Coloration Mechanism of the Acrylonitrile Solution of *N*-Phenylmaleimide and Its Stabilization Method

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ABSTRACT: *N*-Phenylmaleimide (PMI) was used as an acrylonitrile (AN) solution which is convenient to handle because PMI is an irritative solid and difficult to handle. However, the PMI solution tends to color during storage upon heating and its yellow color is apt to become brownish. Impurities contained in the colored PMI solution were isolated and their structures identified. Azobenzene (AZB) and *N,N'*-diphenylhydradine (DPH) are the compounds which cause the color change in the solution. The extent of the coloration of the PMI solution increases with increase in the contents of AZB and DPH. It is considered that AZB and DPH are produced by the oxidation of aniline (ANL) generated by the hydrolysis of PMI in the solution. The addition of the antioxidants under a low concentration of oxygen was examined to prevent coloration of the solution based on the proposed mechanism of the coloration. These conditions proved to be sufficiently effective for stabilization of the solution. Furthermore, it was also confirmed that the extent of coloration of the polymer prepared from the stabilized solution is effectively minimized. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2037–2045, 1997

Key words: acrylonitrile solution; *N*-phenylmaleimide; coloration; stabilization; polymerization

INTRODUCTION

Maleimides are radicaly polymerizable monomers and their polymerization behavior has been extensively investigated.[1–6] Copolymers of maleimide have drawn attention because the incorporation of the maleimide unit into the polymer backbone raises the glass transition point (T_g) of the copolymer.[4–6] *N*-Phenylmaleimide (PMI) has the superior capability of enhancing the T_g by copolymerization. Moreover, it is well known that the copolymer of styrene (St) and PMI is a useful raw material for the heat-resistant acrylonitrile–butadiene–styrene resin (ABS) because the St–PMI copolymer is miscible with styrene–acrylonitrile resin (AS), which is a matrix resin of ABS.[7] A variety of the copolymers involving PMI as one of the components was proposed by Nield et al.[8–10] However, such resins were not commercialized because the technology of industrial production of PMI was not yet established at that time. PMI has been commercialized since 1985, and PMI has been used as one of the key materials for heat-resistant ABS.[11]

PMI, which is made up of yellow crystals having a melting point of 89°C, irritates the skin and eye mucosa. Liquid material is easier to handle without contact to the human body because a pump and flow meter can be used for its transfer. A tank, rail car, tank lorry, etc., are also employed

Table I   Quality of PMI

Item	Criterion
Appearance	Yellow flakes
Melting point (°C)	89.9
Water (wt %)	< 0.05
MAN (wt %)	0.04
PMA (wt %)	0.05
ANL (wt %)	< 0.01
PMI (wt %)	> 99.5

for storage or transportation. However, handling of the solid material, especially powder, without human contact in a closed system is not an easy task, and complicated equipment such as a closed belt conveyer system or a closed bucket conveyer system are necessary for the transfer of such material. Furthermore, a closed container or a closed hopper system is required for storage and transportation. These problems have been pointed out for the handling of PMI because a closed system is preferable for the irritating PMI.

Handling of PMI as an acrylonitrile (AN) solution of PMI in the liquid state was proposed to solve these problems.[12,13] The PMI solution has been widely utilized after it was confirmed that PMI is highly soluble in AN, and the solution exhibits sufficient stability at high temperature despite the polymerizabilities of AN and PMI. AN is a suitable solvent because AN is one of the monomers for ABS resin, and the AN solution of PMI can be directly used for the production of the heat-resistant ABS. The PMI solution can be transferred by a pump, transported in a tank lorry, and stored in a tank as well as can the

Table II   Quality of AN

| Item	Criterion
Appearance	Colorless/transparent
Color No.[a]	< 5
Distillation range	
Initial boiling point (°C)	75.7
Distillation point at 97% (°C)	77.2
Water (wt %)	< 0.5
Acetaldehyde (wt %)	< 10
Hydrogencyanide (wt %)	< 1
Acetone (wt %)	< 10

[a] Color standard number of platinum−cobalt color standards, ASTM D 1209, Ref 16.

Table III   Solubility of PMI

Solvent	Solubility at 25°C (g/100 g of Solvent)
Benzene	28
Toluene	18
Methanol	9
Ethanol	5
Ethyl acetate	29
Butyl acetate	18
Acetone	48
Methyl ethyl ketone	39
Tetrahydrofuran	44
N,N-Dimethylformamide	51
Styrene	21
Acrylonitrile	100
Water	0.01

acrylic ester or St which are handled in the liquid state at room temperature.

ABS should be a colorless or slightly yellowish resin and is utilized as a colored resin upon mixing with pigment for various applications. Accordingly, less colored ABS resin is preferred for easier coloring. The light yellow color of the PMI solution becomes brownish during storage upon heating, and ABS, which is produced from such a colored PMI solution, is also colored. Coloration of the final product cannot be avoided if the colored PMI solution is employed. So, enhanced stability of the PMI solution against such coloration has been required. The present article is concerned with the investigation of the coloring mechanism of the solution based on isolation of impurities closely related to the coloration and development of a stabilization method.
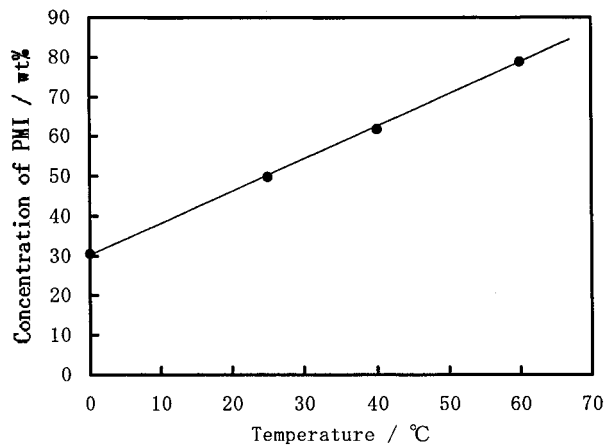
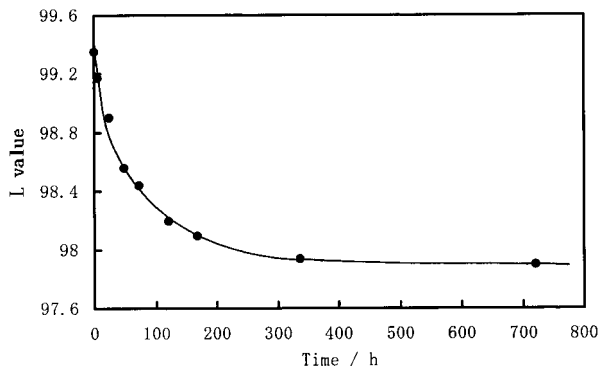**Figure 1**   Temperature dependence of the solubility of PMI in AN.

Figure 2   Change in the *L* value of the solution containing 60 wt % of PMI after storage in air at 55°C.

EXPERIMENTAL

Materials

PMI is a product of Nippon Shokubai Co. AN is a product of Sumitomo Chemical Co. PMI was dissolved in AN at 40°C to prepare a 60 wt % solution of PMI. 3-Anilino-*N*-phenylsuccinimide (APSI) and 3-anilino-*N*-phenylmaleimide (APMI) were synthesized according to the literature.[14] Azobenzene (AZB) and 1,2-diphenylhydrazine (DPH, Wako Pure Chemical Industries) are commercially available.

Storage Test

A 15 g PMI solution and #304 (10 × 50 × 2 mm) stainless steel were placed into a Pyrex test tube having a diameter of 18 mm. The closed test tube with a silicone rubber plug was maintained at 55°C in a water bath after introducing a gas of a fixed composition into the solution to remove any air.
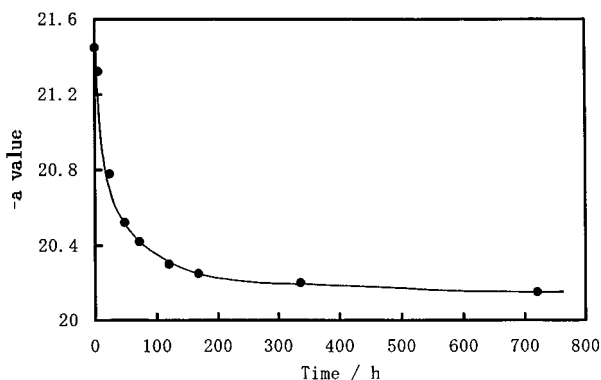
Figure 3   Change in the *a* value of the solution after storage under the same conditions with those in Figure 2.
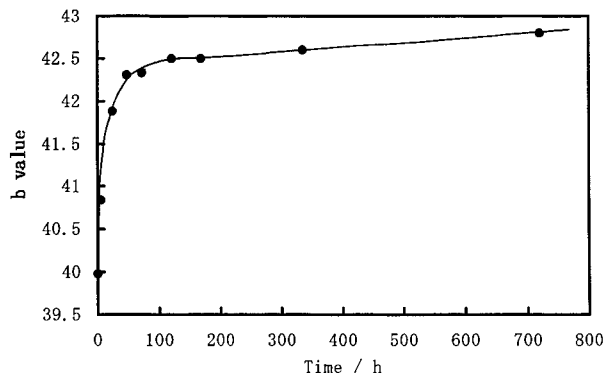
Figure 4   Change in the *b* value of the solution after the storage under the same conditions with those in Figure 2.

Color Measurement of Solution

The color change of the solution was measured after the PMI concentration in the solution was adjusted to 30 wt % using AN and the solution was poured into a cell having a thickness of 10 mm. Color was defined by lightness, saturation, and hue. The color change was expressed using Hunter's *L*, *a*, and *b* values.[15] The *L* value indicates lightness and a larger *L* value indicates a higher lightness. The degree of red becomes stronger as the *a* value increases while the smaller *a* value indicates that the degree of green becomes stronger. An increase in the *b* value shows that the degree of yellow becomes stronger and a decrease in the *b* value indicates that the degree of blue becomes stronger.[15]

Separation of Colored Impurities

A 20 g solution which was kept for 2 months at 55°C was poured into the glass column (20 mm ϕ × 500 mm) packed with 100 g of silica gel C-200 (Wako Pure Chemical Industries). One hundred grams of *n*-hexane was poured into this column for the development of the impurities. Successively, 100 g of an equivalent mixture of *n*-hexane and tetrahydrofuran (THF) was poured, and, finally, 100 g of THF was poured to elute the impurities.

Table IV   Changes in Quality of PMI in the 60 wt % Solution Under Air at 55°C

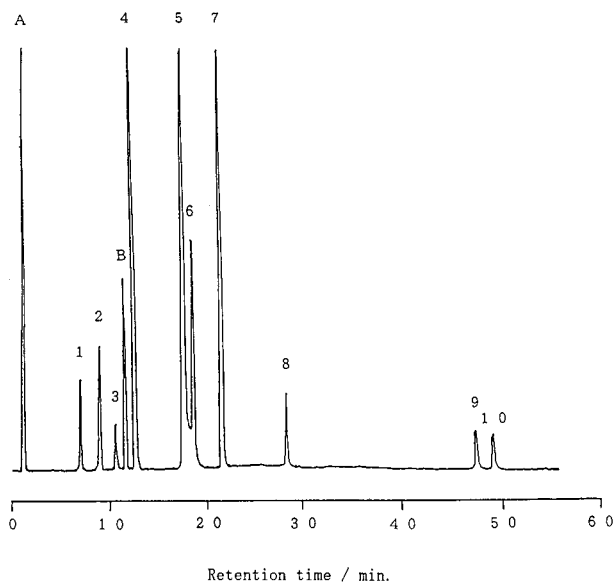| Item	Initial	After 720 h
Melting point (°C)	89.9	89.8
Purity of PMI (wt %)	> 99.5	> 99.5

Figure 5 GC spectrum of impurities separated from the solution. Compounds exhibiting peaks 1–12 are shown in Table VI. A and B are the peaks of THF and BHT dissolved in THF as the inhibitor.

Polymerization

A jacketed reactor, which was equipped with a condenser and stirrer, was employed, and silicone oil was circulated through the jacket for maintaining the temperature. St, 90 g, toluene, 110 g, and *t*-butyl peroxy isopropyl carbonate (BIC, Kayaku Akuzo Corp.), 50 mg, were placed in the reactor and the temperature was adjusted at 100°C. The 60% PMI solution of AN, 50 g, toluene, 50 g, and BIC, 100 mg, were continuously admitted to the above mixture with refluxing for 2 h. The reaction mixture was kept for 1 h at the same temperature.

Color Measurement of Polymerization Solution and Recovered Polymer

The yellow index (YI) of the polymerization solution was measured after adjusting the polymer

Table VI Identification of Isolated Impurities by GC/MS Spectroscopic Analysis

Peak No.	EI-MS (*m/z*)	Molecular Weight	Identified Compound Name
1	56, 77, 118, 133	133	PA
2	26, 54, 98	98	MAN
3	28, 38, 66, 93	93	ANL
4	27, 44, 71	71	AAM
5	26, 54, 103, 129, 173	173	PMI
6	39, 66, 93, 121	121	PF
7	28, 55, 93, 119, 146, 175	175	PSI
8	44, 64, 91, 119, 191	191	PMA
9	51, 77, 117, 144, 264	264	APMI
12	51, 77, 119, 146, 266	266	APSI

concentration to 3 wt % by diluting with chloroform. The polymer was recovered by precipitation with 10 times methanol from the diluted polymerization solution using five times methyl ethyl ketone and then dried. The YI, L, a, and b values were measured using a 3 wt % polymer solution of chloroform.

Measurements

For confirmation of the impurities affecting the coloration, the following conditions were employed for the gas chromatography measurement: column—the PEG megabore column (30 m × 0.53 mm ϕ); column temperature—holding at 80°C for 3 min, elevation to 250°C at a rate of 10°C/min, and holding at 250°C for 30 min; injection temperature—260°C; and load—1 μ. The following conditions were employed for the HPLC measure-

Table V Physical Constants and Spectral Data of Synthesized APMI and ASPI

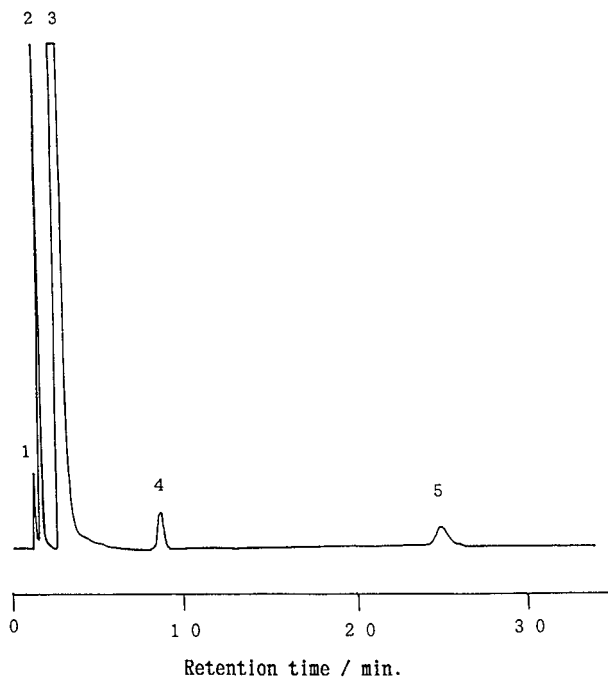| Compound	mp (°C)	MS *m/z* (M⁺)	EI-MS (*m/z*)	IR (KBr) (cm⁻¹)	¹H-NMR DMSO-d_6/δ (ppm)
APSI	210	266	51, 77, 119, 146, 266	3400 (m), 1780 (w), 1710 (vs), 1600 (m), 1500 (m), 750 (m), 690 (m)	7.5 (m, 3H), 7.3 (d, 2H), 7.1 (t, 2H), 6.7 (m, 3H), 6.1 (d, 1H), 4.8 (m, 1H), 3.3 (dd, 2H), 2.6 (dd, H)
APMI	234	264	51, 77, 117, 144, 264	3250 (m), 3050 (m), 1700 (s), 1650 (m), 1630 (m), 1550 (w), 1500 (w), 1400 (m), 750 (s), 690 (s)	9.8 (s, 1H), 7.5 (d, 4H), 7.4 (t, 5H), 7.1 (t, 1H), 5.8 (s, 1H)

Figure 6 HPLC spectrum of impurities separated from the solution. Compounds of peaks 1–5 are shown in Table VII.

ment: column—TSK-gel ODS-120T (4.6 mmϕ × 25 cm); mobile phase—a mixture of the aqueous solution of 0.65% acetic acid and acetone of which the weight ratio was 7 : 3; column temperature—40°C; flow rate—1.0 mL/min; and detector—225 nm. Mass spectra were recorded in the EI mode using a JEOL JMS-AX505WA.

For determination of the contents of aniline (ANL), maleic acid (MA), and *N*-phenylmaleamic acid (PMA), the same HPLC was employed under the following conditions: column—TSK-gel ODS-120T (4.6 mmϕ × 25 cm); mobile phase—a mixture of the aqueous solution of 0.5% orthophos-

Table VII   Identification of Impurities by HPLC/MS Spectroscopic Analysis

Peak No.	EI-MS (*m/z*)	Molecular Weight	Identified Compound
1	26, 27, 29, 45, 54, 55, 72, 99, 116	116	MA
2	44, 64, 91, 119, 191	191	PMA
3	26, 54, 103, 129, 173	173	PMI
4	51, 66, 77, 92, 115, 167, 168, 184	184	DPH
5	51, 77, 105, 153, 182	182	AZB
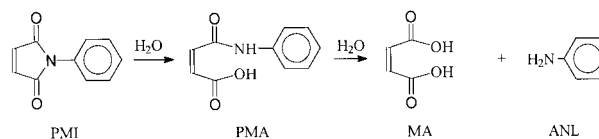
Scheme 1

phoric acid and acetonitrile, the weight ratio of which was 7 : 3; column temperature—40°C; flow rate—0.9 mL/min; and detector—210 nm.

The PMI content remaining in the solution after the polymerization was measured using GC under the following conditions: column—ULBON HR-1 (0.25 ϕ × 50 cm); column temperature—holding at 60°C for 10 min, elevation to 200°C at a rate of 10°C/min, and holding at 200°C for 15 min; and injection temperature—250°C.

The composition of the recovered polymer was determined by elemental analysis and IR spectroscopy using a Yanako CHN MT-3 and a Japan Biorat FTS-7, respectively. The weight-average molecular weight (M_w) was determined by gel permeation chromatography calibrated with polystyrene standards using a Tosoh CCP M-2 with the following conditions employed: column—Tosoh G6000HXL, G5000HXL, G4000HXL, G3000HXL, and G1000HXL; sample—polymer, 5 mg, was dissolved in 2 cc, THF; column temperature—38°C; and mobile phase—1 mL/min. The YI, *L*, *a*, and *b* values were determined using a Nippon Denshoku Kogyo Σ80.

RESULTS AND DISCUSSION

The qualities of PMI and AN were separately determined, and these two monomers were found to be highly pure commercial products as shown in Tables I and II. The solubilities of PMI in various
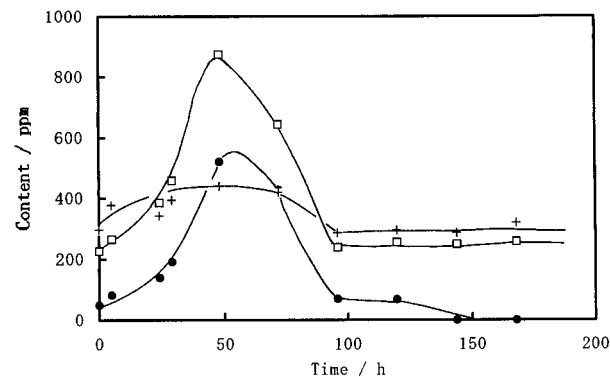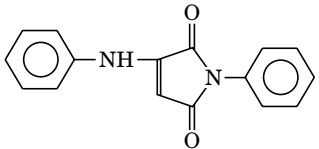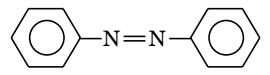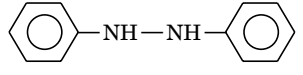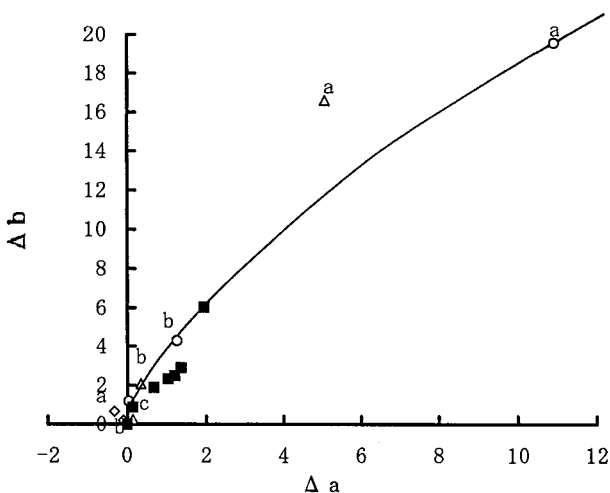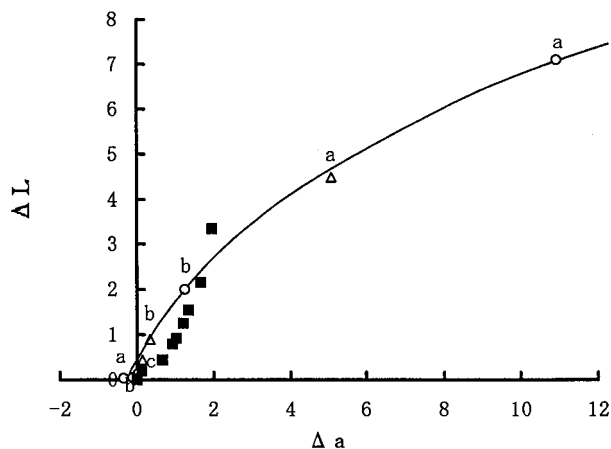

Figure 7 The contents of (●) ANL, (□) MA, and (+) PMA in the solution during storage.

Table VIII Colored Impurities in PMI/AN Solution

Name	Structure	Color
APMI		Orange yellow
AZB		Orange red
DPH		Orange red

Figure 9 A correlation between Δa and ΔL of the solution containing (◇) APMI, (△) DPH, and (○) AZB at (a) 500 ppm, (b) 100 ppm, (c) 10 ppm, and (■) during storage.

solvents and monomers are summarized in Table III. A quite high solubility of PMI in AN was confirmed and AN proved to be a suitable solvent for PMI. The dependence of the PMI solubility in AN on temperature is shown in Figure 1, indicating that the 50–70 wt % PMI solution can be prepared and handled as a homogeneous liquid at 25–50°C.

The difference in color is indicated by the L, a, and b values. Changes in the color of the PMI solution with respect to the L, a, and b values during storage at 55°C are summarized in Figures 2–4. The L value showing lightness tends to decrease with increasing time as shown in Figure 2, and an initial significant decrease in lightness during the first 100 h was found. Changes in the

$-a$ and b values during storage upon heating are illustrated in Figures 3 and 4 which show the coloration of the solution. Red became stronger as the $-a$ value decreased in Figure 3. Yellow also became stronger as the b value increased in Figure 4. Significant changes in the a and b values were also found during the initial 100 h and a gradual change after about 100 h was observed. Purities of PMI contained in the solution before and after heating are shown in Table IV, and it is apparent that the purity did not change during storage. Consequently, it is expected that a small amount of impurities except PMI affect the coloration.

The GC spectrum of impurities isolated from the colored solution shown in Figure 5 exibits many peaks, and the structures of these impurities were confirmed based on the mass spectroscopic data of an authentic compound.[17] The presence of APSI and APMI were confirmed using the spectral data for those separately synthesized. Their physical constants and spectral data are summarized in Table V. Table VI summarizes the GC/MS data for the isolated impurities including APSI and APMI. The impurities which were not identified by GC were also confirmed using HPLC and a mass spectrometer. Figure 6 shows the
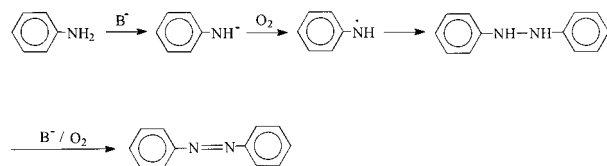

Figure 8 A correlation between Δb and Δa of the solution containing (◇) APMI, (△) DPH, and (○) AZB at (a) 500 ppm, (b) 100 ppm, (c) 10 ppm, and (■) during storage.

Scheme 2

Table IX   Influence of O$_2$ Concentration and Antioxidants on Coloration on the Solution

Run No.	O$_2$ Concentration in Gas Phase[a] (Vol %)	Additives[b]	Period Storage (h)	L	a	b	ΔL^c	Δa^c	Δb^c
1	21 (air)	Non	0	99.35	−21.45	39.98	0	0	0
2	21 (air)	Non	720	97.90	−20.15	42.80	1.45	−1.30	−2.82
3	7 (air−N$_2$ mixture)	Non	720	98.60	−20.86	41.77	0.75	−0.59	−1.79
4	7 (air−N$_2$ mixture)	Added	720	99.09	−21.25	40.44	0.26	−0.20	−0.46

[a] Atmospheric condition in the storage vessel.
[b] Primary antioxidant, 1000 ppm, and peroxide decomposer, 1000 ppm, shown in table X were administrated.
[c] Differences from the respective *L*, *a*, and *b* values of No. 1.

HPLC traces of the solution containing the impurities. AZB and DPH were also identified using the authentic compounds in addition to the confirmation using GC. The HPLC and mass spectroscopic data for the impurities are summarized in Table VII.

We reported that PMI is readily hydrolyzed to PMA, ANL, and MA upon heating as shown in Scheme 1.[18] The changes in the contents of PMA, ANL, and MA in solution were monitored as shown in Figure 7, and the amounts of ANL and MA significantly changed for about 100 h. The color of the solution was also substantially changed after 100 h as shown in Figures 2−4. As a result of these findings, the changes in the amounts of the hydrolyzed compounds of PMI, which are PMA, ANL, and MA, coincided well with the changes in the *L*, *a*, and *b* values of the solution. PA, DPH, AZB, PF, APSI, and APMI, which were identified using GC and HPLC as shown in Tables VI and VII, are produced from

ANL because these compounds include the ANL moiety. AAM was produced from AN.

Among the impurities, APMI, AZB, and DPH were expected to induce coloration because these compounds are strongly colored as shown in Table VIII. Quantification of these colored compounds in the solution was actually impossible because too many compounds in extremely small amounts are involved in the solution. Alternatively, their amounts were estimated based on a comparison of the changes in the *L*, *a*, and *b* values during storage with the induced changes by 10, 100, and 500 ppm of APMI, AZB, and DPH added to the PMI solution.

The correlation between the differences in the *L*, *a*, and *b* values after adding APMI, DPH, and AZB and those during storage are summarized in Figures 8 and 9. The *L*, *a*, and *b* values tend to increase with increase in the contents of DPH and AZB. However, the dependence of the increase of APMI on the coloration is slight. According to

Table X   Additives to Prevent Coloration

Additive	Structure

Primary antioxident (Irganox 245)

Peroxide decomposer (JPP2000)

Table XI Polymerization Result and Characterization of the Polymer

Run No.	Composition of Copolymer (Mol %)[a]			M_w
	St	AN	PMI	
5	59.0	7.1	33.9	22.9
6	58.9	7.3	33.8	22.1
7	58.5	7.5	34.0	22.7
8	58.8	7.2	34.0	22.5

[a] Residual monomeric PMI in the polymerization mixture was confirmed to be below 100 ppm.

these findings, it is deduced that the coloration of the solution is induced by AZB and DPH, and these amounts were estimated to be 10–100 ppm after 700 h storage.

The influence of oxygen on the coloration was expected based on the mechanism of the production of DPH and AZB from ANL as shown in Scheme 2.[19] The changes in the L, a, and b values in the atmosphere of the air–nitrogen gas mixture containing 7 vol % oxygen and air were determined to know the effect of oxygen. The extent of the changes in the L, a, and b values in air are more significant than are those in the mixed gas as shown in Table IX. Apparently, AZB and DPH are produced by the oxidation of ANL because the higher content of oxygen in the atmosphere resulted in a faster coloration of the solution.

Antioxidants such as a primary antioxidant and peroxide decomposer shown in Table X were added to the solution to prevent the color change. The changes in the color were examined after storage for 720 h in the presence of 1000 ppm antioxidants under a nitrogen atmosphere containing 7 vol % oxygen. These results are shown by No. 4 in Table IX. The antioxidant and a reduced oxygen

content efficiently suppressed the coloration of the PMI solution.

The St–AN–PMI copolymer was synthesized using the stabilized solution to confirm the effectiveness of the antioxidant. The polymerization was continued until there was no remaining PMI monomer as determined by the color of PMI results in the yellowish polymerization solution. Antioxidants did not affect the composition of synthesized polymers and its M_w as shown in Table XI. The YI, L, a, and b values of these polymers from the stored solutions of Nos. 1–4 of Table IX were determined as shown in Table XII. It was confirmed that the coloration of the polymer was effectively suppressed by stabilization of the solution, and the proposed mechanism of the coloration was confirmed by the results presented in Table XII.

CONCLUSIONS

The color of the PMI solution changes to brownish from yellow, and the lightness also decreases during storage when heated. Impurities involved in the colored PMI solution were isolated and identified. The changes in the contents of ANL and MA were confirmed to coincide with the changes in the color of the solution. DPH and AZB were predicted to cause the coloration because the changes in the L, a, and b values by admitting DPH and AZB to the solution rationalized the coloration of the solution during storage.

It was postulated that PMI is hydrolyzed to ANL and MA by water involved in AN, and oxidation of ANL yields DPH and AZB. The influence of the oxygen content in the atmosphere on the coloration was found to enhance the coloration.
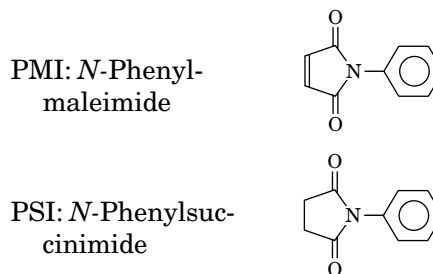
According to the proposed mechanism, the method which prevents coloration of the solution under an atmosphere of low oxygen in the pres-

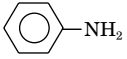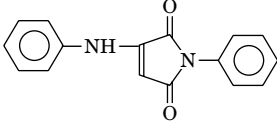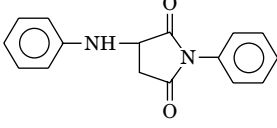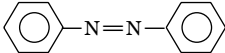**Table XII Influence of the Monomer Solution Color on the Color of Polymer Used**
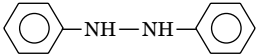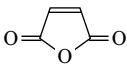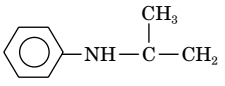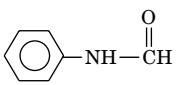
Run No.	PMI Solution				YI of Polymerization Mixture	Polymer Isolated			
	No.[a]	L	a	b		L	a	b	YI
5	1	99.35	−21.45	39.98	2.7	99.02	−0.30	1.12	2.0
6	4	99.09	−21.25	40.44	2.7	98.55	−0.33	1.53	2.7
7	3	98.60	−20.86	41.77	4.8	98.07	−0.49	1.90	3.3
8	2	97.90	−20.15	42.80	5.6	97.62	−0.95	2.07	3.6

[a] PMI solution shown in Table IX used for polymerization.

ence of antioxidants was developed. Moreover, the effectiveness of the stabilized solution to avoid the coloration of the polymer was also confirmed. As a result of the investigation on the mechanism of solution coloration, an effective stabilization method for the solution was established.

PMI: *N*-Phenyl-maleimide

PSI: *N*-Phenylsuc-cinimide

LIST OF ABBREVIATIONS

AAM: Acrylamide $CH_2=CH-CONH_2$

AN: Acrylonitrile $CH_2=CH-CN$

ANL: Aniline   ⬡—NH_2

APMI: 3-Anilino-*N*-phenylmaleimide

APSI: 3-Anilino-*N*-phenylsuccinimide

AZB: Azobenzene   ⬡—$N=N$—⬡

DPH: 1,2-Diphenyl-hydrazine   ⬡—$NH-NH$—⬡

MA: Maleic acid
$$CH-COOH$$
$$\|$$
$$CH-COOH$$

MAN: Maleic anhydride $O=$⬠$=O$

PA: 2-Propenyla-niline

PF: *N*-Phenylforma-mide

PMA: *N*-Phenyl-maleamic acid
$$CH-CONH-⬡$$
$$\|$$
$$CH-COOH$$

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