

The Spectral and Thermal Properties of Styrylquinolium Salts for Disc-Recordable Dyes

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Several styrylquinolium salts were synthesized to investigate their absorption and thermal properties, which had five different *p*-aminobenzene units and three different counter ions (iodide, perchlorate, and hexafluorophosphate anion), respectively. Hydroxy, methoxy, and methyl group in the *meta* position to the amino group led to bathochromic shift, while *N*-ethyl-*N*-chloroethylamino unit instead of *N,N*-diethylamino unit resulted in hypsochromic shift. A dye having a methoxy group in the *meta* position to the amino group had the highest molar extinction coefficient (ϵ), while a dye carrying chloro group in *N*-alkyl chains had the lowest ϵ . The type of counter ions had no effect on spectral properties like the maximum absorption wavelength and ϵ . All styryl dyes had exothermic peaks at decomposition in DSC curves. Among these styryl dyes, S2 series with perchlorate anions showed the strongest exothermic decomposition. From TGA spectra, S3 series with hexafluorophosphate anions had the best thermal stability and the sharpest threshold at thermal decomposition.

key words: styryl dyes, counter ions, spectral properties, thermal properties, DVD-R

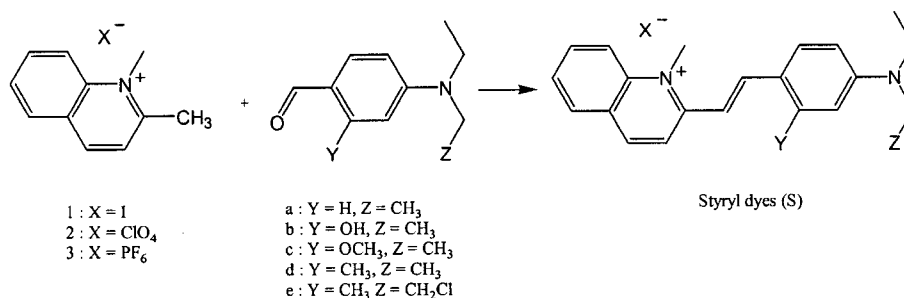
INTRODUCTION

A very variety of styryl dyes have been developed in a variety of fields such as laser dyes [1], probes for monitoring photopolymerization processes [2] and second-order NLO applications [3]. In addition, styryl dyes are used as photosensitizers in biochemistry areas [4] and can be promising candidate materials in the development of optical data storage system or optical switching devices [5].

The organic dyes for optical memory such as compact disc-recordable (CD-R) and digital versatile disc-recordable (DVD-R), require adequate absorption spectra against writing laser, high molar extinction coefficients, dramatic thermogravimetric decomposition threshold, and high thermal and photochemical

stability, etc. The dye compounds satisfying most of requirements would be azo-metal complexes [6], cyanines [7], and styryl dyes [8], etc. Our dye materials are based on the styryl-type dye structure because we can easily modify electron-donating or accepting groups inside the structures so that we can adjust precisely red- or blue-shift in the UV-VIS spectra.

In this paper, we adopted a quinoline moiety to enhance thermal stability of DVD-R dyes and some *p*-aminobenzene derivatives to shift absorption spectra for practical DVD-R application. Three series of 1-methyl-2-(*p*-aminostyryl)quinolium salts were synthesized by condensation reactions between five *p*-aminobenzaldehyde derivatives and three quinolium salts having different counter ions (iodide, perchlorate, and hexafluorophosphate anion) (Scheme 1). We tried to examine which



Scheme 1. The synthesis of styryl dyes

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substituents of *p*-aminobenzene and counter ions of quinolium salts affected their spectral and thermal properties by means of UV-VIS spectroscopy and thermal analysis measurements.

MATERIALS AND METHODS

Measurements. Melting points of starting materials were measured in capillary tubes on a melting temperature apparatus and those of styryl dyes were measured by differential scanning calorimetry (DSC). FT-IR spectra were taken on Galaxy Series FT-IR 6030 spectrometer in potassium bromide pellet. Absorption spectra in methanol solution were recorded on Jasco V-530 UV/VIS spectrophotometer. ¹H-NMR spectra were taken with a 200 MHz Gemini, using tetramethylsilane (TMS) as internal standard and CDCl₃ or DMSO-*d*₆ as a solvent. Thermogravimetric analysis (TGA) plots were taken on TA Instruments TGA 2950 and DSC curves on TA Instruments DSC 2910.

Starting materials. Methyl iodide, phosphorus oxychloride, 2-methylquinoline, 4-(diethylamino)benzaldehyde (a), 4-(diethylamino)salicylaldehyde (b), and 2-(*N*-ethyl-*m*-toluidino)ethanol were purchased from Aldrich Co. and used without further purification.

4-(Diethylamino)-2-methoxybenzaldehyde (c). Into a 100 mL flask with a cooling condenser, 4-(diethylamino)salicylaldehyde 3.27 g (16.9 mmol), potassium carbonate 2.80 g (20.3 mmol), and 30 mL of *N,N*-dimethylformamide (DMF) were added, and stirred at 80°C. Methyl iodide 4.80 g (33.8 mmol) was added slowly and this mixture was reacted under reflux for 6 hours. The reaction mixture was poured into water. The solid precipitate was filtered, dried, and recrystallized from tetrahydrofuran (THF) to give 2.3 g (66% yield) of the desired product as pink crystals : m.p. 84~85°C, ¹H-NMR (CDCl₃); 1.25 (6H, t), 3.45 (4H, q), 3.91 (3H, s), 6.05 (1H, s), 6.33 (1H, d), 7.72 (1H, d), and 10.14 ppm (1H, s) : IR (KBr pellet); 1078, 1271 (C-O), and 1642 cm⁻¹(C=O).

4-(Diethylamino)-2-methylbenzaldehyde (d). Into a flask with 50 mL of DMF, phosphorus oxychloride 21.13 g (137.8 mmol) was added dropwise with stirring at 0°C for 30 min. The portion of *N,N*-diethyl-*m*-toluidine 15 g (91.9 mmol) in DMF was slowly added into the above solution and the resulting mixture was maintained at room temperature. The solution was heated at 80°C for 4 hours, and then poured onto crushed ice/water. The resulting mixture was neutralized with sodium bicarbonate and was extracted with ethyl acetate, and combined organic layers were dried over with anhydrous sodium sulfate, and the solvent was evaporated. The product was purified by column chromatography on silica gel (eluent, ethyl acetate:hexane=1:5, v/v). The product was obtained as yellow viscous oil (15.45 g, 88% yield) : b.p. 136~137°C/2.3 Torr, ¹H-NMR (CDCl₃); 1.20 (6H, t), 2.60 (3H, s), 3.41 (4H, q), 6.39 (1H, s), 6.52 (1H, d), 7.62 (1H, d), and 9.93 ppm (1H, s) : IR (KBr pellet); 1673 cm⁻¹(C=O).

4-[(2-Chloroethyl)(ethyl)amino]-2-methylbenzaldehyde (e). In 30 mL of DMF at 0°C, phosphorus oxychloride 6.42 g (137.8 mmol) was added drop-wise with stirring for 1 hour. The portion of 2-(*N*-ethyl-*m*-toluidino)ethanol 5 g (27.9 mmol) dissolving in

DMF was slowly added into above solution and the resulting mixture maintained at room temperature. The solution was heated at 80°C for 5 hours, and poured onto crushed ice/water. The resulting mixture was neutralized with sodium bicarbonate and was extracted with ethyl acetate, and combined organic layers were dried over with anhydrous sodium sulfate, and the solvent was evaporated. The product was purified by column chromatography on silica gel (eluent ethyl acetate:hexane=1:6,v/v). After evaporation of the solvents, the product was obtained as orange crystals (4.48 g, 71% yield) : m.p. 51~52°C, ¹H-NMR (CDCl₃); 1.23 (6H, t), 2.63 (3H, s), 3.51 (2H, q), 3.61-3.74 (4H, m), 6.44 (1H, s), 6.58 (1H, d), 7.67 (1H, d), and 9.98 ppm (1H, s) : IR (KBr pellet); 1674 cm⁻¹ (C=O).

1,2-Dimethylquinolium iodide (1) [9]. A portion of 2-methylquinoline 10.0 g (70 mmol) was dissolved in 100 mL of acetone and methyl iodide 39.6 g (280 mmol) was added into the solution and reacted at reflux for 1 day. The precipitate was filtered off, washed with acetone, dried, to give 16.11 g (81% yield) of the desired product as bright yellow powder : m.p. 195~196°C, ¹H-NMR (DMSO-*d*₆); 3.10 (3H, s), 4.47 (3H, s), 8.00 (1H, t), 8.14 (1H, d), 8.24 (1H, t), 8.42 (1H, d), 8.61 (1H, d), and 9.12 ppm (1H, d) : IR (KBr pellet); 1226 (C-N⁺) and 2986 cm⁻¹ (C-H, 2-methyl).

1,2-Dimethylquinolium perchlorate (2) [10]. A portion of 1.72 g (12 mmol) of perchloric acid (70%) was added to a hot solution of 1,2-dimethylquinolium iodide 2.85 g (10 mmol) dissolved in 20 mL of methanol. After cooling, the product was obtained as pale brown crystals (2.5 g, 97% yield) : m.p. 152~153°C, ¹H-NMR (DMSO-*d*₆); 3.08 (3H, s), 4.45 (3H, s), 8.00 (1H, t), 8.11 (1H, d), 8.23 (1H, t), 8.40 (1H, d), 8.59 (1H, d), and 9.09 ppm (1H, d) : IR (KBr pellet); 1230 (C-N⁺) and 3050 cm⁻¹ (C-H, 2-methyl).

1,2-Dimethylquinolium hexafluorophosphate (3). A portion of 13.38 g (55 mmol) of hexafluorophosphoric acid (60%) was added to a hot solution of 1,2-dimethylquinolium iodide 14.26 g (50 mmol) dissolved in 120 mL of methanol. The precipitate was filtered, dried and recrystallized from methanol to give 11.9 g (78% yield) of the desired product as pale yellow crystals : mp 157~158°C, ¹H-NMR (DMSO-*d*₆); 3.09 (3H, s), 4.45 (3H, s), 8.00 (1H, t), 8.12 (1H, d), 8.24 (1H, t), 8.40 (1H, d), 8.59 (1H, d), and 9.09 ppm (1H, d) : IR (KBr pellet); 1230 (C-N⁺), 3100 cm⁻¹ (C-H, 2-methyl).

Synthesis of styryl dyes (S1-a ~ S3-e).

1-Methyl-2-(*p*-diethylaminostyryl)quinolium iodide (S1-a). 4-(Diethylamino)benzaldehyde 1.77 g (10 mmol) and 1,2-dimethylquinolium iodide 2.85 g (10 mmol) were mixed in 20 mL of ethanol, and pyridine (0.5 mL) was added. The resulting mixture was heated under reflux for 1 day. The product was precipitated by itself during reaction. The flask was kept in a refrigerator for higher yield. The solid product was separated by filtration and recrystallized from ethanol, to give 2.25 g (50% yield) of the product as fine crystals. The synthetic procedure for compounds **S1-b** ~ **S3-e** was the same as that for the preparation of compound **S1-a**.

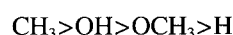
The synthesis of the S3 series was conducted in methanol instead of ethanol. Every styryl dye was obtained as fine crystals and had high purity without further purification.

RESULTS AND DISCUSSION

Styrylquinolium salts were obtained from the condensation of *p*-aminobenzaldehyde derivatives with 2-methyl quinolium salts in the presence of base [11]. The structures of the dyes were characterized by ¹H-NMR and FT-IR spectra. Benzaldehyde peaks (9.9~10.2 ppm, 1640~1680 cm⁻¹) and 2-methyl peaks (3.1 ppm, 2980~3100 cm⁻¹) of 2-methylquinolium salts disappeared in ¹H-NMR and FT-IR spectra of styryl dyes, respectively. Also, ethylene double bond peaks (7.4~7.5 ppm) newly appeared in ¹H-NMR spectra of styryl dyes. Data on yields, melting points, and ¹H-NMR spectra are summarized in Table

1. From these results, we confirmed that the condensation of *p*-aminobenzaldehyde derivatives with 2-methyl quinolium salts gave the expected styryl dyes.

As shown in Table 2, styryl dyes containing different substituents in the *meta* position to the *N,N*-diethylamino group and *N*-alkyl chain exhibited different absorption wavelength maxima (λ_{max}) and molar extinction coefficients (ε). The order of bathochromic effect order induced by the substituents on the *meta* position was as follows :



The highest ε values were obtained for compounds having methoxy group in the *meta* position (**S1-c**, **S2-c**, **S3-c**). Bathochromic shift was responsible for the introduction of electron donating groups (hydroxy, methoxy, and methyl group) in the *meta* position to the diethylamino group. This effect can

Table 1. Yields, melting points, and ¹H-NMR data of styryl dyes.

	Yield(%)	mp(°C)	¹ H-NMR
S1-a	50.7	212	1.16 (6H, t), 3.48 (4H, q), 4.43 (3H, s), 6.80 (2H, d), 7.50 (1H, d), 7.83 (3H, d), 8.07 (1H, t), 8.21-8.53 (4H, m), 8.76 (1H, d)
S1-b	59.4	-	1.15 (6H, t), 3.42 (4H, q), 4.32 (3H, s), 6.20 (1H, d), 6.39 (1H, d), 7.50 (1H, d), 7.72-7.80(2H, m), 8.02 (1H, t), 8.15-8.39 (4H, m), 8.63 (1H, d), 10.53 (1H, s)
S1-c	46.9	218	1.18 (6H, t), 3.51 (4H, q), 3.98 (3H, s), 4.35 (3H, s), 6.22 (1H, d), 6.46 (1H, d), 7.49 (1H, d), 7.75-7.85 (2H, m), 8.04 (1H, t), 8.18-8.41 (4H, m), 8.67 (1H, d)
S1-d	54.1	222	1.17 (6H, t), 2.55 (3H, s), 3.49 (4H, q), 4.44 (3H, s), 6.63 (1H, d), 6.69 (1H, d), 7.47 (1H, d), 7.84 (1H, d), 8.05-8.32 (4H, m), 8.42 (1H, d), 8.58 (1H, d), 8.78 (1H, d)
S1-e	42.7	202	1.16 (3H, t), 2.55 (3H, s), 3.55 (4H, q), 3.80 (2H, t), 4.46 (3H, s), 6.69 (1H, d), 6.74 (1H, d), 7.54 (1H, d), 7.86 (1H, t), 8.04-8.30 (4H, m), 8.44 (1H, d), 8.61 (1H, d), 8.82 (1H, d)
S2-a	75.3	-	1.15 (6H, t), 3.46 (4H, q), 4.41 (3H, s), 6.78 (2H, d), 7.48 (1H, d), 7.80 (3H, d), 8.06 (1H, t), 8.18-8.48 (4H, m), 8.74 (1H, d)
S2-b	76.2	217	1.16 (6H, t), 3.41 (4H, q), 4.31 (3H, s), 6.19 (1H, d), 6.36 (1H, d), 7.49 (1H, d), 7.71-7.80 (2H, m), 8.02 (1H, t), 8.15-8.38 (4H, m), 8.62 (1H, d), 10.55 (1H, s)
S2-c	67.8	228	1.18 (6H, t), 3.51 (4H, q), 3.97 (3H, s), 4.34 (3H, s), 6.22 (1H, d), 6.44 (1H, d), 7.48 (1H, d), 7.74-7.83 (2H, m), 8.04 (1H, t), 8.16-8.39(4H, m), 8.68 (1H, d)
S2-d	65.6	221	1.15 (6H, t), 2.52 (3H, s), 3.47 (4H, q), 4.44 (3H, s), 6.59 (1H, d), 6.65 (1H, d), 7.43 (1H, d), 7.83 (1H, d), 8.01-8.28 (4H, m), 8.38 (1H, d), 8.54 (1H, d), 8.73 (1H, d)
S2-e	61.1	-	1.15 (3H, t), 2.53 (3H, s), 3.54 (4H, q), 3.78 (2H, t), 4.44 (3H, s), 6.66 (1H, d), 6.71 (1H, d), 7.49 (1H, d), 7.84 (1H, t), 8.02-8.28 (4H, m), 8.42 (1H, d), 8.57 (1H, d), 8.80 (1H, d)
S3-a	72.4	256	1.15 (6H, t), 3.46 (4H, q), 4.41 (3H, s), 6.78 (2H, d), 7.47 (1H, d), 7.80 (3H, d), 8.05 (1H, t), 8.18-8.48 (4H, m), 8.72 (1H, d)
S3-b	56.0	221	1.16 (6H, t), 3.41 (4H, q), 4.32 (3H, s), 6.20 (1H, d), 6.38 (1H, d), 7.49 (1H, d), 7.71-7.80 (2H, m), 8.02 (1H, t), 8.15-8.38 (4H, m), 8.62 (1H, d), 10.52 (1H, s)
S3-c	86.6	243	1.18 (6H, t), 3.49 (4H, q), 3.96 (3H, s), 4.32 (3H, s), 6.19 (1H, d), 6.42 (1H, d), 7.46 (1H, d), 7.73-7.81 (2H, m), 8.02 (1H, t), 8.15-8.38 (4H, m), 8.64 (1H, d)
S3-d	76.2	220	1.15 (6H, t), 2.53 (3H, s), 3.47 (4H, q), 4.41 (3H, s), 6.60 (1H, d), 6.66 (1H, d), 7.44 (1H, d), 7.82 (1H, d), 8.02-8.29 (4H, m), 8.39 (1H, d), 8.55 (1H, d), 8.74 (1H, d)
S3-e	49.4	210	1.15 (3H, t), 2.54 (3H, s), 3.54 (4H, q), 3.79 (2H, t), 4.44 (3H, s), 6.68 (1H, d), 6.73 (1H, d), 7.51 (1H, d), 7.85 (1H, t), 8.03-8.29 (4H, m), 8.43 (1H, d), 8.58 (1H, d), 8.80 (1H, d)

S1-b, S2-a, and S2-e had no melting points

Table 2. Absorption spectral results for styryl dyes

	λ_{max} (nm) ^a	$\log \epsilon$ ^b		λ_{max} (nm)	$\log \epsilon$		λ_{max} (nm)	$\log \epsilon$
S1-a	535	4.81	S2-a	535	4.83	S3-a	535	4.78
S1-b	547	4.86	S2-b	547	4.85	S3-b	547	4.88
S1-c	544	4.89	S2-c	544	4.91	S3-c	544	4.90
S1-d	548	4.80	S2-d	548	4.79	S3-d	548	4.83
S1-e	527	4.79	S2-e	527	4.74	S3-e	526	4.75

^aIn methanol. ^bMolar absorption coefficient (ϵ)

be explained by their ability to stabilize the excited states by sharing the positive charge on the terminal nitrogen atom [12]. According to this result, electron donating groups (hydroxy, methoxy, and methyl group) which had larger size than hydrogen atom had little influence on the coplanarity of dye molecules.

On the other hand, dyes (**S1-e**, **S2-e**, **S3-e**) with *N*-ethyl-*N*-chloroethylamino group instead of *N,N*-diethylamino group had the lowest absorption wavelength maxima, resulting in hypsochromic shift because $-I$ inductive effect of chloro group tends to reduce the $+I$ inductive effect of the alkyl group [12].

However, the kind of counter ions for styryl salts had no influence on λ_{max} and ϵ ($\Delta\lambda_{\text{max}}=1$ nm, $\Delta\log \epsilon=0.05$). All dyes had high molar extinction coefficients in the range of 4.75–4.91 ($\log \epsilon$).

Figure 1 shows the DSC curves of styryl dyes in this study. The melting temperatures (T_m) for all series of styryl dyes were in the range of 202–256°C. Three compounds (**S1-b**, **S2-a**, **S2-e**) did not show melting points. All styryl dyes had exothermic peaks on decomposition. Among three series of styryl dyes, **S2** series with perchlorate anions showed the

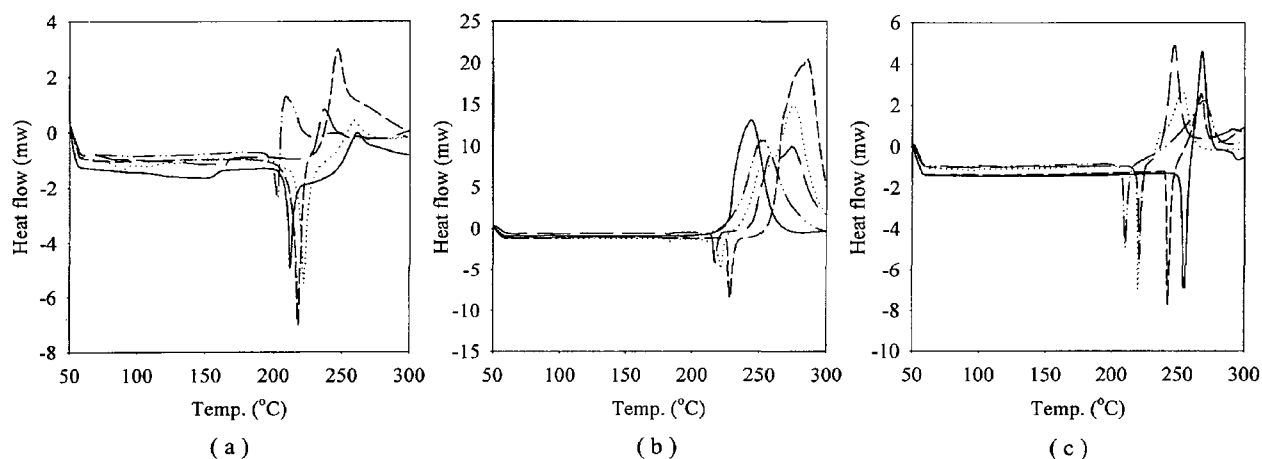


Figure 1. DSC curves of styryl dyes (— : Sa, — — : Sb, — — — : Sc, ····· : Sd, — ··· : Se) (a) Series 1 (b) Series 2 (c) Series 3.

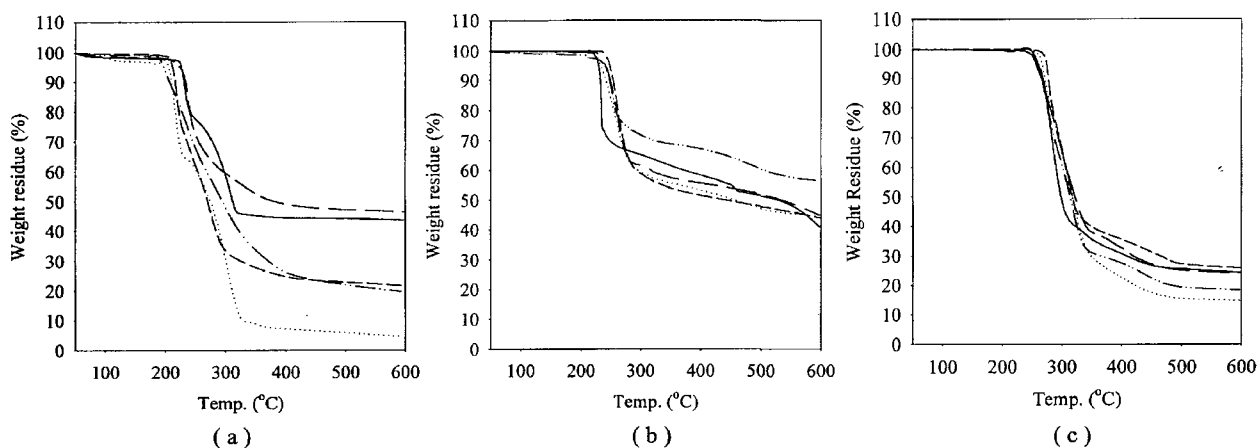


Figure 2. TGA curves of styryl dyes (— : Sa, — — : Sb, — — — : Sc, ····· : Sd, — ··· : Se) (a) Series 1 (b) Series 2 (c) Series 3.

Table 3. T_d and W_L of styryl dyes

	T_d^a	W_L^b		T_d	W_L		T_d	W_L
S1-a	226	0.88	S2-a	235	0.39	S3-a	264	1.74
S1-b	230	0.82	S2-b	242	0.76	S3-b	256	1.02
S1-c	231	1.25	S2-c	246	1.02	S3-c	271	1.54
S1-d	227	1.15	S2-d	237	0.82	S3-d	262	1.36
S1-e	206	0.80	S2-e	242	0.21	S3-e	261	1.18

^aInitial decomposition temperature. ^b40% weight loss (from 100% weight)/ ΔT (%/°C)

strongest exothermic decomposition. In TGA curves of Figure 2 and the summarized results of Table 3, it was found that S3 series with hexafluorophosphate anions had the highest initial decomposition temperatures. The highest value of W_L (weight loss per temperature) as shown in Table 3 indicated that S3 series had the sharpest threshold on thermal decomposition of styryl dyes. From these results, it was found out that the counter ions affected considerably the thermal stability of dyes, while they did not affect the spectral properties. The order of thermal stability of three series of styryl dyes was as follows.

S3 series > S2 series > S1 series

Among various dyes in this study, we measured a recording characteristic of **S2-a** with ClO_4^- as an anti-ion. The reflectivity (R_{top}) and optimum writing power (OWP) were about 55% and about 13 mW, respectively. The eye pattern was recorded by 8/16 multipulse. As a result, the jitter value and the modulated amplitude (I_{14}/I_{14H}) of the dye were 21% and 0.30. The jitter value was not fully satisfactory in terms of all DVD-R specification because the required specification is below 9%, however, it is expected that the jitter can be increased by the shift of UV-VIS spectrum through a modification of the molecular structure.

CONCLUSIONS

Three series of 1-methyl-2-(*p*-aminostyryl)quinolium salts were prepared and characterized by UV-VIS spectroscopy and thermal analysis. We could observe that the introduction of electron donating groups (hydroxy, methoxy, and methyl group) in the *meta* position to the diethylamino group led to bathochromic shift, while electron accepting substituent (chloro group) into *N*-alkyl chains led to hypsochromic shift. A dye having methoxy group in the *meta* position to the diethylamino group had the highest ϵ . However, the type of counter ions did not affect spectral properties. In DSC analysis, S2 series with perchlorate anions showed the strongest exothermic reaction on decomposition. On the other hand, S3 series with hexafluorophosphate anions showed the stiffest decomposition behavior despite of the highest initial decomposition temperature. It was found that the counter ions had a considerable influence on the thermal stability. These results can be applied to the shift of UV-VIS spectra and thermal stability enhancement of

practical DVD-R dyes.

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