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Improvement of the storage stability and photostability of colored latex prepared by miniemulsion polymerization

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Abstract Polymer particles containing oil-soluble dyes (colored latex) were prepared by miniemulsion polymerization. The dye preservation properties of colored latex loaded with different types of dye were studied; preservation depended on the rate of dye diffusion and thus on the size of the dye molecules and the hardness of the polymer matrix in the latex particles. Hindered amine stabilizers (HAS) were used to improve the photostability of colored latex. The effect of HAS in colored latex was investigated both as an additive and as a comonomer. The photostability of latex particles containing a simple mixture of dye and HAS was improved with increasing HAS content up to 20% in particles. In the case of colored latex particles combined with HAS by a covalent bond, the optimal amount of HAS for photostability improvement was between 8 and 20%.

Keywords Miniemulsion polymerization · Particle · Hindered amine stabilizer · Colored latex · Photostability · Dye migration

Introduction

Miniemulsion polymerization is carried out by polymerizing the monomer droplets prepared by miniemulsification [1]. The polymerization of miniemulsions 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 particle growth.

In our previous work [2], we prepared "colored latex" with high dye content by miniemulsion polymerization for the purpose of the development of a third colorant, that is, in addition to dye and pigment. Colored latex is latex loaded with oil-soluble dye. We adjusted the particle size to 30–100 nm, much shorter than the wavelength of visible light, in order to achieve high color brilliance. Colored latex with strong color depth was prepared using different kinds of dye. In the case of colored latex containing copper phthalocyanine dyes, dye molecules were found to form dye dimers or larger assemblies inside the latex particles at higher concentrations. As to the colored latex containing styryl dyes, we obtained latexes that contained dyes up to 43.7 wt% and showed enough strong color depth and brilliance. But the absorption coefficient value of styryl dye was found to decrease during storage. Colored latex must keep dyes 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.

One of the most important properties of a dye is its fastness to light and many efforts have been made for the purpose of photostability improvement. Not only has the correlation between light fastness and the dye structure been studied [3, 4], but also stabilizers have been commonly used to protect dyes and the host polymer against photodegradation [5]. There are some kinds of stabilizer which preferentially absorb the UV component of sunlight, accept the transfer of energy from an excited dye or polymer, or quench the effects of singlet oxygen. Included in the third category are the hindered amine stabilizers (HAS) that are useful antioxidants in the protection of polyolefins, especially polypropylenes.

Compatible and mobile stabilizers usually give the best protection, but low molecular weight stabilizers are easily lost from the polymer particles through migration, evaporation, or extraction. Surface grafting of stabilizers has been reported as a convenient technique for attaching a stabilizer to the polymer in a permanent manner [6]. It was shown that the photostabilizing efficiency of surface-anchored HAS was superior to that of HAS melt-blended in polyolefins. Azo dyes containing a built-in hindered amine moiety were also synthesized and it was reported that such moieties enhanced the photostability of dyes in polymer matrices [7].

In this paper, the storage stability and photostability of colored latexes were studied. First, the dye migration properties of colored latex with different types of dye were investigated to improve the storage stability of colored latexes. Then, latex particles containing azo dyes and HAS were prepared in attempts to improve the photostability of colored latex. The photostabilities of colored latex were discussed with respect to photofading of colored latex films on substrates.

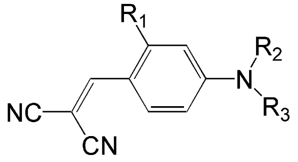
Experimental

Materials

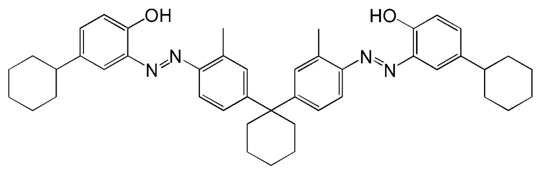
Styryl dyes, Dye I (HSY-2068) and Dye II (Disperse Yellow 201) (Fig. 1), were supplied by Mitsubishi Chemical Co. and Dai Nippon Printing Co., respectively. One of the azo dyes, Dye III (Fig. 1), was supplied by Orient Co. as Oil Yellow 129. The other azo dyes were supplied by Mitsubishi Chemical Co. as HSR2310 and HSR2150. A hindered amine stabilizer HAS I (Fig. 2) was supplied by Sankyo Co. as Sanol LS-440. A polymerizable hindered amine stabilizer HAS II (Fig. 2) was supplied by Asahi Denka Co. as Adekastab LA-82. Other chemicals used in this work include styrene, sodium hydrogen carbonate ($NaHCO_3$), hexadecane (HD), and tetrahydrofuran (THF) from Junsei Chemical Co., methyl methacrylate (MMA), methacrylic acid, *N*-cetyl pyridinium chloride, and stearyl methacrylate (SMA) from Tokyo Kasei Kogyo Co., sodium dodecyl sulfate (SDS) from Nacalai Tesque, potassium persulfate (KPS) from Kishida Chemical Co., and 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50), 2,2′-azobis(isobutylonitrile) (AIBN) from Wako Pure Chemical Industries. All chemicals were used as received. Water was deionized before use.

Preparation of miniemulsions

The monomer solution of dyes (containing HD or SMA, HAS, and AIBN in some cases) was added to the aqueous surfactant solution 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% intensity for 15 min under ice cooling.

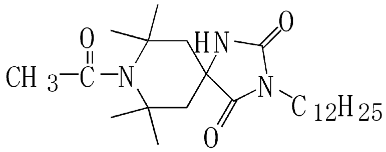


a) DyeI (R_1:CH_3, Mw.343.47)
DyeII (R_1:H, Mw.399.54)

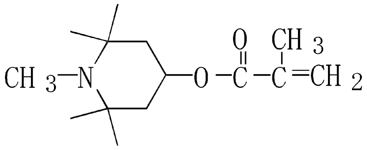


b) DyeIII

Fig. 1a,b Molecular structure of dyes. **a** Dye I (R_1: CH_3, Mw 343.47), Dye II (R_1: H, Mw 399.54). **b** Dye III



a) HASI



b) HASII

Fig. 2a,b Molecular structure of HAS. **a** HAS I. **b** HAS II

Polymerization process

The monomer 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 heated to 70–80 °C under nitrogen flow. The reaction mixture was stirred at 200–300 rpm during the polymerization. The reaction was initiated by injection of KPS or V-50 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. The theoretical solid content of the colored latex is approximately 20%.

Droplet and particle size

The average size and size distribution of monomer droplets were obtained from dynamic light scattering (DLS), using a Microtrac UPA (Honeywell Co.) instrument. 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. In the case of the measurement of polymer particle size, the latex was diluted with deionized water.

Dye migration properties

The dye content in colored latex particles at t_0 (storage time $t=0$) was measured immediately after latex preparation. Then, the latex was kept in an oven at 25 °C and the dye contentof the particles was measured at various storage times. The measurement by absorptiometry was carried out as follows.

Colored latex was filtered through 200-nm microfilters to remove solids such as aggregates of dye molecules, aggregates of particles, and extremely large size particles. Then the filtered latex was dried on a hot plate. Dried polymer particles were dissolved in THF and the concentration of the solution was adjusted to 0.1 mg/mL. The visible absorption spectra of the THF solution of the colored latex were measured with 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 the absorption maximum ($\lambda_{\max}$) of colored latex immediately after preparation was regarded as the 100% value of residual dye. The values for the amounts of residual dye in colored latex after storage were calculated by Eq. 1:

$$\text{Residual dye}(\%) = A_t/A_0 \times 100 \tag{1}$$

where A_t = absorbance at $\lambda_{\max}$ of colored latex (THF solution) at storage time t and A_0 = absorbance at $\lambda_{\max}$ of colored latex (THF solution) at storage time $t=0$.

Light fastness

The photostability of colored latex was evaluated by an irradiation experiment. The solid content of colored latex was adjusted to the stated value by dilution with deionized water. A paper was coated with the colored latex using a bar-coater (No. 4) and dried at room temperature (r.t.). The latex film on paper thus obtained was irradiated by a xenon weatherometer (Atlas Co.) for 40 h under the condition where the light intensity at 360 nm was 0.5 W/cm^2, the temperature 60 °C, and the relative humidity 50%. Before and after the irradiation, the reflectance of each sample was measured with an absorptiometer (Hitachi Spectrophotometer U-3500). The reflectance spectrum was analyzed into L^*, a^*, and b^* by a CIELAB color system. The values of L^*, a^*, and b^* indicate the positions of colors in the CIELAB coordinates. E^*, ΔE^*, and relative % fading were calculated using the following Eqs. 2, 3, and 4:

$$E* = \left[(L*)^2 + (a*)^2 + (b*)^2\right]^{1/2} \tag{2}$$

$$\text{Color difference } \Delta E* = \left[(L*' - L*)^2 + (a*' - a*)^2 + (b*' - b*)^2\right]^{1/2} \tag{3}$$

$$\text{Relative\%fading} = (\Delta E*/E*) \times 100 \tag{4}$$

where $L^{*\prime}$, $a^{*\prime}$, and $b^{*\prime}$ are the values for the latex after light exposure, whereas L^*, a^*, and b^* are those before light exposure.

Results and discussion

Dye migration properties

Colored latex must keep dyes inside the latex particles for a long storage time, so dye migration from the colored latex particles must be minimized. But it is apt to become a severe issue as the dye concentration increases in the latex particles. In some cases, dyes inside latex particles migrate to the aqueous phase and precipitate as dyestuff aggregates. Dye migration in colored latex was studied in order to clarify the cause and prevent it. To evaluate 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.

The relation between residual monomer inside particles and the dye migration properties was investigated first. Latex particles containing Dye I and different amounts of residual monomer were prepared by controlling monomer conversion in the system Dye I/styrene/HD/AIBN/SDS/H$_2$O = 4/16/1/0.06 or 0.3/1.84/80 g. HD was used as a hydrophobe to stabilize the miniemulsion. The conversion of styrene was controlled to 75, 95, and 100% by adjusting the amount of AIBN, reaction temperature, and reaction time during the polymerization. In the colored latex whose monomer conversion was 75%, most of the dye escaped from the particles, formed dye molecular clusters, and precipitated in the aqueous phase within one week after preparation (Fig. 3). With decreasing residual monomer in the latex, the viscosity inside the particle increased and the colored latex exhibited more resistance to migration of dye molecules, as supposed from Eq. 5:

$$D = kT/(r\eta) \tag{5}$$

where D is the diffusion constant, k a constant, T the absolute temperature, r the radius of the solute, and η the viscosity of the matrix. The result in Fig. 3 shows that, even if there was no monomer remaining in the latex particles, migration of Dye I could not be prevented perfectly at 25 °C.

Equation 5 suggests that the radius of the dye molecule also affects the migration of dye. Therefore we next investigated the correlation between the size of the dye molecule and dye migration. The dyes chosen for this study were Dye I, Dye II, and Dye III. Dye I and Dye II are both styryl dyes and the molecular size of

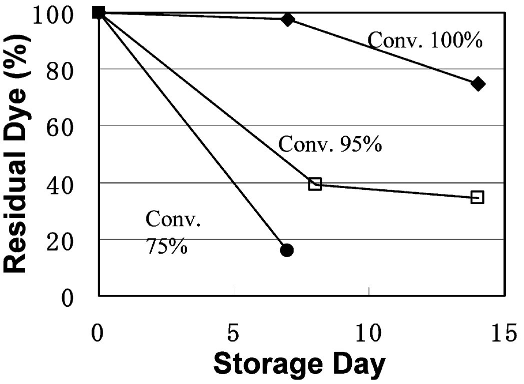


Fig. 3 Dye migration properties of colored latex containing different amounts of monomer (dye content 20 wt%, const.)

Table 1 Characteristics of colored latex loaded with different types of dyes

Colored latex	Dye	Monomer	AIBN (g)*	Diameter (nm)	Conversion (%)	A_0 (λ_{max})
Y1	I	Styrene	0.06	69.1	100	2.000 (443 nm)
Y2	II	Styrene	0.06	56.3	100	1.295 (439 nm)
Y3	III	MMA/MAA	0.3	14.1	97	0.941 (345 nm)

Dye/monomer/HD/AIBN/SDS/H_2O = 4/16/1/*/1.84/80 (g)
MMA/MAA = 15/1 (g)
A_0 = absorbance at λ_{max} of colored latex (THF solution 0.1 mg/mL) immediately after the preparation

Dye II is larger than that of Dye I (the molecular weights of Dye I and Dye II are 343 and 400, respectively). Colored latexes containing Dye I and Dye II were prepared under the same polymerization conditions (Y1 and Y2 in Table 1). Table 1 indicates that Dye II-containing particles were smaller in size than Dye I-containing ones, or that the specific surface area (proportional to the surface/volume ratio) for Dye II-containing particles is larger than that for Dye I-containing particles. These facts may suggest that Dye II molecules inside the particle can reach the surface faster and escape from the particle more easily than Dye I molecules. But this was not the case. Colored latex loaded with Dye II had a better dye retention than colored latex loaded with Dye I, as shown in Fig. 4. This was attributed to the larger molecular size of Dye II.

Dye III was employed in this study as a representative dye with a large molecular size. It contains two color-producing functional groups and is about two times bulkier than Dye I and Dye II. Of course, attention must be paid to the facts that Dye III is an azo dye and the type is different from Dye I and Dye II. Reflecting these situations, polymerization containing Dye III was carried out under different conditions from those for Dye I and Dye II systems.

For example, the monomer was not styrene but methyl methacrylate/methacrylic acid and the amount of initiator was quite large for the Dye III-containing system. The product of this system had a remarkable feature in terms of particle size, perhaps due to the effect of methacrylic acid. The size of colored latex particles loaded with Dye III (Y3) was extremely small (14.1 nm, shown in Table 1). In addition, the average size and size distribution of latex particles measured by DLS were almost overlapped with those of the monomer droplets before polymerization (Fig. 5). This indicated that Y3 was mainly produced by the miniemulsion polymerization mechanism. Now, Dye III migration was compared with that of Dye I and Dye II. The results are shown in Fig. 4. Y3 could keep most dye inside the particles for more than six months (although Fig. 4 shows only the result up to 30 days). As mentioned above, the decrease in the diameter of latex particles causes an increase in the ratio of surface area to volume (S/V) of particles and the acceleration of dye molecule escape from the particle. Although the S/V ratio of Y3 was the largest among the three, Y3 exhibited the best dye retention (Fig. 4). This could be attributed mainly to the bulkiness of Dye III as was true in the relation between Dye I and Dye II systems. But very good compatibility of Dye III with the PMMA matrix would probably be an additional cause for negligible migration of Dye III.

It is known that copper phthalocyanine dye has a planer molecular structure and is likely to form dyestuff aggregates by van der Waals attraction [8, 9, 10]. In our previous work, it was confirmed that phthalocyanine dye formed aggregates inside the latex particles. This colored

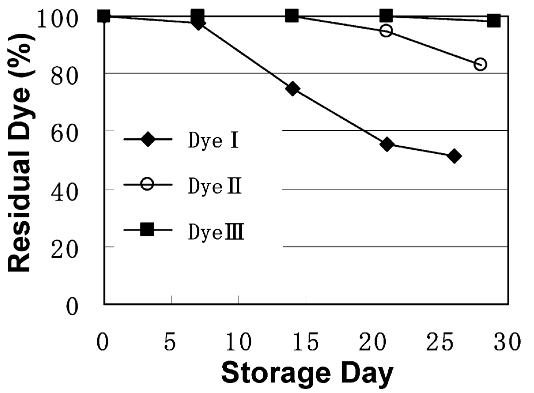


Fig. 4 Dye migration properties of colored latex containing different dyes (dye content 20 wt%, const.)

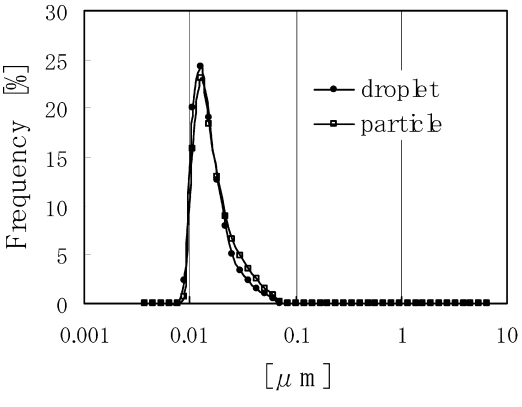


Fig. 5 Size distribution of miniemulsion (Y3) before and after polymerization

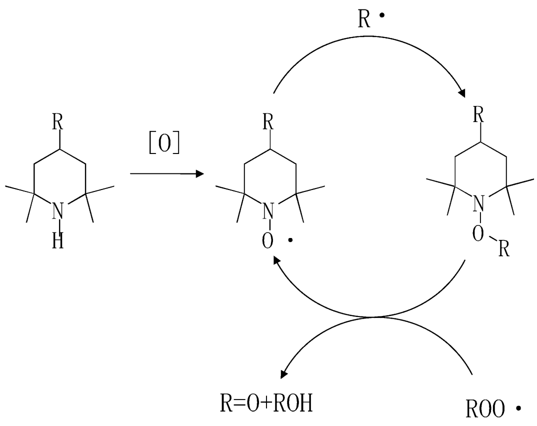


Fig. 6 Denisov cycle

latex could maintain the dye inside the particles for several months. This is believed to result from the fact that the rate of diffusion of dyestuff aggregate is lower than that of dye monomer.

The conclusion in this section is that dye migration depends on the diffusion rate of dye molecules inside the latex particles, so incorporation of bulky dye molecules in a hard polymer matrix without residual monomer would be the best way to get colored latexes with high dye preservation properties.

Improvement of light fastness

HAS was used to improve the photostability of colored latex containing azo dyes. HAS is a tetramethylpiperidine derivative and works as a radical scavenger [11]. Various types of HAS have been developed and commercialized as plastics additives. The stabilizing mechanism by scavenging polymer radicals has not been clarified completely. But the stabilization by HAS is probably attributed to the oxidation of amine and the change to a nitroxy radical, and is explained by the Denisov cycle as shown in Fig. 6.

The photostabilities of colored latex were studied with respect to photofading of latex films prepared from colored latex on substrates (papers). Colored latex containing magenta dyes (HSR2310/HSR2150 3:1 by wt.) was prepared by miniemulsion polymerization (Table 2). First, we studied the effect of the latex film thickness on the photofading measurements, using colored latex without HAS as reference (R1 in Table 2). The thickness of latex films on paper (substrate) was controlled by the solid content of the latex using a barcoater (No. 4). The thickness can be roughly estimated by Eq. 6. (Since the latex permeates the paper to some degree, the thickness calculated by Eq. 6 will not necessarily accord with the real value.)

$$\text{Thickness of film } (\mu\text{m}) = \text{bar} - \text{coater No.} \times 1.5 \times \text{solid content}(\%)/100 \qquad (6)$$

As the latex film became thicker, the photostability of the sample was higher (Fig. 7). Therefore, photostability was evaluated as relative % fading ($\Delta E^*/E^*$) at each film thickness under the condition where the dye content in the film was kept ca. 20%.

In the preparation of HAS-containing latexes, stearyl methacrylate (SMA, water-insoluble comonomer) was used as a reactive hydrophobe to stabilize the miniemulsion. Two types of HAS, a mixed stabilizer and a polymerizable stabilizer, were employed to investigate the effect of immobilization of HAS in colored latex.

Application of HAS I as an additive

HAS I is a white solid, not polymerizable. An oil phase that consisted of an MMA solution of dyes and HAS I was miniemulsified in the aqueous phase, and the miniemulsion was polymerized. Dye-loading miniemulsions were prepared with different contents of HAS I in the monomer phase, under the condition where dye contents were ca. 20 wt.% (Table 2). In this way, latex particles containing a simple mixture of dye and HAS I were obtained.

The effect of HAS I content was studied at a fixed film thickness. With increasing HAS I content in latex particles, $\Delta E^*/E^*$ decreased and the photostability was improved (Fig. 8). Colored latex R4 exhibited the best photostability and the efficiency of HAS I in color development was better than others.

In general, the physical state of the dye within its substrate is believed to be a determining factor for the

Table 2 Characteristics of colored latex loaded with HAS I

Colored latex no.	Dye/HAS I/MMA (wt.%)	Hydrophobe	Initiator (g)	Conversion (%)	Diameter (nm)	Solid content (%)
R1	20:0:80	HD	0.1 (V-50)	85	74.9	19.1
R2	20:10:70	SMA	0.2 (KPS)	93	31.0	21.4
R3	20:15:65	SMA	0.3 (KPS)	92	29.9	21.4
R4	20:20:60	SMA	0.3 (KPS)	83	28.2	20.5

Dye: HSR2310:HSR2150 = 3:1

R1: Dye/MMA/hydrophobe/V-50/*N*-cetyl pyridinium chloride/H_2O = 4/16/1/0.1/1.84/80 (g)

R2, 3 ,4: Dye/HAS + MMA/hydrophobe/KPS/$NaHCO_3$/SDS/H_2O = 4/16/1/0.2 or 0.3/0.068 or 0.101/1.84/80 (g)

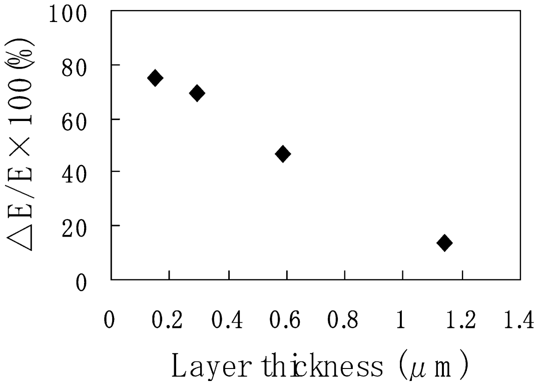


Fig. 7 Relative % fading vs thickness of layer consisting of colored latex (R1)

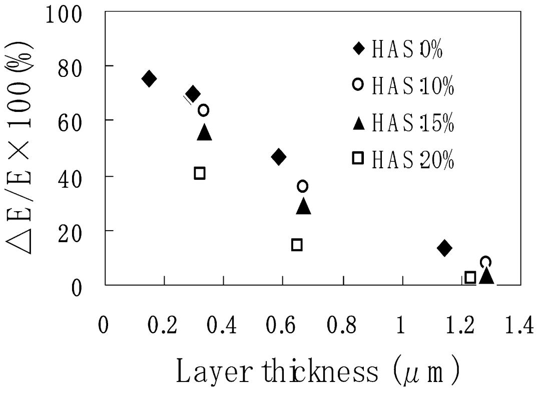


Fig. 8 Effect of HAS I content on photostability of colored latex

photostability of the dye. It was confirmed from electron micrographs that dye aggregates existed in the polymer particle for the colored latex with good light fastness [5]. If the total content of dye and HAS I in MMA monomer is over the solubility limit, the dye will be inclined to form aggregates in latex particles. A part of the dye in latex particles R4 might exist as aggregates.

In conclusion, the higher the HAS I content in latex particles was, the better the photostabilty of colored latex became. But on increasing the HAS I content, dyes tended to form aggregates in latex particles. Therefore, it is desirable that the total content of dye and HAS I in MMA monomer be below the solubility limit.

Application of HAS II as a comonomer

HAS II is a polymerizable stabilizer having a tetramethylpiperidine group and is an almost colorless liquid. The polymerization behavior of 2,2,6,6-tetramethylpiperidinyl methacrylate with MMA was reported by Lee et al. [12]. Dye solutions consisting of azo dyes, HAS II, MMA, and HD were miniemulsified in an aqueous phase and the miniemulsions were polymerized. Dye-loading miniemulsions were prepared with different contents of HAS II but constant dye content (ca. 20%). HAS II was copolymerized with MMA to incorporate stabilizer onto latex particles by a covalent bond. Magenta-colored latex containing HAS II could be obtained in this way.

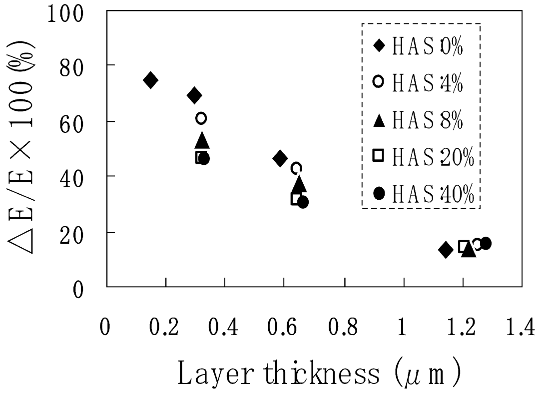


Fig. 9 Effect of HAS II content on photostability of colored latex

In the range of film thickness >1μm, the effect of HAS II was not recognized, and $\Delta E^*/E^*$ values of all latexes were almost equal regardless of HAS II content (Fig. 9). Under the condition in which the latex film was thinner than 1μm and the photostability was relatively low, HAS II decreased the $\Delta E^*/E^*$ and consequently increased the photostability of each sample. Close examination of the effect of HAS II content revealed that $\Delta E^*/E^*$ tended to decrease with increasing HAS II in the range of HAS II content up to 20 wt.%, but $\Delta E^*/E^*$ values were almost equal when the HAS II content exceeded 20 wt.% (R7 and R8). It indicated that the optimal amount of HAS for photostability improvement was between 8 and 20%. As HAS II can be homopolymerized, colored latex consisting of homopolymer of HAS II was prepared without PMMA. The dye content in the latex particles was a maximum of 10% due to the low solubility of azo dye in poly-HAS II. The photostability of this colored latex was not improved compared with R8.

Now the feature of two systems, **a** (HAS I) and **b** (HAS II), is compared. The photostability of colored latex was improved by both **a** and **b**. But, in the case of **a,** the migration of HAS became a severe issue with increasing HAS content in the latex particles.

Conclusions

The dye migration properties of colored latex loaded with different types of dye were investigated. Dye contents inside latex particles were measured as a function of storage time *t* at 25 °C. With decreasing residual monomer in the latex, colored latex exhibited better dye preservation properties. Dyes that have a bulky molecular structure or are likely to form aggregates could stay inside latex particles for several months. This indicated that dye migration depends on the diffusion rate of dye molecules in latex particles. Therefore, in order to obtain good dye preservation, it is suggested that bulky dye molecules be selected for preparation of colored latex.

HAS was used to improve the photostability of colored latex. Two types of HAS were added to colored latexes, and the photostability of the latex was studied with respect to photofading of the films prepared from colored latexes on substrates. The photostability of latex films containing a simple mixture of dye and HAS was improved with increasing HAS I content in the particles. In the case of colored latexes containing HAS combined with matrix polymer by a covalent bond, the optimal amount of HAS for photostability improvement was between 8 and 20% and the effect was prolonged compared with the simply mixed HAS I system.

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