

Self-Curable Aqueous Polymeric Dyes for Printing and Dyeing Applications

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ABSTRACT: An epoxy resin (NPES-904, epoxy equivalent weight is 815) with a repeating unit, $n > 4$ was selected as a polymer backbone of polymeric dye. Water-reducible epoxy resin was prepared by a semiesterification of its secondary hydroxy group with succinic anhydride and then dispersed to aqueous phase after it was neutralized with triethylamine. An aqueous polymeric dye was obtained from a ring opening reaction of that epoxy resin with amino group of a direct dye (soluble dye such as C. I. Acid Blue 62, C. I. Direct Orange 39 or C. I. Direct Red 2). These aqueous polymeric dye dispersions carried the average particle sizes

between 50 and 90 nm. A polyaziridine was added as a latent curing agent and forming a self-curable system of aqueous polymeric dye solution, which was stable in aqueous phase when its pH remained above 8.0. This aqueous polymeric dye was self-cured on drying at ambient temperature and results in the formation of waterproof and solvent-resistant polymeric dye. These self-curable polymeric dyes had potential for jet ink printing and dyeing applications. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1919–1931, 2006

Key words: self-curable; polymeric dye; aqueous epoxy resin

INTRODUCTION

The direct dye is water-soluble, which is useful for writing and jet ink. Its excellent water solubility is the natural property that is due to the presence of ionic group (e.g., sulfonate and etc.) However, its good water solubility also limits its application areas.

A market available epoxy resin (eew is 815) with a repeating unit, $n > 4$ was chosen as polymer backbone of a self-curable aqueous polymeric dye. Water-reducible aqueous-based epoxy resin dispersion was prepared through a semiesterification of succinic anhydride with its secondary hydroxyl group of the epoxy resin, followed by neutralization with triethylamine and addition of water. The stable aqueous-based epoxy resin contained both carboxyl and epoxy groups, which were reactive functional groups. A self-curable aqueous-based epoxy resin system was prepared by adding a polyaziridine (e.g., TMPTA-AZ) as a latent curing agent into the aqueous epoxy resin dispersion. Upon drying, the liberated carboxyl group in the aqueous epoxy resin reacted with polyaziridine to form an amino ester via a ring-opening reaction.^{1–4}

Water-soluble dye comprises amino group and sulfonate such as C. I. Acid Blue 62, C. I. Direct Orange 39 and C. I. Direct Red 2 were selected for preparation of aqueous

polymeric dyes, respectively. A ring-opening reaction took place between amino group of dye and epoxide end-groups of water-reducible epoxy resin and its resulting aqueous polymeric dye was chemically bonded with a water-soluble dye and remained water-reducible. The average particle size distribution of these aqueous polymeric dyes were between 50 and 90 nm. The UV-visible absorption spectrum of polymeric dye was similar to that of the original water-soluble dye because the water-reducible epoxy resin had little inductive effect toward the electronic structure of dye chromophore.

A curing agent, polyaziridine,^{1–10} (e.g., TMPTA-AZ), was added as a latent curing agent for self-curable system of aqueous polymeric dye, which was stable when its pH remained above 8.0. The self-curing reaction occurred between aziridine of trimethylolpropane triacrylate (TMPTA)-AZ and carboxyl group of water-reducible epoxy resin on drying at ambient temperature. This self-curing reaction took place only on polymeric backbones and left dye moiety untouched.^{11,12} The final self-cured polymeric dye became waterproof and organic solvent became resistant. This self-curable system of nano-size aqueous polymeric dye dispersion would have the potential for dyeing, jet ink printing, and other color applications.¹³

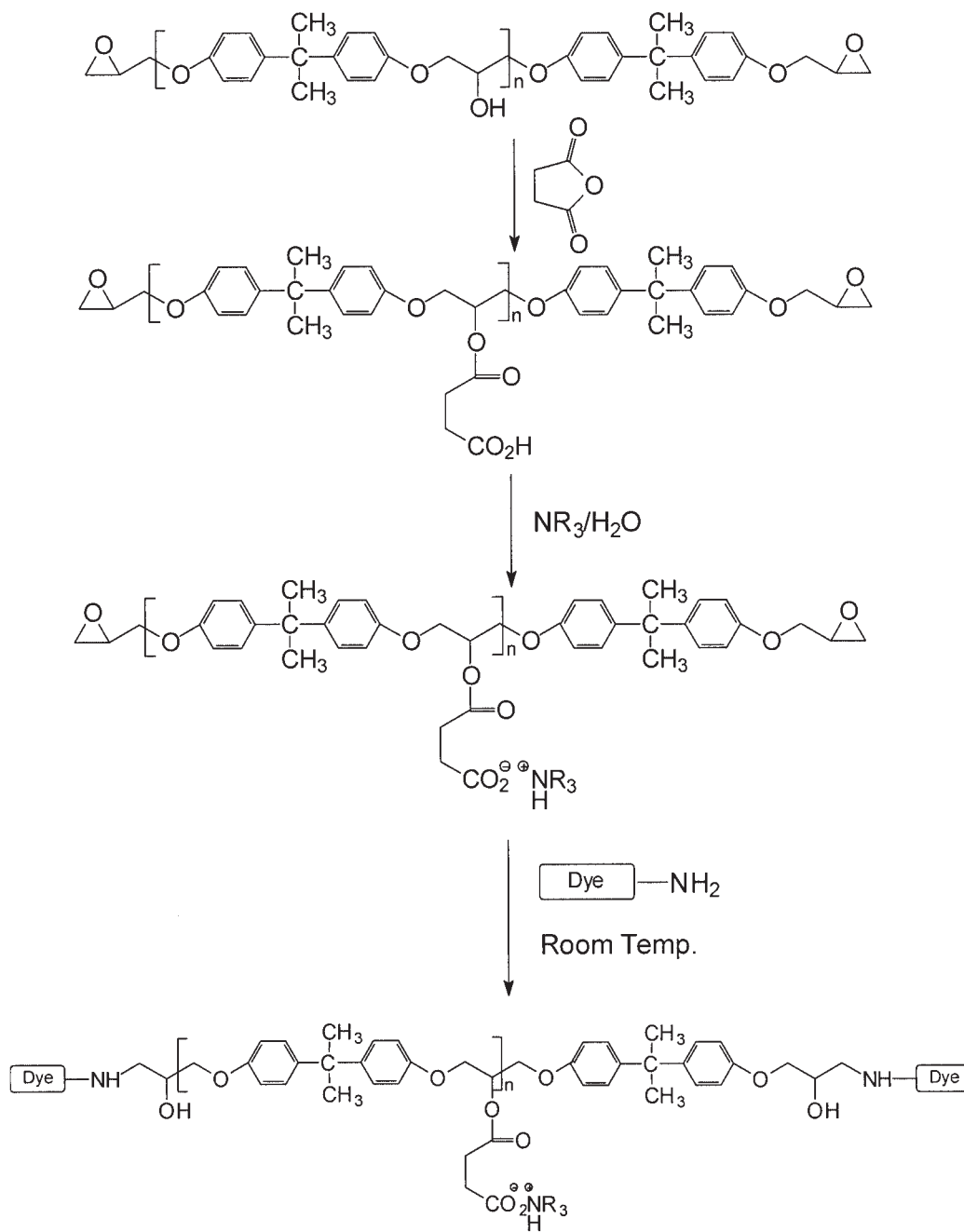
Experimental

Materials

Water-soluble dyes, C.I. Acid Blue 62, C.I. Direct Orange 39, and C. I. Direct Red 2 were obtained from Aldrich Chemical Co. Epoxy resin, NPES-904 (815

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Aqueous Polymeric Dye

Scheme I Preparation of aqueous polymeric dye.

ew), was supplied by Nan-Ya Plastics Co., Taiwan. They were used as received without further purifications. Solvents such as acetone, methyl isobutyl ketone (MIBK), toluene, tetrahydrofuran (THF), and etc. were dried and freshly distilled before use.

Instruments

Thermogravimetric data were measured by a Hi-Resolution TGA 2950 Thermogravimetric Analyzer,

TA. Color strength of each dye was measured by an X-Rite SP62 Sphere Spectrophotometer. UV-visible absorption spectra of aqueous solution of direct dye and its polymeric dye were measured, respectively, by a HP UV-Agilent 8453 UV-visible Spectrophotometer. NMR spectra were measured by a Bruker AC-300 FT-NMR photometer. FTIR spectra were obtained from a Bio-Rad FTS-135 Infrared spectrometer.

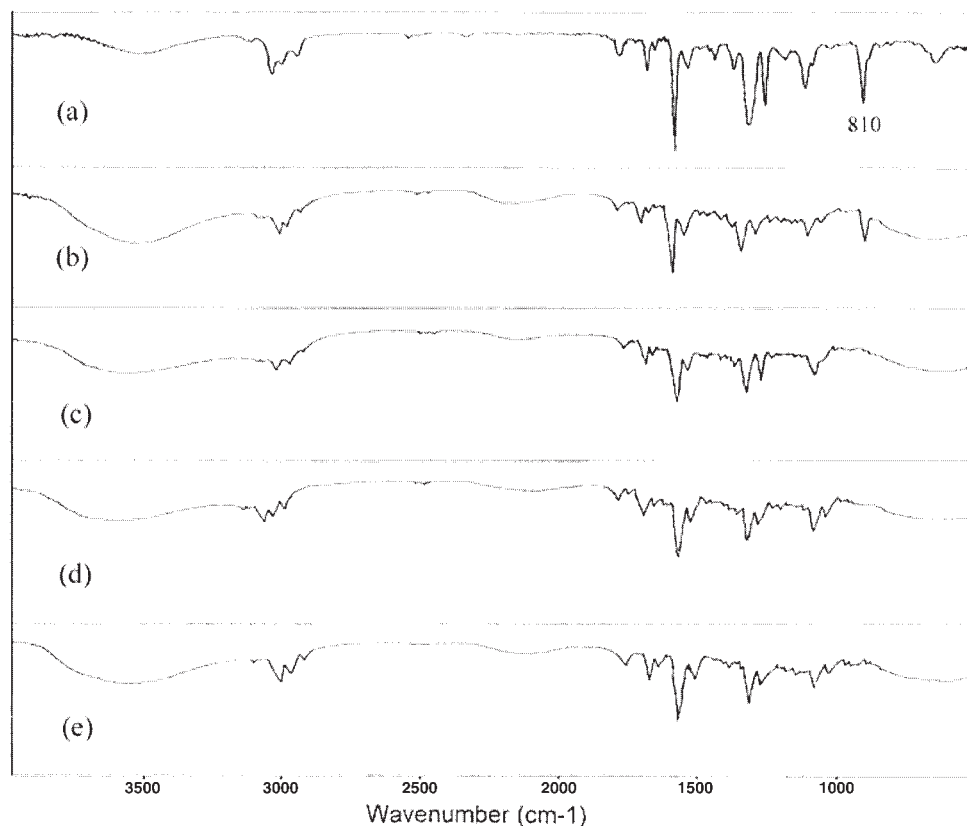


Figure 1 Infrared spectra of epoxy resin and its polymeric dyes. (a) Epoxy resin oligomer (NPES 814); (b) water-reducible epoxy resin oligomer; (c) polymeric Red 2 dye; (d) polymeric Blue 62 dye; (e) polymeric Orange 39 dye.

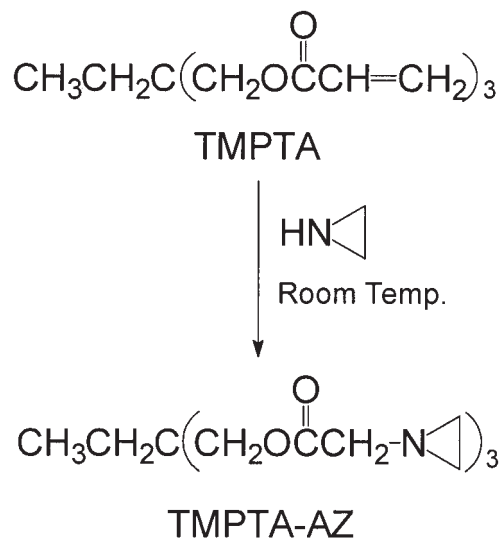
Preparation of water-reducible epoxy oligomer¹ and its polymeric dye (Scheme I)

An epoxy resin oligomer (50 g, NPES-904 with 815 eew) and 12 g of succinic anhydride were mixed with methyl isobutyl ketone (MIBK, 50 mL) in a 500-mL three-necked flask and two drops of T-12 was added as a catalyst. The semiesterification reaction was carried out and kept at 120°C for about 18 h. The product was cooled to room temperature and the unreacted succinic anhydride was removed by THF extraction. A water-reducible epoxy resin dispersion was prepared by neutralization of this final reaction mixture with triethylamine (TEA) and then it was dispersed in 45 mL de-ionized water with agitation.^{14,15} An aqueous polymeric dye was obtained from a reaction of amino containing dye (0.5 g) with the epoxide end-groups of this water-reducible epoxy resin dispersion (dye/epoxy resin = 1/100, w/w) (Fig. 1). Among the water-soluble dyes, those that comprised of amino group and sulfonate, such as C. I. Acid Blue 62 (m.w. 421), C. I. Direct Orange 39 (m.w. 299), and C. I. Direct Red 2 (m.w. 692),¹⁶ were used, respectively.

Preparation of polyaziridine, TMPTA-AZ (Scheme II)

Aziridine (ethylenimine) was prepared and modified from the published literature⁵⁻⁷. A quantitative amount

of freshly prepared aziridine was added slowly into acetone solution of trimethylolpropane triacrylate (TMPTA) at ambient temperature and agitated for 5 h until the absorption peak of acrylate double bond stretching frequency at 1638 cm⁻¹ in IR spectrum disappeared (Fig. 2).^{1-4,15} Acetone was removed from the reaction mixture under reduced pressure and the remained residue of



Scheme II Preparation of TMPTA-AZ.

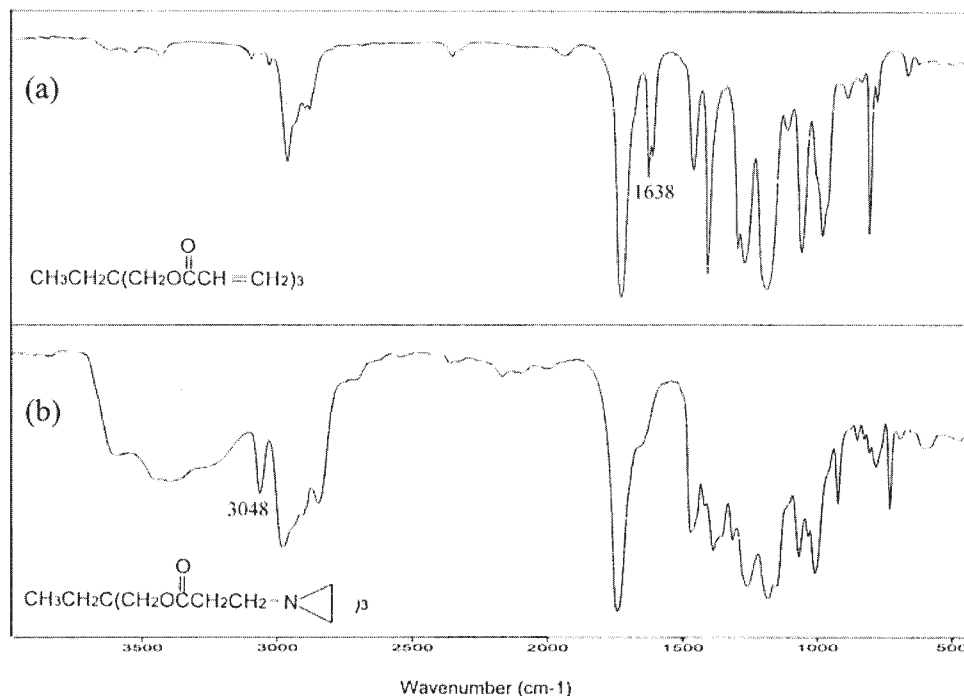


Figure 2 Infrared spectra: (a) TMPTA and (b) TMPTA-AZ.

TMPTA-AZ was proved by its NMR spectra (Figs. 3 and 4), which was stable under nitrogen atmosphere.

Self-curable system of aqueous polymeric dye

The aqueous polymeric dye dispersion was mixed with a latent curing agent (e.g., TMPTA-AZ, 5 phr)

and became a single pack self-curable system of polymeric dye dispersion, which was a stable aqueous dispersion with 25% solid content while its pH value was kept above 8.0. The self-curing reaction of aqueous polymeric dye occurred on drying and resulted in a water-insoluble with networked polymeric dye formation (Scheme III).

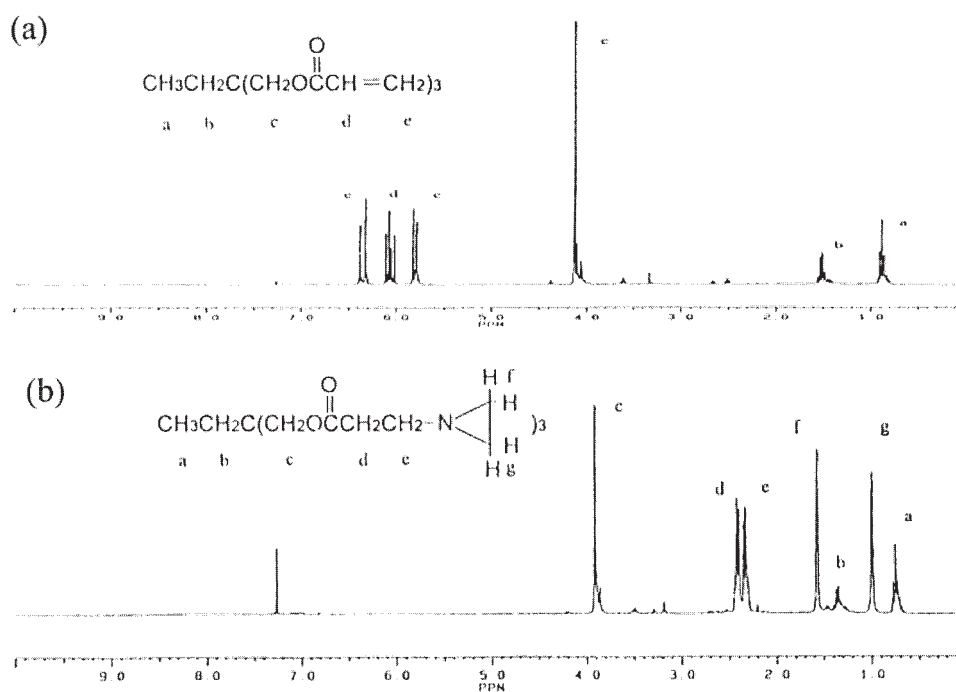


Figure 3 ¹H NMR spectra: (a) TMPTA and (b) TMPTA-AZ.

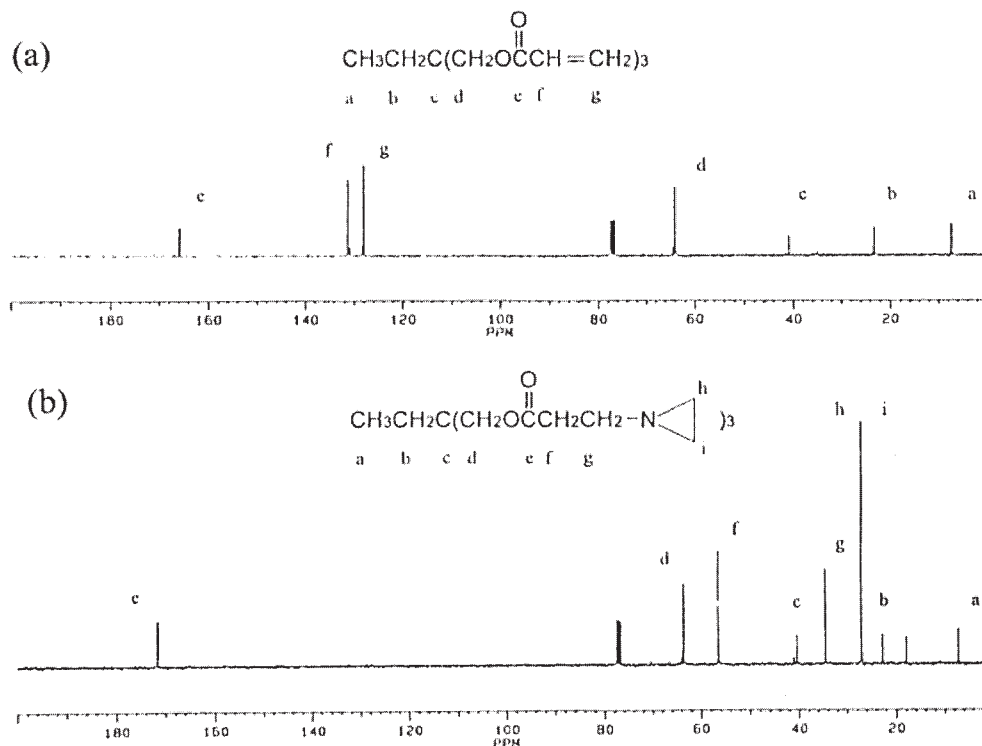


Figure 4 ^{13}C NMR spectra: (a) TMPTA and (b) TMPTA-AZ.

UV-visible absorption spectra of water-soluble dye and its polymeric dye

UV-visible absorption spectra of water-soluble dye and its polymeric dye were measured in aqueous solution, respectively, by a UV-visible Spectrophotometer at ambient temperature (Figs. 5–7).

Physical properties of self-cured polymeric dyes (Tables I and II)

Gel content

A known weight of oven-dried polymeric dye was placed in a Soxhlet extractor for continuous extraction with THF for 24 h. The remained polymeric gel after extraction was dried and calculated according to the tests results. Three tests were carried out and averaged out for each sample.

Water-uptake

A known sample weight (W_0) of oven-dried self-cured polymeric dye was measured before it was immersed in a de-ionized water bath for a week. The weight (W_1) of towel wiped dry polymeric dye and the weight (W_2) of oven-dried sample were obtained. Water-uptake ($W_w\%$) and weight loss ($W_x\%$) of the polymeric dye in water were calculated according to the following equation.

$$W_w\% = [(W_1 - W_2) / W_2] \times 100$$

$$W_x\% = [(W_0 - W_2) / W_0] \times 100$$

W_w was the amount of water-uptake by polymeric dye.

W_x was the amount of polymeric dye dissolved into water.

Ethanol absorption

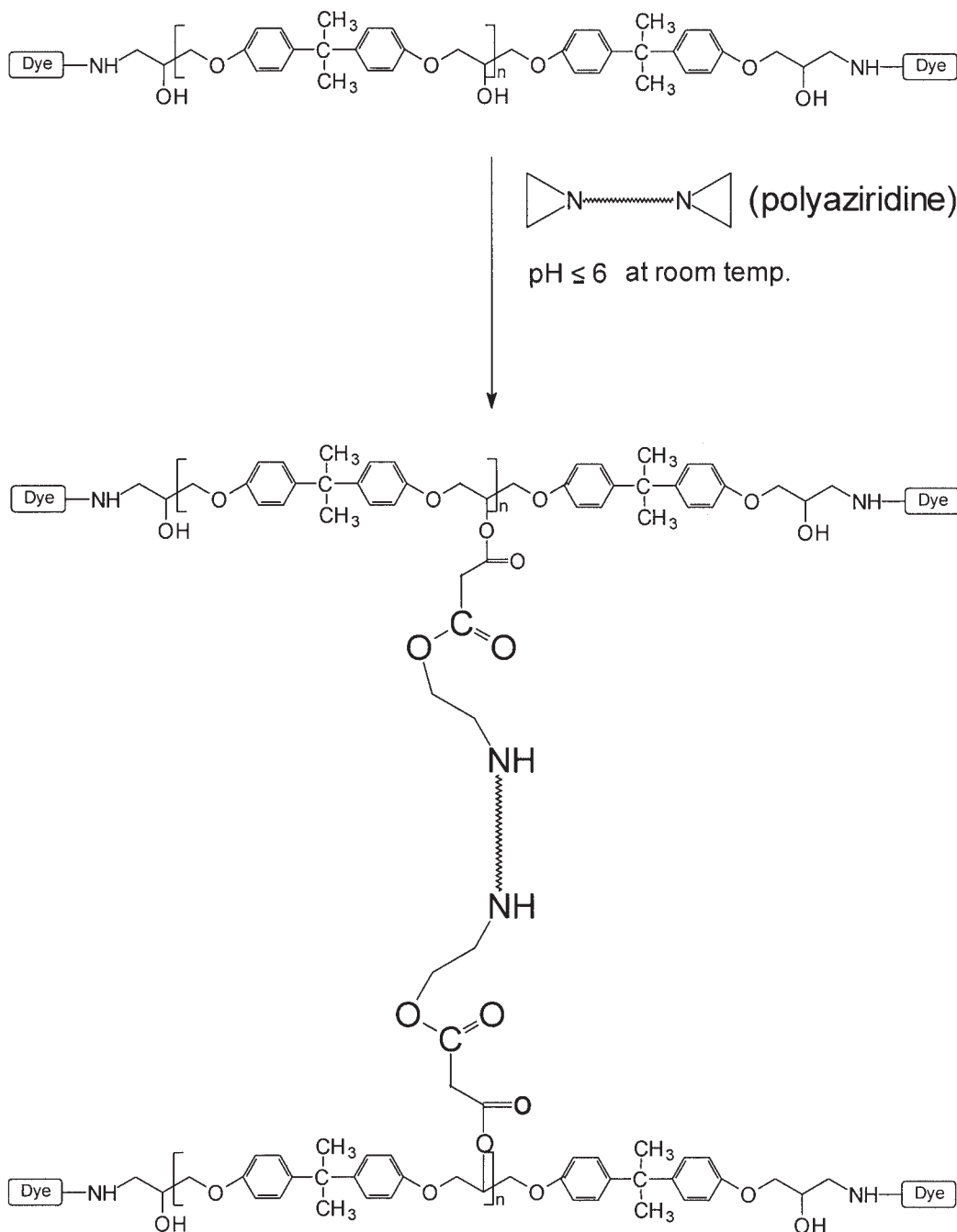
A known sample weight (W_0) of dried self-cured polymeric dye was immersed in a 95% ethanol bath for 24 h. The weight (W_1) of towel wipe dry polymeric dye and the weight (W_2) of oven dry sample were obtained. Ethanol absorption ($W_e\%$) and weight loss ($W_y\%$) of self-cured polymeric dye in ethanol were calculated according to the following equation.

$$W_e\% = [(W_1 - W_2) / W_2] \times 100$$

$$W_y\% = [(W_0 - W_2) / W_0] \times 100$$

W_e was the amount of ethanol absorption by polymeric dye.

W_y was the amount of polymeric dye dissolved into ethanol.



Self-cured Polymeric Dye

Scheme III Self-curing of aqueous polymeric dye.

Appearance color strength

The polymeric dye film was obtained from the self-curing system of aqueous polymeric dye by cast dry at ambient temperature. The treated polymeric dye films were dipped in water and ethanol bath for 24 h and then dried, respectively. The appearance color strength of original untreated and treated polymeric dye films were

obtained from the measurements of a Sphere Spectrophotometer. The appearance color strength of original untreated sample was set in Table III at 100%.¹⁶⁻¹⁸

Thermogravimetric analysis (TGA)

The conditioned samples were measured with a Thermogravimetric analyzer at a heating rate of 10°C/min

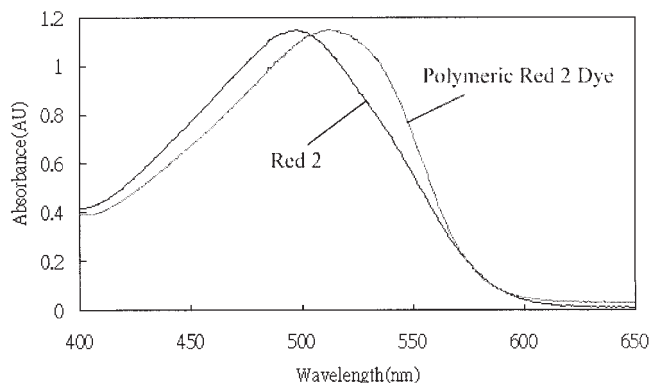


Figure 5 UV-visible spectra of aqueous solution of Red 2 and its polymeric dye.

and it was heated from ambient temperature to 800°C. The thermal stability measurements of the self-cured polymeric dyes were carried out under a nitrogen atmosphere. (Figs. 8–13).

Application of polymeric dye for dyeing and printing

A piece of white micro-fiber cloth was dipped into an aqueous self-curable polymeric dye solution (or water-soluble dye solution) at 80°C for 5 min and the excess dye solution was squeezed out. Then, this dyed cloth was dried and tumble-washed with cold water for 4 cycles. And the appearance color strength of each dyed cloth before and after washing was measured by a Sphere Spectrophotometer.

A self-curable aqueous polymeric dye solution was printed on regular white paper (which is acidic with a pH about 6) as a printing ink and dried at ambient temperature.

RESULTS AND DISCUSSION

An anionic water-reducible aqueous epoxy resin dispersion was prepared through the semiesterification

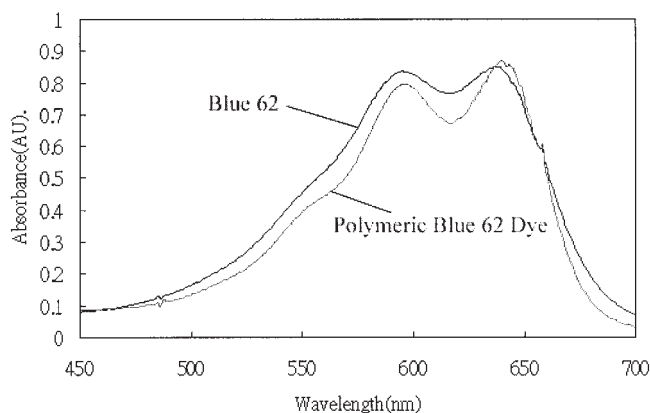


Figure 6 UV-visible spectra of aqueous solution of Blue 62 and its polymeric dye.

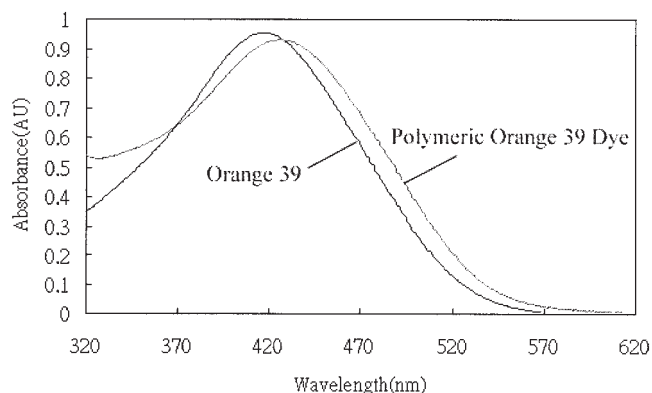


Figure 7 UV-visible spectra of aqueous solution of Orange 39 and its polymeric dye.

reaction between a dicarboxylic acid anhydride (e.g., succinic anhydride) and the secondary hydroxy group of an epoxy resin, followed by neutralization of the carboxylic acid, which introduced into the epoxy resin with triethylamine (TEA), and then adding only water, without the need of any emulsifier, to the resulting hydrophilic amine salt of the carboxylic acid. The stable aqueous epoxy resin contained both carboxyl and epoxy groups as the main reactive functional groups. A single pack self-curable aqueous epoxy resin system was prepared by adding a polyaziridine (e.g., TMPTA-AZ) as latent curing agent into the aqueous epoxy resin dispersion. Upon drying, the liberated carboxyl group in aqueous epoxy resin reacted with the polyaziridine to form an amino ester via a ring-opening reaction. The result of this curing reaction took place on drying, which formed a polymer film with networked epoxy resin.^{1–4}

Direct dye is water-soluble that was excellent in color-extension, but poor in color-fastness on applications. However, its poor color-fastness limited its applications on dyeing and printing.

A water-soluble dye could be chemically bonded with aqueous-based polymer to make it a part of polymer. This dye-containing aqueous polymer could be crosslinked as a networked structure with waterproof character by postcuring. Among the water-soluble dyes, those that consisted of amino group, such as C. I. Acid Blue 62, C. I. Direct Orange 39, or C. I. Direct Red 2 were selected (Scheme IV). The amino group of dye reacted with epoxide-end groups of water-reducible epoxy resin, which resulted in a formation of aqueous polymeric dye (Scheme I). This polymeric dye was treated with a latent curing agent, polyaziridine (e.g., TMPTA-AZ),^{1–10} and formulated as a single pack self-curable system of aqueous polymeric dye that was self-cured on drying. This self-cured polymeric dye became waterproof and solvent resistant, which had the potential for dyeing, printing, and other color applications.

TABLE I
Physical Properties of Polymeric Dye Films without Curing^a

Direct dye phr in WEP ^b	WEP (0) ^a	Red 2			Blue 62			Orange 39		
		0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Gel content ^c (%)	0	43.9	45.6	47.3	46.4	53.7	56.4	45.1	46.8	47.7
Water uptake (%)	53.8	67.0	73.6	80.4	46.7	63.9	91.7	66.7	73.9	95.6
Polymer wt. dissolved in water (%)	13.3	10.1	8.9	7.2	15.8	13.4	9.7	9.3	7.5	6.3
Ethanol absorption (%)	50.6	51.7	58.6	63.2	49.0	56.3	66.1	48.9	56.6	62.7
Polymer wt. dissolved in ethanol (%)	12.5	10.2	8.8	6.9	15.4	12.5	9.6	13.9	11.1	9.7

^a WEP and polymeric dye films are cast from water-reducible epoxy oligomer and its polymeric dye, respectively without curing.

^b The polymeric dyes are obtained from various dye dosages (0.5, 1.0, and 2.0 phr).

^c Gel content is obtained from a continuous Soxhlet extraction with tetrahydrofuran.

Infrared spectra of polymeric dye

Infrared (IR) spectra of water-reducible epoxy resin and its polymeric dyes were identical except that the C—O stretching frequency of epoxide at 810 cm⁻¹ disappeared after the reaction with dye amino group (Fig. 1). The azo N=N and sulfonate S—O stretching vibration bands were covered by the strong absorption peaks of epoxy resin and became invisible.

Latent curing agent TMPTA-AZ

Latent curing agent, TMPTA-AZ, was prepared by aziridine via Michael addition toward trimethylolpropane triacrylate (TMPTA) at ambient temperature (Scheme II). The acrylate absorption peak of 1638 cm⁻¹ on infrared spectrum (Fig. 2) disappeared after Michael addition was completed. Their chemical shifts due to the effect of acrylate double bonds in the range of 5.8–6.4 ppm vanished and new chemical shifts at 2.3, 2.4, 1.6, and 1.0 ppm appeared on ¹H NMR spectrum (Fig. 3) of TMPTA-AZ. The chemical shifts on

¹³C NMR spectrum indicated aziridine carbons on 27 ppm (Fig. 4). This compound (TMPTA-AZ) was served as a latent curing agent, which was stable in the solution with a pH value at 8.0 or above. It was demonstrated by constant particle size distribution of its self-curable polymeric dye dispersion.^{5–10}

Self-curable system of polymeric dye with latent curing agent

The curing agent (TMPTA-AZ) was added into aqueous polymer dye and resulted in a formation of self-curable system of polymeric dye that was stable with a pH value at 8.0 or above. The curing reaction in which aziridine of TMPTA-AZ reacted with the carboxyl groups of epoxy resin took place only on drying. This self-cured polymeric dye had amino ester bonds formation between epoxy main chains without disturbing dye moiety of the polymeric dye (Scheme III).

TABLE II
Physical Properties of Self-cured Polymeric Dye Films

Direct dye phr in WEP	WEP (0) ^b	TMPTA-AZ (5 phr) ^a								
		Red2 ^c			Blue 62 ^c			Orange 39		
		0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Gel content ^d (%)	75.4	85.4	87.3	89.8	78.9	81.5	82.1	77.3	78.8	80.4
Water uptake (%)	41.3	64.8	66.7	70.5	35.2	54.5	82.2	55.3	61.8	94.2
Polymer wt. dissolved in water (%)	11.7	8.8	6.9	5.5	12.5	10.6	7.2	6.5	5.2	4.9
Ethanol absorption (%)	39.8	44.5	47.2	51.6	42.1	50.7	58.3	40.4	48.8	55.9
Polymer wt. dissolved in ethanol (%)	9.1	8.5	6.6	3.3	7.5	5.9	3.1	5.5	4.2	3.8

^a Self-cured polymeric dye films are obtained from the self-curable system of aqueous polymeric dyes with a polyaziridine latent curing agent, TMPTA-AZ (5 phr), respectively.

^b WEP film is obtained from self-cured water-reducible epoxy oligomer.

^c The polymeric dye system with various dye dosages (0.5, 1.0, and 2.0 phr).

^d Gel content is obtained from a continuous Soxhlet extraction with tetrahydrofuran.

TABLE III
Color Strength of Polymeric Dye Films

Polymeric dye ^a with 1.0 phr in WEP	Polymeric dye color strength (%) ^b	
	Water ^c	Ethanol ^c
Polymeric Red 2 dye	106.6	110.2
Cured polymeric Red 2 dye ^d	108.1	112.4
Polymeric Blue 62 dye	115.3	121.8
Cured polymeric Blue 62 dye ^d	129.1	143.2
Polymeric Orange 39 dye	102.5	125.2
Cured polymeric Orange 39 dye ^d	111.6	137.9

^a Polymeric dye is obtained from aqueous polymeric dye, which is prepared by direct dye (1.0 phr) with water-reducible epoxy resin.

^b Color strength is 100% of each polymeric dye before water or ethanol treatment.

^c Color strength of each polymeric dye film is obtained after that is immersed into water or ethanol for 24 h and then dried.

^d Each self-cured polymeric dye with curing agent, TMPTA-AZ (5 phr).

Physical properties of self-cured aqueous polymeric dye

Polymeric film was obtained from water-reducible epoxy resin dispersion (without curing) that was dissolved into THF completely (its gel content is 0) (Table I). Dye-contained sulfonate (Red 2, Blue 62, or Orange 39) was soluble in water but not in tetrahydrofuran (THF). The polymeric dye films were casted from aqueous polymeric dyes (without curing) with various

dosages of dye, which had the gel contents more than 43.9% (Table I). These demonstrated that the amino group of dye reacted with epoxide end-group of epoxy resin and its secondary amine reacted further with other epoxy group as a chain-extender that contributed the increasing gel contents of polymeric dyes.

Self-cured polymeric dye films with a latent curing agent, TMPTA-AZ (5 phr), which had the gel contents, increased to 89.8 (Red 2), 82.1 (Blue 62), and 80.4% (Orange 39), respectively (Table II). These results proved that self-curing reaction carries out within aqueous polymeric dye system and formed a waterproof and organic solvent resistant (both THF and ethanol) polymeric dye or ink.¹⁸

UV-visible absorption spectra of aqueous dye solution

UV-visible absorption spectra of aqueous solution of polymeric dyes had a little red shift from that of its original direct dye. For example, C.I. Red 2 had λ_{\max} : 496 nm, and that of its polymeric dye was 512 nm (Fig. 5). C. I. Orange 39 had the similar phenomena of red shift (Fig. 6). It was due to an inductive effect toward its diazo chromophore caused by epoxy resin. C. I. Blue 62 had two λ_{\max} peaks, the one remained the same, however, the other one with higher absorbance (λ_{\max}) at 637 nm, and that of its polymeric dye shifts to 640 nm (Fig. 7). It indicated that the polymer moiety had a little inductive effect on the electronic structure of

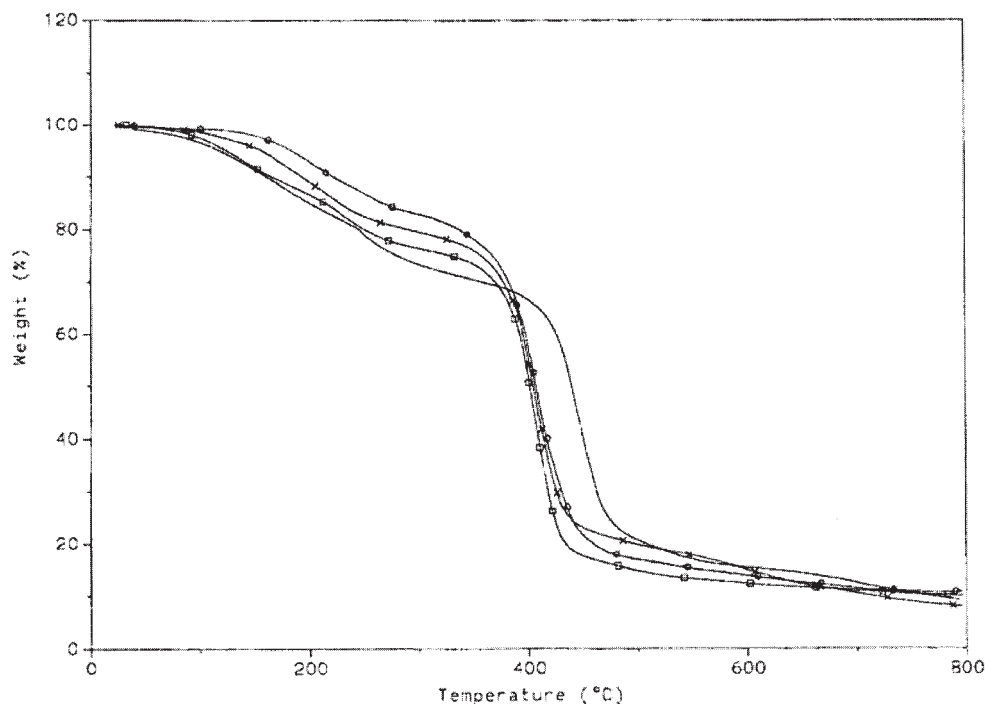


Figure 8 TGA of polymeric dyes with various dosages of Red 2 dye under nitrogen; 0.5 (□); 1.0 (×); 2.0 (○) comparing to original water-reducible epoxy resin, WEP (—).

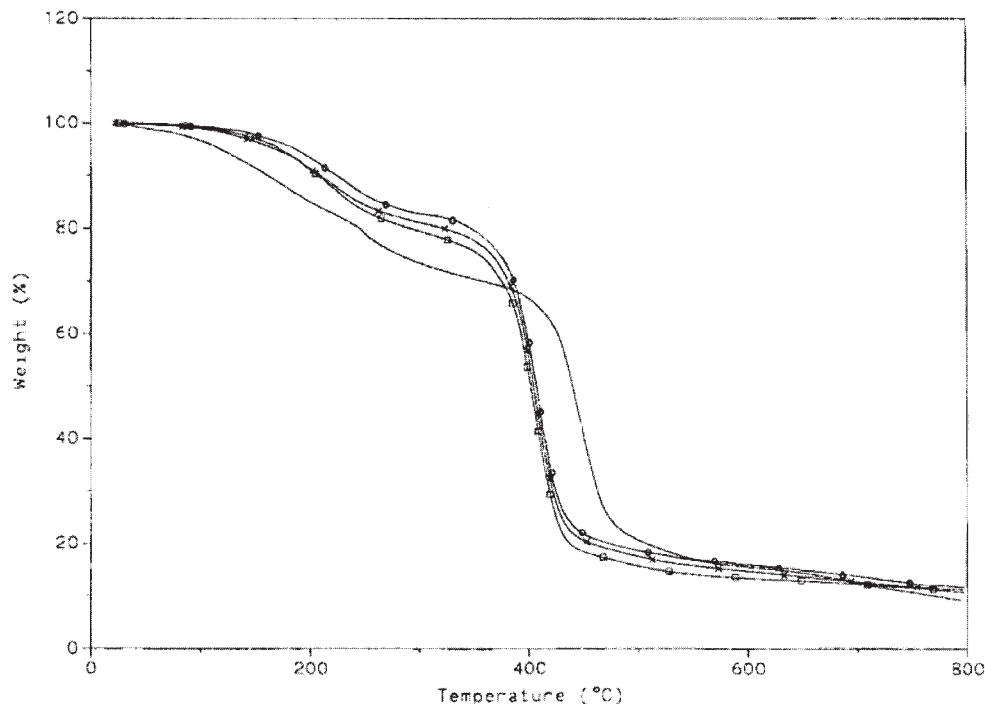


Figure 9 TGA of polymeric dyes with various dosages of Blue 62 dye under nitrogen; 0.5 (\square); 1.0 (\times); 2.0 (\circ) comparing to original water-reducible epoxy resin, WEP (—).

azo dye chromophore for polymeric dyes Orange 39 and Red 2, but not on that of polymeric dye Blue 62.

Thermal behaviors of polymeric dye

Thermogravimetric analysis (TGA) thermograms indicated that aqueous polymeric dye had a better

thermal stability than the original water-reducible epoxy resin (Figs. 8–10). And its thermal stability increased (at the range below 400°C) with increasing dye dosage to the epoxy oligomer. That might be due to a chain-extension reaction between epoxy resin oligomer with amino group containing dye. These results coin-

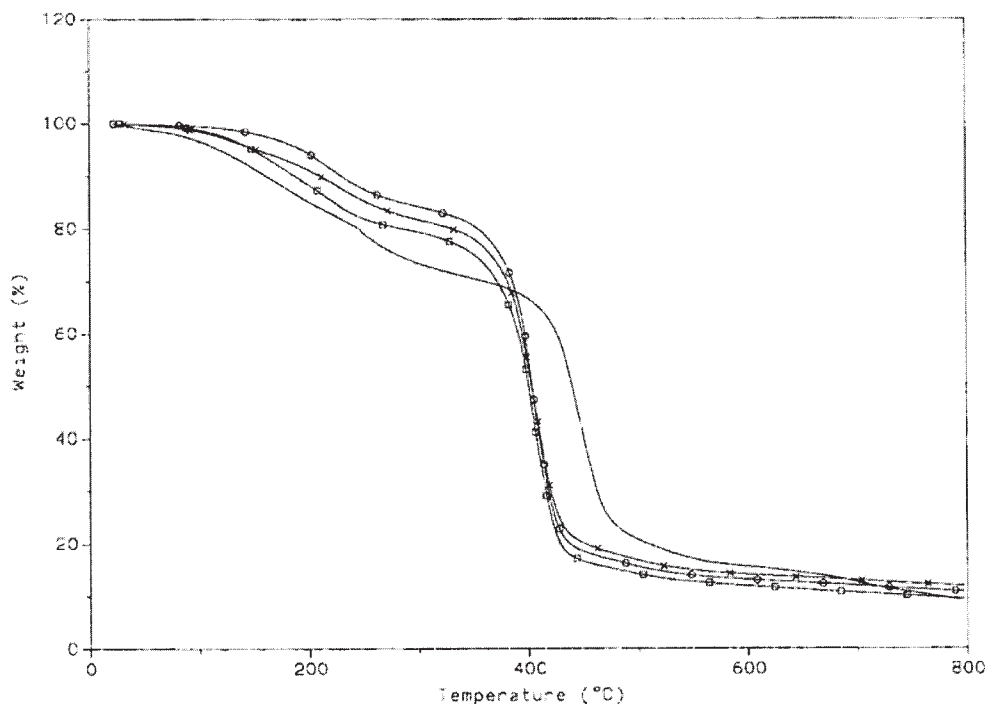


Figure 10 TGA of polymeric dyes with various dosages of Orange 39 dye under nitrogen; 0.5 (\square); 1.0 (\times); 2.0 (\circ) comparing to original water-reducible epoxy resin, WEP (—).

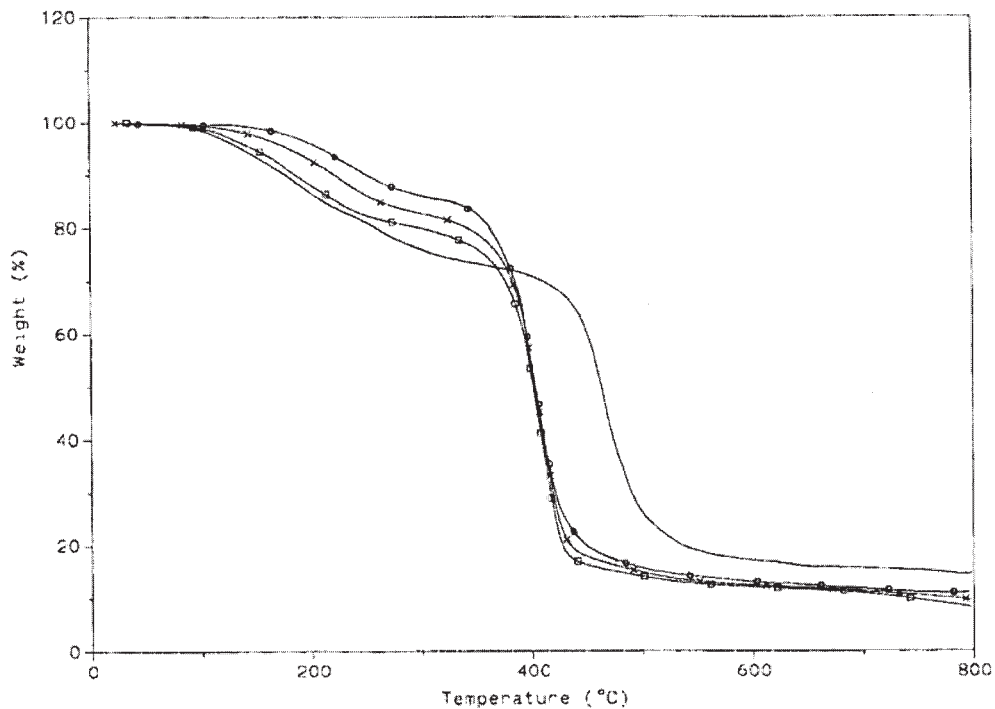


Figure 11 TGA of self-cured polymeric dyes with various dosages of Red 2 dye under nitrogen; 0.5 (□); 1.0 (×); 2.0 (○) comparing to original water-reducible epoxy resin, WEP (—).

cided with the gel contents of polymeric dyes shown in Table I.

The thermal stability of each self-cured polymeric dye (Figs. 11–13) was slightly higher than that of

polymeric dye without curing (Figs. 8–10). These were the same trend of their gel contents shown in Table II. This self-curing reaction promoted the interpenetrating polymeric network (IPN) formation

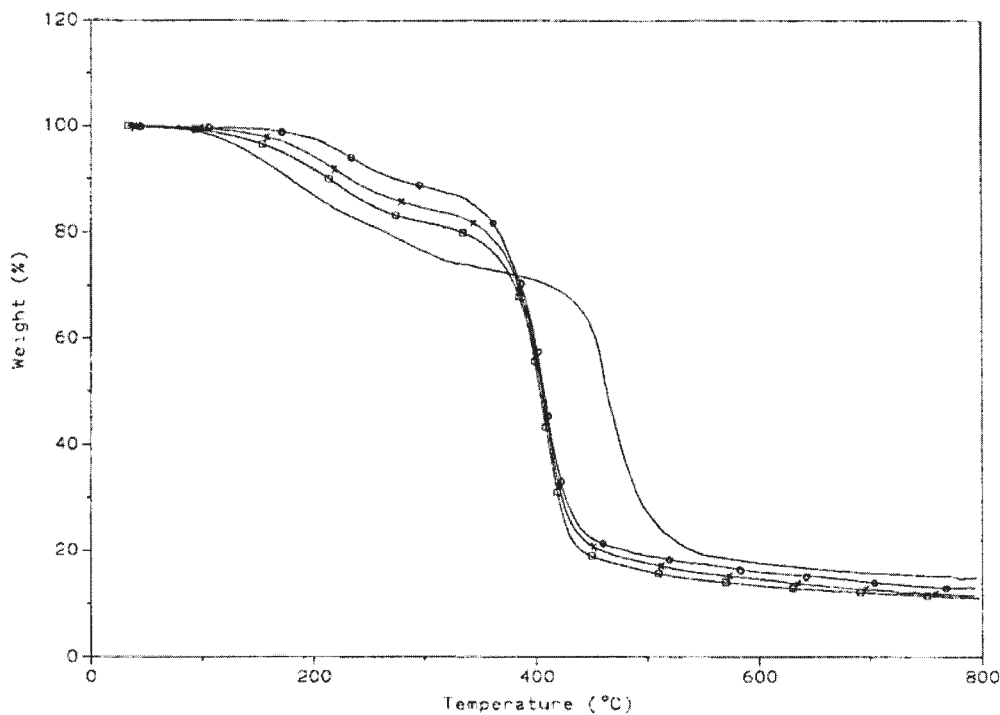


Figure 12 TGA of self-cured polymeric dyes with various dosages of Blue 62 dye under nitrogen; 0.5 (□); 1.0 (×); 2.0 (○) comparing to original water-reducible epoxy resin, WEP (—).

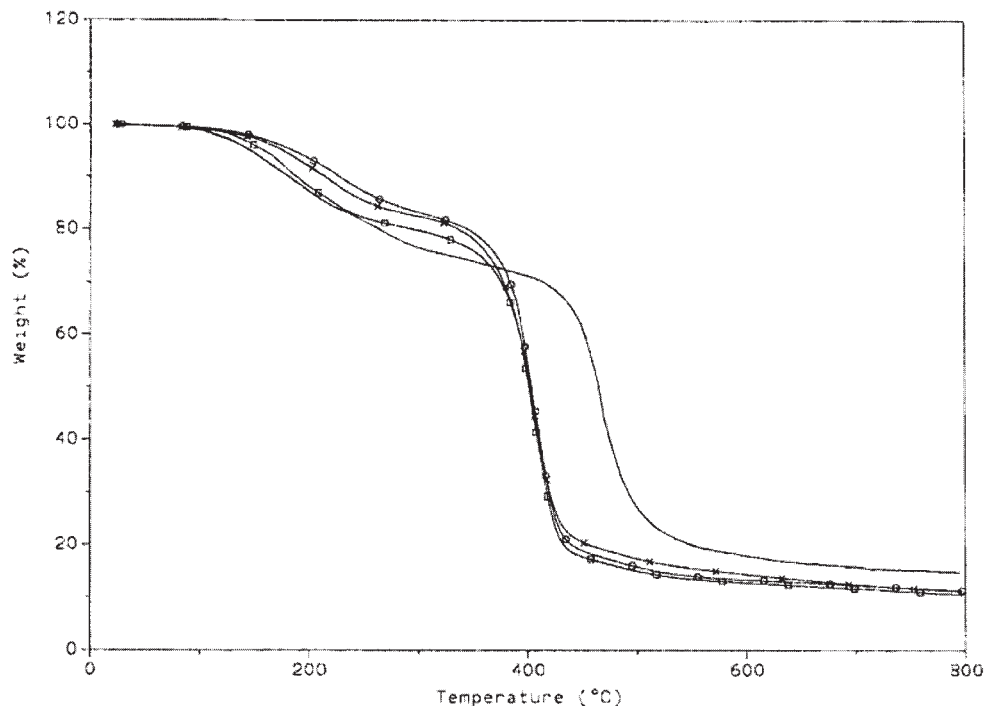
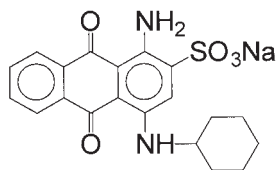


Figure 13 TGA of self-cured polymeric dyes with various dosages Orange 39 dye under nitrogen; 0.5 (\square); 1.0 (\times); 2.0 (\circ) comparing to original water-reducible epoxy resin, WEP ($—$).

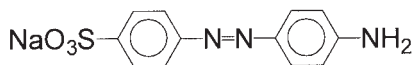
between polymeric dyes and also increased its thermal stability.

Appearance color strength of polymeric dye

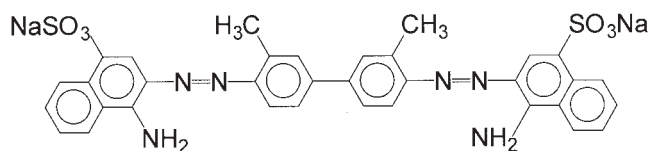
Appearance strength was 100% scale for each polymeric dye film before dipping in water or ethanol.



C.I. Acid Blue 62



C.I. Direct Orange 39



C.I. Direct Red 2

Scheme IV Water-soluble dyes.

Most of dried polymeric dye films after dipping in either water or ethanol demonstrated a greater value of appearance strength than that of original untreated film. This was possible because most of the polymeric dyes were crosslinked and waterproof (or ethanol resistant), and some fractions of epoxy resin without dye were washed away by water (or ethanol) and the polymeric dye remained with a higher color strength. Furthermore, the self-cured polymeric dye molecules were brought closer by the crosslinking reaction. Therefore, color strength of treated polymeric dye film was more intense than that of original polymeric dye film. The color strength of water-treated polymeric dyes was 6.6–29.1% higher than that of original polymeric dye. The ethanol-treated samples were 10.2–43.2% higher than that of the original polymeric dyes (Table III). A higher appearance color strength of the polymeric dye film after water (or ethanol) treatment than that of the original untreated sample indicated that good color fastness was generated by self-curing reaction of polymeric dye.

Applications of polymeric dye

Dyed micro-fiber cloth with self-cured aqueous polymeric dye was treated with cold water washing for 4 cycles. The appearance color strength of dyed cloths remained on 69.3, 70.7, and 73.1% with Direct Orange 39, Direct Red 2, and Acid Blue 62, respectively, after water wash. That was due to the self-cured polymeric dye with networked polymeric structure anchored in

micro-fiber cloth. Comparing with those dyed cloths with original water-soluble dyes will be washed away completely after water washing.

The self-curable aqueous polymeric dye solution was printed on a regular white paper. Water content of aqueous polymeric dye solution was absorbed by paper immediately through capillary and its polymeric dye turned into waterproof and solvent-resistant printed ink on drying. It was due to the acidity of paper (which is acid paper with a pH about 6) that catalyzed the self-curing reaction of polymeric dye and its polymeric dye became waterproof instantly after it was printed on paper. This self-curable aqueous polymeric dye solution had the potential for jet printing ink applications.

CONCLUSIONS

A nano-size aqueous polymeric dye dispersion was obtained from the ring-opening reaction of water-reducible epoxy resin, with amino group containing water-soluble dyes; C. I. Direct Red 2, C. I. Acid Blue 62, and C. I. Direct Orange 39 were used, respectively. A self-curable system of aqueous polymeric dye was formulated with a polyaziridine as a latent curing agent, which was stable at pH above 8.0. Its self-curing reaction took place on drying at ambient temperature, and the final self-cured polymeric dye was waterproof and organic resistant. It was not only an environmental-friendly product, but also solved the handicaps of water-soluble dyes on their applications. This self-

curable system of nano-size aqueous polymeric dye dispersion could have the potential for jet ink printing, dyeing, and other color applications.

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