

Synthesis of Conjugated Copolymers with phenothiazine and Azomethine Units and their Electro-Optic Properties

Hyeon Jin Seo^a, Byeung Jo Jang^a, Jin Gyu Chang^b, and Lee Soon Park^{a*}

Abstract

Three types of conjugated polymers, poly(PZ-Pi), poly(PZ-BPI) and poly(PZ-NPI) were synthesized by Schiff-base reaction. These new conjugated polymers exhibited improved solubility in common organic solvents due to the presence of alkyl side chains as well as azomethine groups. Double layer LEDs made with the synthesized polymers as emitting layer and Alq₃ as electron transporting layer exhibited enhanced EL emission and efficiency compared to those of single layer LEDs. Double layer LEDs exhibited gradual shift in the emission peak with the single layer LED, made of only Alq₃ as the emitting layer as the thickness of Alq₃ layer increased.

Keywords : azomethine group, electroluminescence, light-emitting diode(LED), electro-optical properties

1. Introduction

A number of conjugated polymers have been used as light emitting layers since R. H. Friend[1] reported of electroluminescence devices made of poly(*p*-phenylene vinylene)s. Recently, Tao et al. reported on the synthesis metal complex polymer with Schiff base structure in the main chain and its electroluminescence property.[2] In this work, conjugated polymers which have both phenothiazine moiety and azomethine linkage in the main chain were synthesized by using Schiff-base reaction.[3, 4] Light emitting diodes were fabricated with these conjugated polymers as light emitting layer and

Alq₃ as electron transporting layer and their electro-optical properties were examined.

2. Experiments

2.1 Monomer synthesis

Synthesis of aromatic dialdehyde monomer, N-(2-ethylhexyl)-3,6-diformylphenothiazine(DFPZ) containing phenothiazine moiety is shown in Fig. 1.

2.1.1 N-(2-Ethylhexyl)phenothiazine (EHPZ)

Phenothiazine(6 g, 0.03 mol) was added to a suspension of sodium hydroxide(7.2 g, 0.18 mol) in 60 ml dimethyl sulfoxide(DMSO) which was prepared by vigorous stirring for 0.5 hr under nitrogen atmosphere. After stirring for 1 hr, 2-ethylhexylbromide(5.8 g, 0.03 mol) was added. The reaction was carried out for 3 hrs at room temperature.[5,6] The resulting mixture was concentrated under reduced pressure utilizing rotary evaporator, and then extracted with water and dichloromethane. The collected organic layer was concentrated and the residue was purified by using

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* Member, KIDS.

Corresponding Author : Hyeon Jin Seo

a. Department of Polymer Science, College of Engineering, Kyungpook National University, #1370 Sangyuk-dong, Daegu, 702-701, Korea.

b. Department of Chemical Industry, Donggwi Institute of Technology, Pusan 614-715, Korea.

E-mail : lspark@bh.knu.ac.kr Tel : +53 950-5627 Fax : +53 950-6616

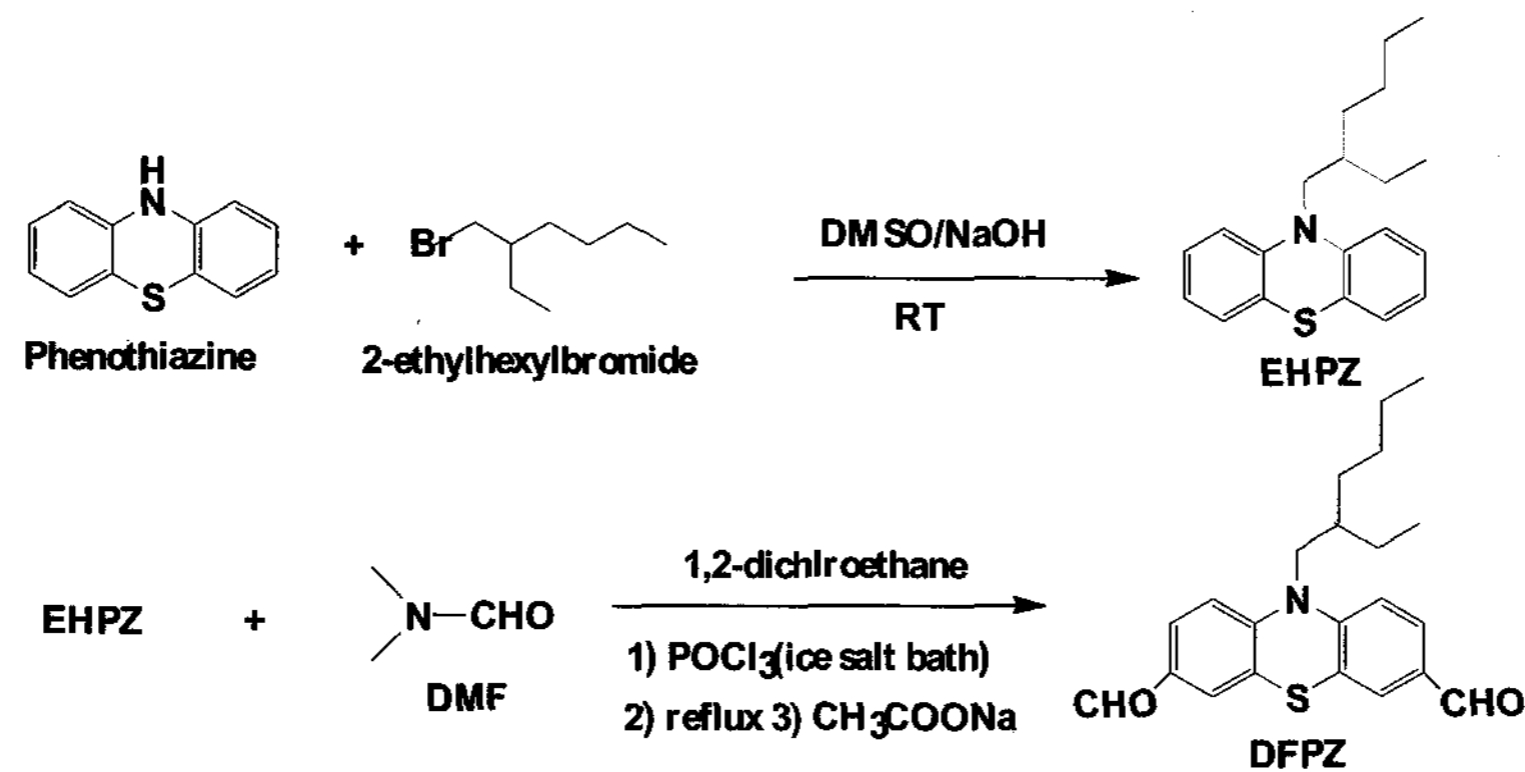


Fig. 1. Synthesis of dialdehyde compound as a monomer.

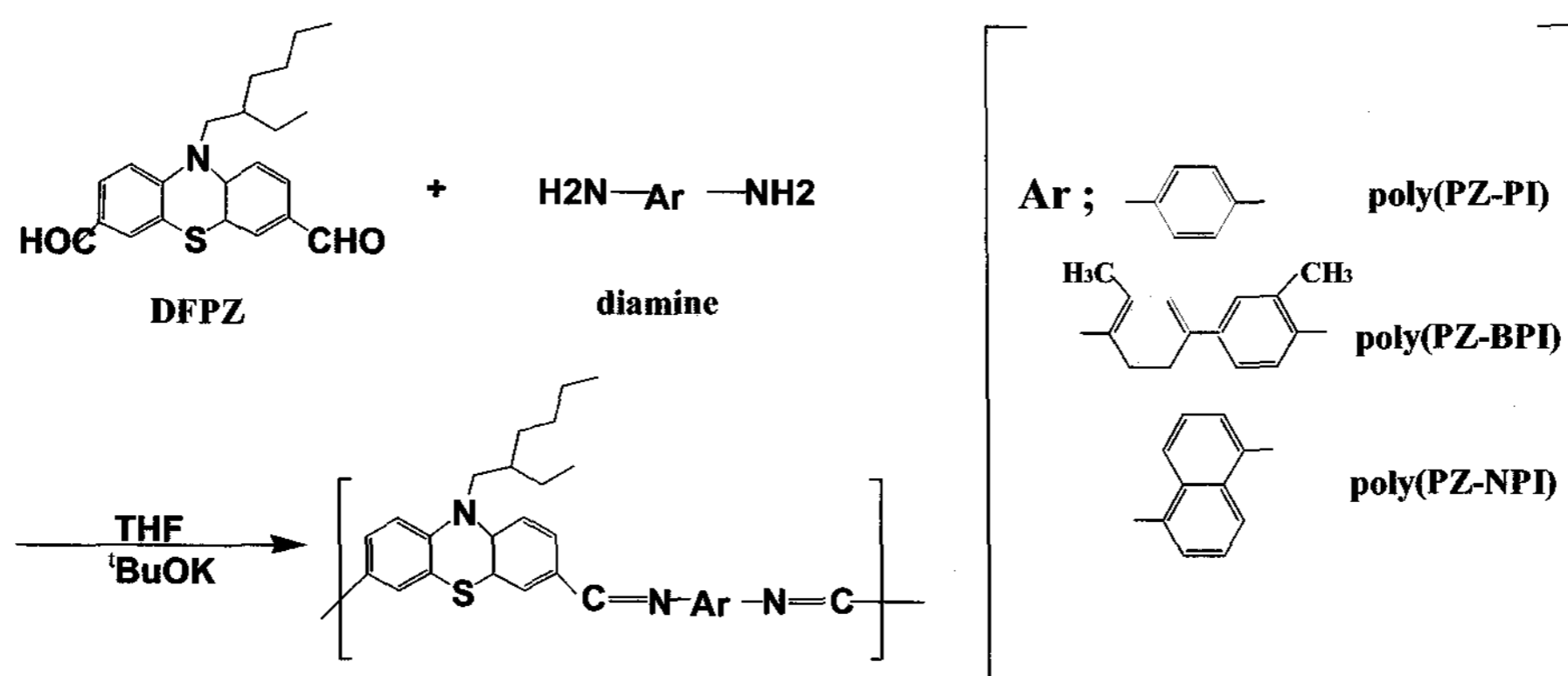


Fig. 2. Synthesis of conjugated polymers containing phenothiazine moiety and azomethine linkage.

silicagel column (eluent; *n*-hexane:petroleum ether = 2:1). After removing the eluent EHPZ was obtained in liquid form with 73 % yield.

¹H-NMR(CDCl₃), δ : 6.87, 7.12(m, 8H, Ar-H), 3.70(m, 2H, >N-CH₂-), 1.93(t, 1H, >CH-), 1.22-1.44(m, 9H, -CH₂-), 0.83-0.87(m, 6H, -CH₃), IR(KBr), cm⁻¹: 3064(Ar CH), 2926(aliphatic CH), 2857(>N-CH₂-), 1593, 1485(Ar C=C).

2.1.2 *N*-(2-Ethylhexyl)-3,6-diformylphenothiazine (DFPZ)

Vilsmeier-Haack formylation [7] was used to synthesize DFPZ. Phosphoryl chloride(122.7 g, 0.8 mol) was added dropwise over a period of 0.5 hr to a mixture solution of EHPZ(12.36 g, 0.04 mol) and dimethylformamide(DMF) (58.5 g, 0.8 mol) in 1,2-dichloroethane(15 ml) in an ice bath. The solution was then heated to reflux temperature. After refluxing for 72 hr, the

solution was cooled to room temperature. The solution was poured into a 33 wt% sodium acetate(27.8 g) aqueous solution, and stirred for 4 hrs to complete the hydrolysis. The resulting mixture was concentrated under reduced pressure and poured into acetone. Insoluble salts in acetone were filtered off, causing filtrate to become concentrated. The residue was extracted with water and dichloromethane, and the collected organic layer was concentrated. After purification by silicagel column(eluent; *n*-hexane : petroleum ether = 2:1) and evaporation of eluent, DFPZ was obtained in liquid form with 69 % yield.

¹H-NMR(CDCl₃), δ : 9.73(m, 2H, aldehydic hydrogen), 6.88, 7.56(m, 6H, Ar H), 3.73(t, 2H, >N-CH₂-), 1.17-1.85(m, 9H, -CH₂-, >CH-), 0.76-0.82(m, 6H, -CH₃), IR(KBr), cm⁻¹: 3048(Ar CH; weak signal), 2927(aliphatic CH), 2857(>N-CH₂-), 2724(aldehydic

hydrogen), 1688(C=O), 1600, 1465(Ar C=C).

2.2 Polymerization

Schiff-base reaction was used to obtain various conjugated copolymers containing azomethine linkage and phenothiazine moiety.[3,8] The synthetic scheme is shown in Fig. 2.

2.2.1 Poly(PZ-PI)

1,4-Phenylenediamine(1.1 g, 0.01 mol) was added dropwise to a mixture solution of DFPZ(3.67 g, 0.01 mol) in benzene(60 ml) at room temperature under nitrogen atmosphere. The solution was then heated to reflux temperature. The resulting mixture was concentrated under reduced pressure, and the residue was washed with methanol and water. After filtration and vacuum drying at 50 °C for 48 hrs, the poly(PZ-PI) was obtained in the form of orange color powder.

Yield : 68 %, IR(KBr), cm^{-1} : 3027(Ar CH), 2924 (aliphatic CH), 2857(>N-CH₂-), 1616, 1467(-N=C-), 1580, 1467(Ar C=C).

2.2.2 Poly(PZ-BPI)

3,3-Dimethylbenzidine(2.1 g, 0.01 mol) was added dropwise to a mixture solution of DFPZ(3.67 g, 0.01 mol) in benzene(80 ml) at room temperature under nitrogen atmosphere. The solution was then heated to reflux temperature. The resulting mixture was concentrated under reduced pressure, and the residue was washed with methanol and water. After filtration and vacuum drying at 50 °C for 48 hrs the poly(PZ-BPI) was obtained in the form of red color powder.

yield: 78 %, IR(KBr), cm^{-1} : 3018(Ar CH), 2925(aliphatic CH), 2856(>N-CH₂-), 1601, 1481(-N=C-), 1579, 1481(Ar C=C).

2.2.3 poly(PZ-NPI)

1,5-Diaminonaphthalene(1.6 g, 0.01 mol) was added dropwise to a mixture solution of DFPZ (3.67 g, 0.01 mol) in benzene (80 ml) at room temperature under nitrogen atmosphere. The solution was then heated to reflux temperature. The resulting mixture made to become was concentrated under reduced pressure, and the residue was washed with methanol and water. After filtration and vacuum drying at 50 °C for 48 hrs the

poly(PZ-NPI) was obtained in the form of yellow color powder.

Yield: 61%, IR(KBr), cm^{-1} : 3042(Ar CH), 2926(aliphatic CH), 2857(>N-CH₂-), 1620, 1468(-N=C-), 1578, 1469(Ar C=C).

2.3 LED Device fabrication and measurement

2.3.1 Single layer LEDs

Single layer LEDs were made by using the synthesized conjugated polymers as emitting layer that have good solubility in common organic solvents. Indium-tin oxide coated(ITO) glass with a sheet resistance of 30 Ω/\square was cut into 2.0 × 2.0 cm², and electrode area was prepared by photo-etching technique. It was cleaned successively with acetone, methanol, and mixture of isopropyl alcohol and water(1:1 by vol.) in an ultrasonic bath. Filtered solutions of conjugated polymer in benzene were cast on patterned ITO glass by spin coating and the solvent was evaporated to give emitting layers with thickness of about 600 Å measured by scanning probe microscope(Nanoscope Multimode SPM & Bio Scope). Thin Mg film was deposited at a rate of 20 Å/sec on top of the emitting layer as cathode (approximately 0.4 cm²) by using the E-beam method to about a thickness of 4000 Å.

2.3.2 Double layer LEDs with Alq₃ as electron transport layer

Double layer LEDs were also fabricated with Alq₃ as electron transporting layer between emissive layer and metal electrode. After spin coating and drying of polymeric emission layer, vacuum deposition of Alq₃ was performed on top of emissive layer at a rate of 3-5 Å/sec yielding a thickness of 200 Å. The Mg metal was deposited on Alq₃ thin film to give ITO/conjugated copolymer /Alq₃/Mg type double layer LEDs.

2.3.3 Characterization and measurement

The ¹H-NMR and FT-IR spectra of synthesized compounds were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. Molecular weight of conjugated copolymer was measured by Waters gel permeation chromatograph(GPC) equipped with a 410 differential refractometer, 510 HPLC pump, and Styragel HR 5E column using THF as eluent against polystyrene standards at room temperature. Thermal analysis was performed with differential scanning calorimeter(DSC) (TA Instruments, TA4000/Auto DSC

2910 system) and thermogravimetric analyzer(TGA) (Seiko instruments Inc., TG/DTA 320) with heating rate of 20 °C/min under nitrogen atmosphere. UV-visible absorption spectra of the copolymers were obtained by Shimadzu UV-2100.

Electroluminescence(EL) spectra and color coordinates were measured by using Spectroscan PR 704 (Photoresearch Inc.). Current and luminance vs. voltage profiles were obtained by using a DC power supply connected with Model 8092A Digital Multimeter(Hyun Chang Product Co. Ltd) and luminance meter(Minolta LS-100) equipped with close-up lens(No. 110, Φ 40.5 mm) at room temperature, respectively.

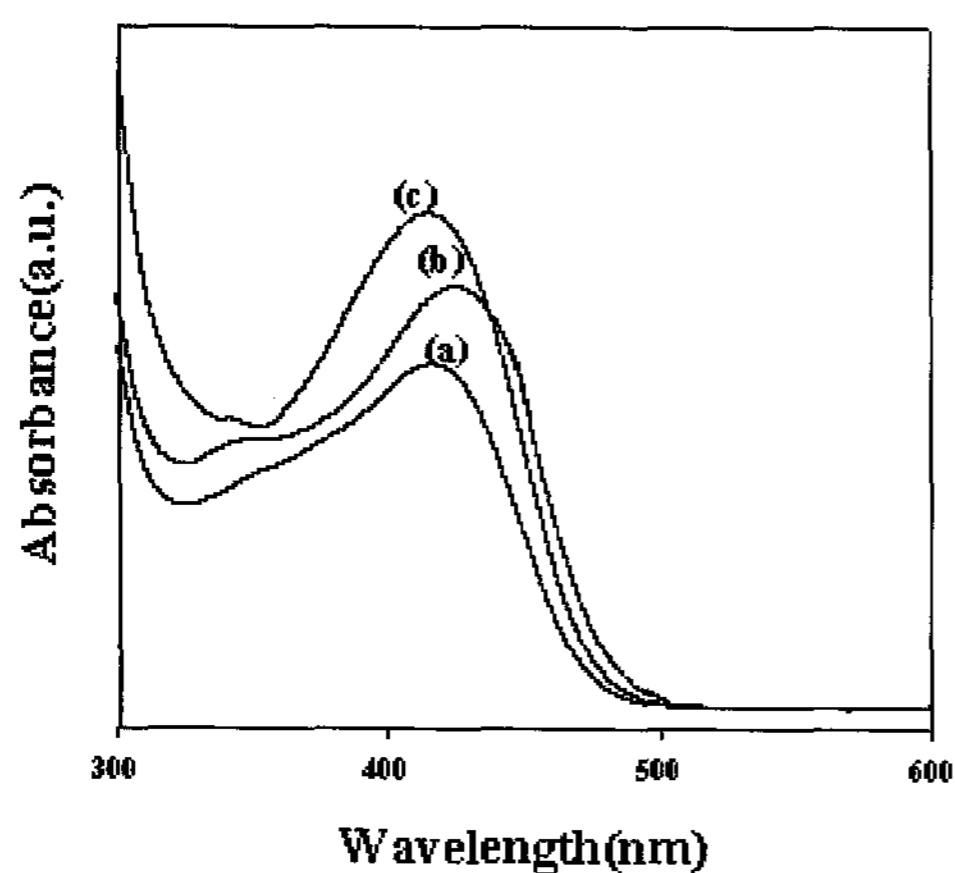


Fig. 3. UV-visible absorption spectra of (a) poly(PZ-PI), (b) poly(PZ-BPI), and (c) poly(PZ-NPI).

3. Results and Discussion

The solubility of the synthesized polymers was dependent on the microstructure of polymers. The data on the solubility of synthesized polymers are listed in Table 1. The poly(PZ-PI) was soluble in such organic solvent as tetrahydrofuran, N,N-dimethylformamide, 1,1,2,2-tetrachloroethane and N-methyl-2-pyrrolidone at room temperature. Poly(PZ-BPI) and poly(PZ-NPI) were soluble in benzene, tetrahydrofuran, 1,1,2,2-tetrachloroethane and N-methyl-2-pyrrolidone at an elevated temperature (about 40 °C). No precipitation of polymer was observed when the solution was cooled down to room temperature. LED devices therefore could be easily made with these polymers as light-emitting layers.

The UV absorption spectra of synthesized copolymers are shown in Fig. 3. The absorption maxima

($\lambda_{\max,UV}$) for poly(PZ-PI), poly(PZ-BPI), and poly(PZ-NPI) appeared at $\lambda_{\max,UV} = 413$ nm, $\lambda_{\max,UV} = 427$ nm, $\lambda_{\max,UV} = 415$ nm, respectively. Fig. 4 shows EL spectra of single layer LEDs made with the synthesized polymers. The maximum of EL spectra appeared at $\lambda_{\max,EL} = 576$ nm, $\lambda_{\max,EL} = 568$ nm, and $\lambda_{\max,EL} = 608$ nm for the LED's made with poly(PZ-PI), poly(PZ-BPI), and poly(PZ-NPI) as emitting materials, respectively.

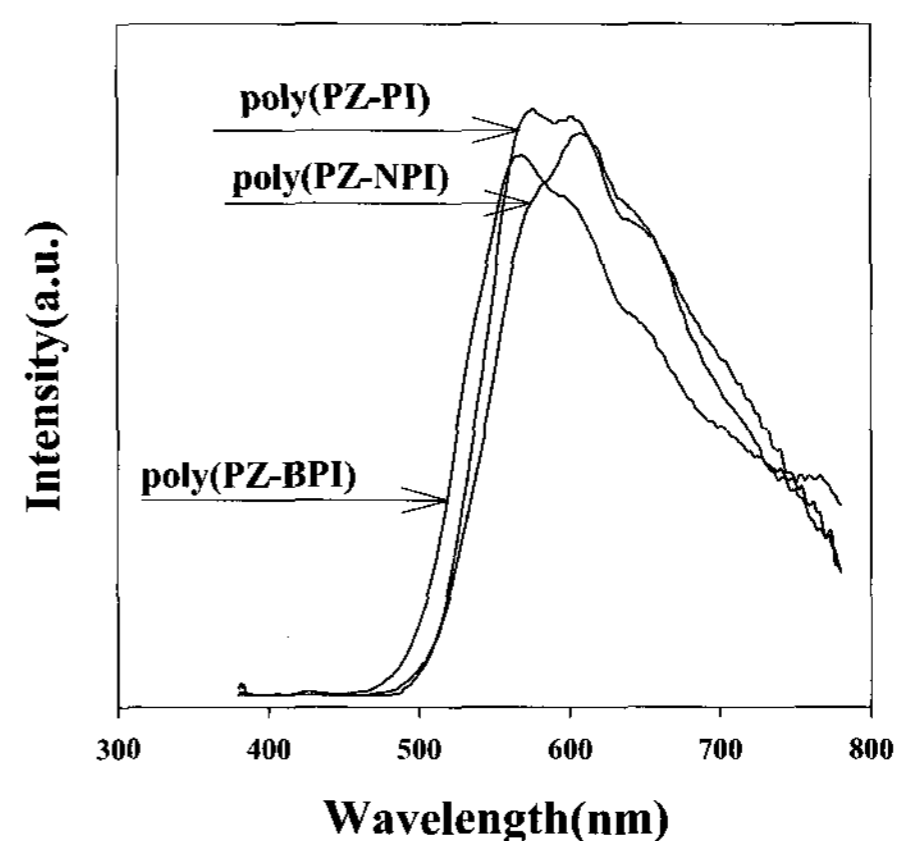


Fig. 4. EL spectrum of single layer LED's made of conjugated polymers.

The electro-optical properties such as maximum π - π^* transition ($\lambda_{\max,UV}$), HOMO-LUMO band gap energy ($\lambda_{\text{edg},UV}$) and emission maximum ($\lambda_{\max,EL}$) obtained from UV-visible and EL spectra are summarized in Table 2. It is noted that Poly(PZ-NPI) exhibits EL maximum at a longer a wave length than the other two emitting polymers due to increased conjugation length involving naphthalene ring.

Fig. 5 shows the luminance vs. voltage profile of single and double layer LEDs made with newly synthesized copolymers. Double layer LED's with Alq₃ as electron transporting layer exhibited both enhanced emission intensity and efficiency compared to the single layer LED's. Besides the threshold voltage of ITO/poly(PZ-PI)/Alq₃(100 Å)/Mg devices (7 V) was lower than that of ITO/poly(PZ-PI)/Mg device (10 V). These results indicate that conjugated copolymers synthesized had hole transporting and electron working property under the induced electric field. This may be due to the presence of alkyl substituted phenothiazine units in these polymers since the aromatic amines are well known to be a hole transport agent in the EL

Table 1. Solubility properties of conjugated copolymers.

solvent	poly(PZ-PI)	poly(PZ-BPI)	poly(PZ-NPI)
Chloroform	○	△	△
DCM	○	△	△
Benzene	○	○	○
THF	○	○	○
DMF	○	△	○
DMSO	△	×	△
TCE	○	○	○
NMP	○	○	○

Table 2. Electro-optical properties of conjugated copolymers.

Conjugated polymers	$\lambda_{\max,uv}$ (nm/eV)	$\lambda_{\text{edg},UV}^1$ (nm/eV)	$\lambda_{\max,EL}$ (nm/eV)
Poly(PZ-PI)	413/3.00	510/2.43	576/2.15
Poly(PZ-BPI)	427/2.90	512/2.42	568/2.18
Poly(PZ-NPI)	415/2.98	508/2.44	608/2.04

¹: onset point of UV-visible absorption spectrum

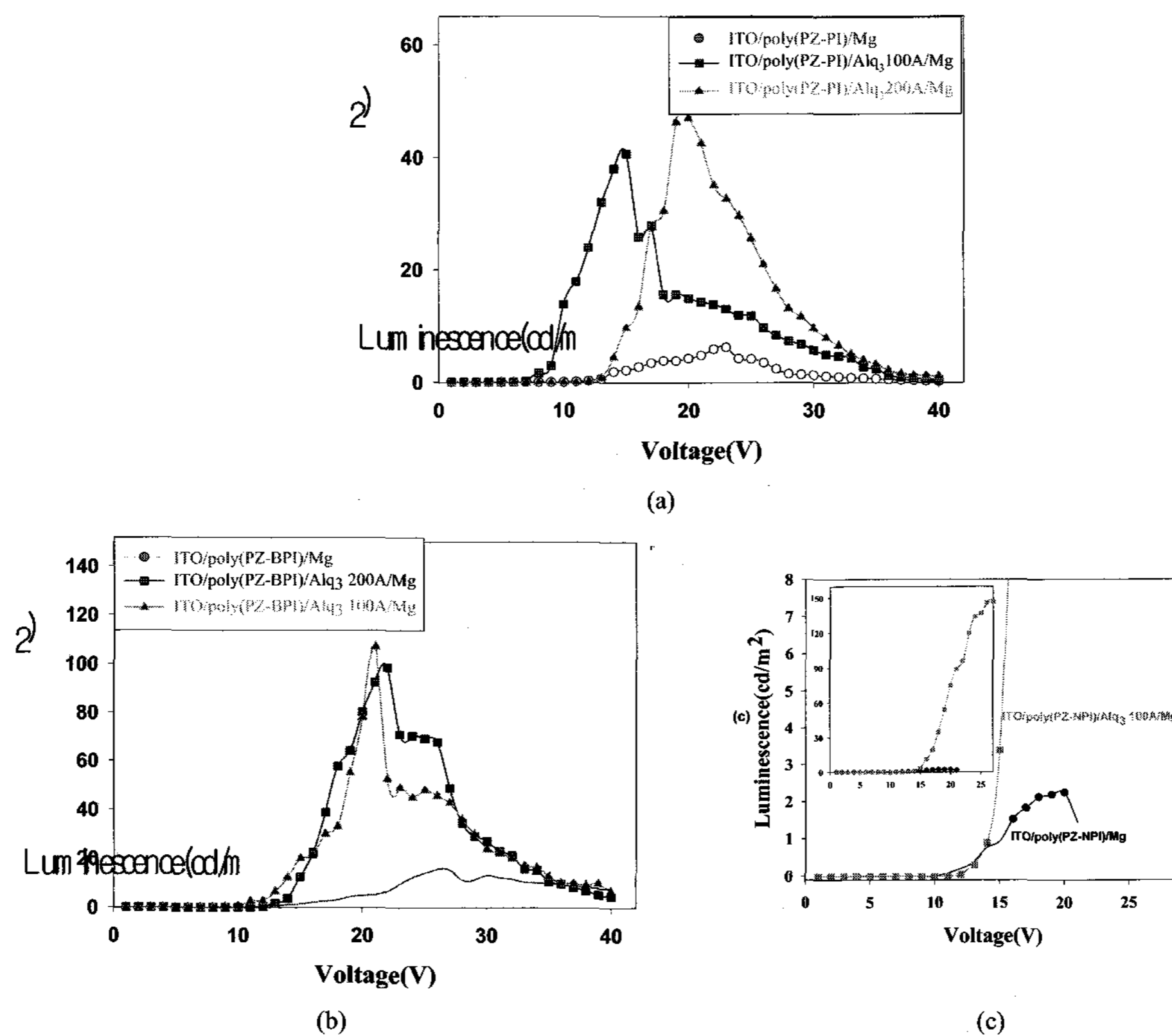


Fig. 5. Luminescence versus voltage profile of single and double layer LED's fabricated with (a) poly(PZ-PI), (b) poly(PZ-BPI), (c) poly(PZ-NPI) as light emitting layer.

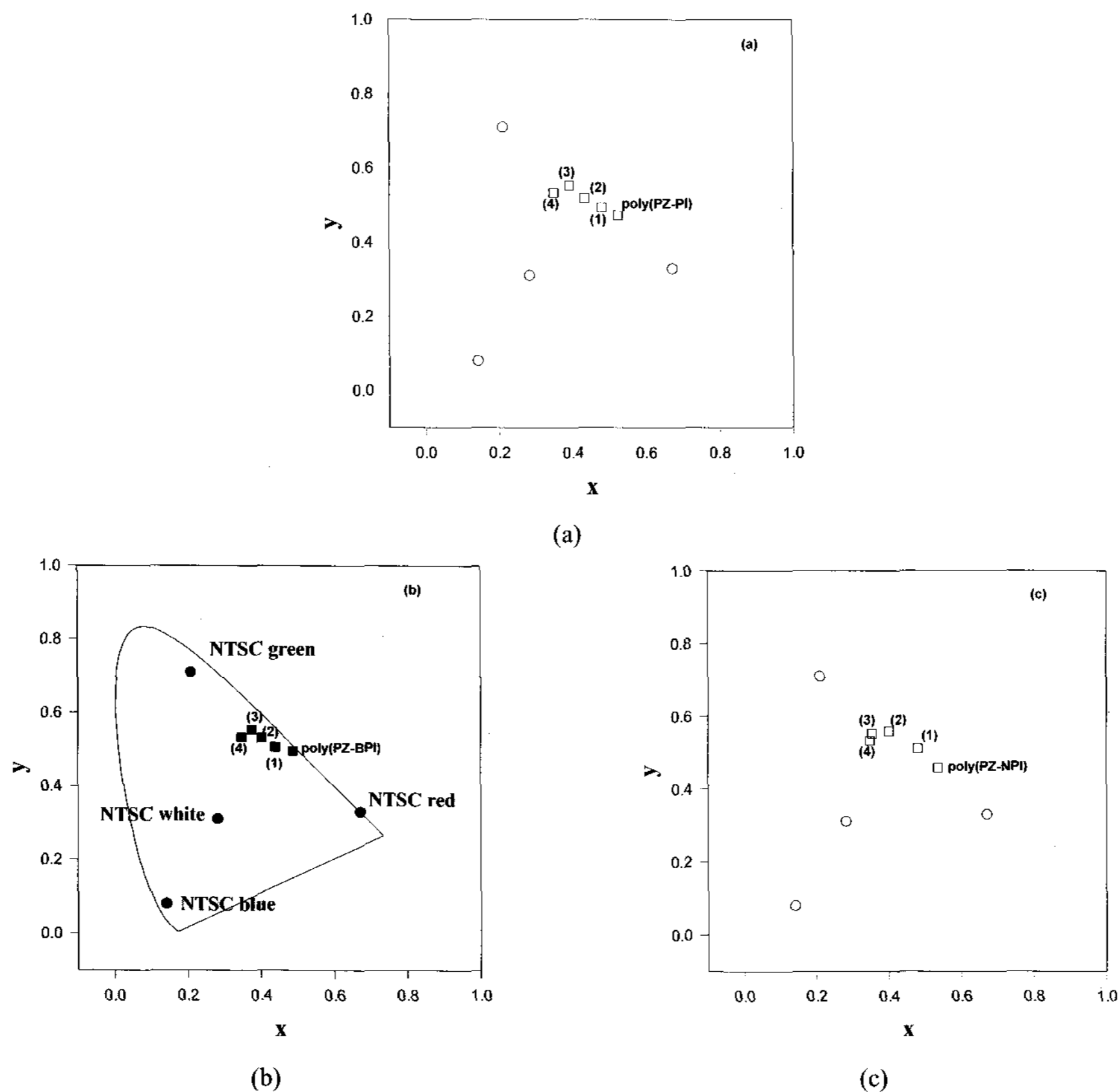


Fig. 6. Effect of thickness of Alq_3 layer in the CIE chromaticity diagram of LED's made with (a)poly(PZ-PI), (b)poly(PZ-BPI) and (c)poly(PZ-NPI) as emitting layer ; (1) Alq_3 100 Å, (2) Alq_3 200 Å, (3) Alq_3 400 Å, (4) single layer LED made with Alq_3 .

devices.[9]

EL emissions of double layer LED's with Alq_3 as electron transport layer to a different thickness are shown in the NTSC chromaticity diagram in Fig. 6.[10] As the thickness of Alq_3 layer increased, the emission color of double layer LEDs approached to that of single layer LEDs made with only Alq_3 as light emitting layer. This result indicates that recombinations of holes and electrons occur close to the Alq_3 layer as the thickness of Alq_3 layer was increased. Such a phenomenon is another evidence of the synthesized conjugated copolymers having a good hole transporting property.

4. Conclusions

Conjugated copolymers containing phenothiazine moiety and azomethine (-C=N-) linkage in the main chain could easily be synthesized by Schiff-base type reaction. The polymers exhibited good solubility in

common organic solvents due to the polar azomethine linkages. Double layer LED's made with the synthesized polymers as emitting layer and Alq_3 as electron transporting layer exhibited enhanced EL emission and efficiency compared to those of single layer LED's. As the thickness of the Alq_3 layer increased, the emission color of double layer LED's approached to that of single layer LED's made with only Alq_3 as emitting layer indicating that the synthesized copolymers have good hole transporting property.

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