene. λ_{max} of phthalocyanine dyes depends on the centered metal but the substituent groups of dyes do not affect the λ_{max} so much. Some phthalocyanine dyes are combined to increase the dye content in colored latex. Phthalocyanine dyes used for this purpose (Dye I and Dye II) have different substituent groups but the colors accord very well, as shown in Fig. 3.

If the dye concentration in the monomer is far over the solubility limit, the mini-emulsion cannot keep its stability during polymerization and the latex product becomes polydisperse and color quality decreases. Therefore, it is necessary to select dyes whose solubility in monomer is high and which can be combined each other to increase the concentration of dissolved dyes in styrene monomer. The colored latex containing different amounts of Dye I and Dye II was prepared as indicated in Table 2. The amounts of dyes (27, 30, and 33 wt%) are based on total oil phase. The latex products showed homogeneous dark blue. In the binary system consisting of Dye I and Dye II, the absorbance at certain wavelength of mixed dyes is provided by the Eq. 3 under the condition where the concentration of dyes is low enough to obey Beer's law.

$$A(\lambda) = C_1A_1(\lambda) + C_2A_2(\lambda) \tag{3}$$

Here C_1 and C_2 are the concentrations of Dye I and Dye II, and A_1 and A_2 are the absorbance per unit concentration of the respective dyes at wavelength λ. The calibration curve of the absorption at 669 nm is theoretically calculated from the absorption coefficient of each dye. Theoretical absorption coefficients of mixed

Table 2 Characteristics of colored latex containing phtalocyanine dyes

Colored Latex	Dye I (g)	Dye II (g)	Styrene (g)	SDS (g)	Absorption coefficient[a]	Conversion (%)	Diameter (nm)	Absorbance[b]	Dye content (wt%)
B5	1.76	0.4	5.84	0.184	93.7	92	79.2	2.045	21.8
B6	2.0	0.4	5.6	0.276	92.8	95	52.4	2.585	27.9
B7	2.32	0.32	5.36	0.276	90.6	90	63.2	2.790	30.8

$KPS/NaHCO_3/H_2O = 0.021/0.007/32$ g

[a] Theoretical absorbance of THF solution of mixed dyes (1.0 g/l) at λ_{max} 669 nm

[b] THF solution of dried particles (0.1 mg/ml), λ_{max} 669 nm

dyes are shown in Table 2. The amount of dye incorporated into the latex particles is determined from the calibration curve of the mixed dye. The absorption coefficient of Dye II is larger than that of Dye I (Fig. 3), but Dye I is more soluble in styrene monomer than Dye II. Therefore, the content of Dye II used in the binary system is limited. Table 2 shows that the dye content in the latex products increased with the content of dyes in the oil phase. The absorption spectra of the diluted latex were also measured. The absorption peaks of the latex particles containing mixed dyes are higher than those of the latex particles containing single dye with the same amount (Tables 1 and 2), because the Dye II has a larger absorption coefficient. The spectra indicated that the dyestuff aggregates have been formed inside the latex particle. In the range of 21.8–30.8 wt% dye content in the latex particle, the absorption peak derived from the dyestuff aggregates is higher than that of the dye monomers, but the dependence of the relative intensities of these two bands on the dye content is not observed clearly. The photograph of colored latex B7 and THF solution of dyes is shown in Fig. 8. Although formation of dyestuff aggregates has disadvantages in point of color quality and dyeability, colored latex containing oil-soluble phthalocyanine dyes showed more brilliant color than commercial ink consisting of phthalocyanine pigment. The stability of the latex product during storage is good for more than 1 year. In conclusion, we could obtain colored latex with deep color by blending copper phthalocyanine dyes.

Fig. 8 *a* Colored latex containing phthalocyanine dyes (B7). *b* THF solution of phthalocyanine dyes. The dye contents of *a* and *b* are equal. *c* and *d* show the color of *a* and *b* spread on paper

Synthesis of colored latex containing styryl dyes

Yellow colored latex containing styryl dye was also prepared by mini-emulsion polymerization (Table 3). Styryl dyes have relatively high solubility in styrene monomer. But, since these styryl dyes hardly stabilize the mini-emulsion, hexadecane is used as a hydro-

Table 3 Characteristics of colored latex containing styryl dyes

Colored latex	Dye III (g)	Dye IV (g)	Styrene (g)	Absorption coefficient[a]	Conversion (%)	Diameter (nm)	Absorbance[b]	Dye content (%)
Y1	1.6	0	6.4	178.8	100	69.1	2.000	–
Y2	0	1.6	6.4	139.7	100	56.3	1.312	–
Y3	0	3.2	4.8	139.7	100	67.3	1.742	39.4
Y4	0.8	2.8	4.4	148.4	100	60.8	2.232	43.7

Y1, 2, 3: $Hexadecane/AIBN/SDS/H_2O = 0.4/0.024/0.736/32$ g

Y4: $Hexadecane/KPS/NaHCO_3/SDS/H_2O = 0.4/0.024/0.008/0.736/32$ g

[a] Absorbance of THF solution of dyes (1.0 g/l) at λ_{max} 439 nm

[b] THF solution of dried particles (Y1, 2:0.1 mg/ml, Y3, 4:0.05 mg/mL), λ_{max} 439 nm

phobe for mini-emulsion polymerization. Styryl dyes (Dyes III, IV) are used alone, or combined to increase the concentration of dissolved dyes. Dyes III and IV have different substituent groups, but they have similar chromophoric groups and their colors accord well (Fig. 9). The latex products showed homogeneous yellow color and the data of DLS indicated that the latex products hardly included bulk aggregates. The colored latex was filtered through 200 nm and the filtered latex was dried. Nitrogen (N) contents in dried latex particles (Y3 and Y4) were determined by elemental analysis. Molecules of two kinds of styryl dyes, Dye III and Dye IV, contain N of 12.23 wt% and 10.52 wt%, respectively, and the dye content of polymer particles can be calculated from the N content in particles. N content in latex particles Y3 was 3.89%. As the theoretical value of N content in Y3 was 3.93%, it was ascertained that most of dye molecules (99%) were incorporated into latex particles. (Although Y3 contained not only dye but also AIBN as N source, N content attributed to AIBN was very little.) N content in latex particles Y4 was 4.34% and the theoretical value of N content in Y4 was 4.44%. Most of Y4 molecules (98%) were also incorporated into latex particles.

The absorption spectra of THF solutions of dried particles were measured. The absorbance at $\lambda_{\max}$ was smaller than the estimation from dye content determined by elemental analysis, and the absorption intensity was less than the values expected from the calibration curve. It appeared that the absorption coefficients of styryl dyes in latex products decreased during polymerization. In other words, some of the dye molecules lost color. Styryl dyes are probably damaged in the course of the polymerization process. After polymerization, absorption coefficients of styryl dyes decrease, but change of color is not recognized. Styryl dye molecules cannot be polymerized with styrene monomers, but radical transfer to the dye molecule may occur in the course of the polymerization process. The conversion of styrene monomer coexisting with styryl dyes finally reached 100% for 2–3 h, but the polymerization rate was lower than that of styrene without styryl dyes.

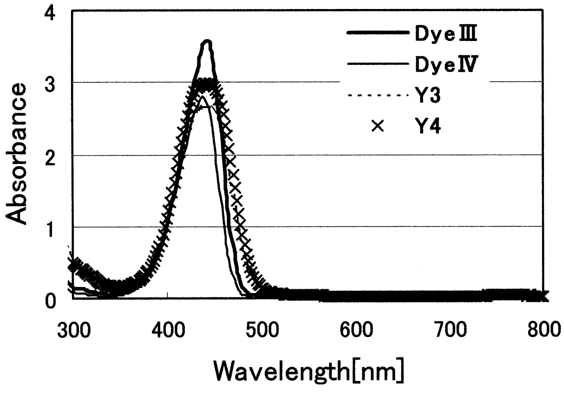


Fig. 9 *Dye III*, *Dye IV* Absorption spectra of THF solutions of styryl dyes (0.02 mg/ml). *Y3*, *Y4* Absorption spectra of colored latex containing styryl dyes (0.1 mg/ml)

The color strength of the latex product was estimated from the absorption spectrum of the latex particles (the diluted latex). The absorption peak of the latex particles is slightly broad in comparison with that of dye solution (Fig. 9). It is supposed that the degree of aggregation of styryl dyes in latex particles is much lower than that of phthalocyanine dyes. The aggregation of dye molecules is a crucial factor for dyeability and color quality, because formation of dyestuff aggregates has disadvantages in point of coloration and brilliant color. Therefore, colored latex without dyestuff aggregates can produce color effectively.

The stability of the latex product during storage was unsatisfactory, since the migration of dyes from the latex particles occurred. The dye molecules that migrate from the latex to the aqueous phase form dyestuff aggregates in water and they precipitate after several days. In the case of colored latex containing copper phthalocyanine dyes, the migration of dye molecules is not a severe issue. Perhaps, the difference in the diffusion velocity between copper phthalocyanine and styryl dyes can be explained by the difference in size of dye molecules or aggregates. The diffusion velocity of dyestuff aggregates is so low that colored latex containing phthalocyanine dye is stable without the migration of dyes.

Conclusions

The mini-emulsion polymerization method is more suitable for the synthesis of colored latex with high dye content than conventional emulsion polymerization.

Colored latex containing phthalocyanine dyes up to 30 wt% has been prepared. The dyes suitable for colored latex were selected and blended so that colored latex showed enough strong color depth as a colorant. The absorption spectra of the latex products indicated that dyestuff aggregates were formed inside the latex particle by π-π interaction.

Yellow colored latex containing styryl dyes was also prepared. Styryl dye content determined by elemental analysis of latex particles was more than 40 wt%. Judging from the color strength of commercial aqueous ink for inkjet printers, the color of the latex product containing styryl dyes is strong enough for practical use.

The conditions of dyes suitable for introduction into latex particles are high solubility in monomer, large absorption coefficient per unit weight, and small radical transfer coefficient.

We have succeeded in obtaining colored latexes (with diameter of less than 100 nm) which contain dyes up to 43.7 wt% by developing a mini-emulsion polymerization technique. The colored latexes showed enough strong color depth and excellent brilliance.

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