

## ORIGINAL ARTICLE

# Synthesis and properties of *N*-substituted maleimides conjugated with 1,4-phenylene or 2,5-thienylene polymers

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$\pi$ -Conjugated polymers are particularly interesting in the field of electro-optic materials because of their desirable properties such as electrical conductivity, nonlinear optics and electroluminescence. Coupling polymerizations of 2,3-dibromo-*N*-substituted maleimide (DBrRMI) (*R*=benzyl, phenyl, cyclohexyl, *n*-hexyl and *n*-dodecyl) were carried out using palladium or nickel catalysts. The number-average molecular weights of poly(RMI-*alt*-Ph) obtained by Suzuki–Miyaura cross-coupling polymerizations of DBrRMI with benzene-1,4-boronic acid or 2,5-thiophene diboronic acid were 680–1270 by gel permeation chromatographic analyses. By contrast, Yamamoto coupling polymerizations of DBrRMI with diiodobenzene gave random poly(RMI-*co*-Ph) results. Poly(RMI-*co*-Ph)s exhibited a higher thermal stability than monomer and poly(RMI-*alt*-Ph). Copolymers showed strong photoluminescence from yellow to light blue colors in tetrahydrofuran.

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**Keywords:** conjugated polymer; coupling polymerization; fluorescence emission; *N*-substituted maleimide; thermal stability

## INTRODUCTION

Conjugated polymers have been of interest in the field of organic optoelectronic materials for products such as polymeric light-emitting diodes.<sup>1–5</sup> Many synthetic methods, including transition metal-catalyzed polymerization, have been reported and applied to the preparation of  $\pi$ -conjugated polymers. The Suzuki–Miyaura cross-coupling of boronic acid derivatives with halide compounds by palladium catalyst and Yamamoto coupling reaction of aryl halide compounds using bis(1,5-cyclooctadiene)nickel (Ni(COD)<sub>2</sub>) as zerovalent nickel complexes have been widely used because of relatively high yields and mild reaction temperatures.<sup>6–13</sup>

*N*-Substituted maleimide derivatives (RMIs) and their polymers have been known to exhibit excellent thermal stability and electron-withdrawing properties based on a rigid five-membered ring in the backbone. In addition, cyclic imide derivatives and their polymers have been reported for *n*-type organic semiconducting materials as organic transistors.<sup>14–19</sup> Although Liu and Chen<sup>7</sup> reported that 3,4-diphenylmaleimide copolymers exhibit orange to red photoluminescence and electroluminescence, the monomer was difficult to synthesize.<sup>7</sup> We expect that  $\pi$ -conjugated poly(RMI) derivatives will show electron-deficient heterocyclic arenes such as polyphthalimide and polynaphthalimide and that their  $\pi$ -conjugated states can be controlled to *N*-substituent on maleimide rings and comonomer units such as phenylene and thienylene. 2,3-Dibromo-*N*-substituted

maleimide (DBrRMI) derivatives were easily synthesized in two steps from known RMIs.<sup>20</sup> The authors have systematically investigated the synthesis and polymerizations of various RMIs.<sup>21–43</sup>

In this paper, we describe the alternating and random copolymerizations of DBrRMIs (*R*=benzyl, phenyl, cyclohexyl, *n*-hexyl and *n*-dodecyl) with dibromo or diboronic acid derivatives and the thermal and fluorescence emission properties of their  $\pi$ -conjugated polymers.

## EXPERIMENTAL PROCEDURE

### Measurements

<sup>1</sup>H (270 MHz) and <sup>13</sup>C (68 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a JEOL-EX270 spectrometer (JEOL, Tokyo, Japan) using tetramethylsilane (TMS) (<sup>1</sup>H NMR,  $\delta$  0.00) or CDCl<sub>3</sub> (<sup>13</sup>C NMR,  $\delta$  77.0) as internal reference peaks at room temperature. Splitting patterns were designated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet) or *br* (broad). Infrared (IR) spectra were recorded on an FT-IR Jasco 4100 spectrophotometer (JASCO, Tokyo, Japan). Melting points (m.p.) were determined on a YANAGIMOTO micromelting point apparatus (YANAGIMOTO, Kyoto, Japan). Gel permeation chromatographic analyses were carried out on an LC-10AS and CHROMATOPAC C-R7A plus (Shimadzu Corporation, Kyoto, Japan), using HSG-40H, HSG-20H, HSG-15H and HSG-10H columns (tetrahydrofuran (THF) as an eluent, flow rate of 1.0 ml min<sup>-1</sup>, 50 °C) and equipped with an ultraviolet (UV) detector SPD-10A (Shimadzu Corporation), on the basis of standard polystyrene samples. Thermogravimetric analyses were carried

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out using an MS-Tg/DTA220 (JEOL) at a scanning rate of 10 °C min<sup>-1</sup> under nitrogen (100 ml min<sup>-1</sup>). Elemental analyses were carried out on MICRO CORDER JM10 (J-SCIENCE, Kyoto, Japan).

## Materials

All chemicals were used without any further purification. Tetrakis-(triphenylphosphine)palladium(0), 2-thiopheneboronic acid and 1,5-cyclooctadiene were purchased from TCI (Tokyo, Japan). *N*-Benzyl-2,3-dibromomaleimide and benzene-1,4-diboronic acid were purchased from Aldrich (St Louis, MO, USA). Maleic anhydride, dodecylamine, 2,5-thiophendiboronic acid and 2,5-dibromothiophene were purchased from Wako Pure Chemical Industries (Osaka, Japan). *n*-Hexylamine, potassium carbonate and 2,2'-bipyridyl ( $\alpha,\alpha'$ -) were purchased from KISHIDA REAGENTS CHEMICALS (Osaka, Japan). Hexamethyldisilazane was purchased from Azmax (Chiba, Japan) and 1,4-diiodobenzene was purchased from MERCK (Gibbstown, NJ, USA). Bromine, triethylamine and anhydrous magnesium sulfate were purchased from NAKALAI TESQUE (Kyoto, Japan). Bis(1,5-cyclooctadiene) nickel (0), phenylboronic acid, 4-biphenylboronic acid, zinc chloride and sodium sulfate were purchased from Kanto Chemical (Tokyo, Japan). *n*-Hexane, ethyl acetate, THF, *N,N*-dimethylformamide, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were dried according to standard procedure and distilled under nitrogen.

Analytical thin-layer chromatography was performed on the Merck silica gel plate 60F<sub>254</sub>. Column chromatography was performed with silica gel 60 (0.063–0.200 mm, MERCK).

RMI was prepared from maleic anhydride and the corresponding primary amine by usual methods.<sup>44,45</sup> Compounds of DBrRMI were prepared following published procedures.<sup>20</sup>

## Synthesis of monomer

***N*-Phenyl-2-bromomaleimide.** This compound is a pale yellow solid, according to literature.<sup>20</sup>

Mp 150–152 °C (lit. 150–153 °C);<sup>20</sup> <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 7.03 (1H, s, HC=CBr), 7.32–7.50 (5H, m, Ph).

***N*-Phenyl-2,3-dibromomaleimide.** This compound is a pale yellow solid, according to literature.<sup>20</sup>

Mp 146–148 °C (lit. 160–166 °C);<sup>20</sup> <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 7.32–7.52 (5H, m, Ph).

***N*-Cyclohexyl-2-bromomaleimide.** *N*-Cyclohexyl-2-bromomaleimide

(BrCHMI) (5.58 g, 21.6 mmol) was obtained as a colorless solid at a 96% yield from CHMI (4.02 g, 22.5 mmol) with bromine (2.0 ml, 32.7 mmol), according to the procedure describing BrPhMI.

R<sub>F</sub> 0.25 (*n*-hexane/ethyl acetate 20/1 v/v); m.p. 108–110 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 1.15–1.41 (3H, m, cyclohexyl), 1.66–1.70 (3H, m, cyclohexyl), 1.83–1.99 (2H, m, cyclohexyl), 1.98–2.11 (2H, m, cyclohexyl), 3.90–4.02 (1H, m, -CH-), 6.81 (1H, s, HC=CBr).

***N*-Cyclohexyl-2,3-dibromomaleimide.** *N*-Cyclohexyl-2,3-dibromomaleimide (2.20 g, 6.53 mmol) was obtained as a colorless solid at a 94% yield from BrCHMI (1.78 g, 6.89 mmol) with bromine (0.70 ml, 11.5 mmol), according to the procedure describing DBrPhMI.

R<sub>F</sub> 0.49 (*n*-hexane/ethyl acetate 20/1 v/v); m.p. 152–154 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 1.40–1.57 (3H, m, cyclohexyl), 1.88–1.93 (3H, m, cyclohexyl), 2.04–2.09 (2H, m, cyclohexyl), 2.23–2.27 (2H, m, cyclohexyl), 4.16–4.27 (1H, m, -CH-).

Anal. Calcd. for C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub>Br<sub>2</sub>: C, 35.64; H, 3.29; N, 4.16. Found: C, 35.23; H, 3.03; N, 4.07.

RMI was synthesized from maleic anhydride and primary amine according to a method reported previously.<sup>44,45</sup>

***N*-Hexylmaleamic acid.** A solution of *n*-hexylamine (4.37 g, 43.2 mmol) in dry ethyl acetate (80 ml) was added dropwise to a solution of maleic anhydride (5.08 g, 51.8 mmol) in dry ethyl acetate (50 ml) at 0 °C, and then the mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure to obtain *N*-*n*-hexylmaleamic acid (10.3 g, 51.7 mmol, quant.) as a colorless solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.89 (3H, t, *J*=6.7 Hz, -CH<sub>3</sub>), 1.23–1.40 (6H, m, hexyl), 1.55–1.65 (2H, m, hexyl), 3.34–3.41 (2H, m, -CH<sub>2</sub>-), 6.32 (1H, d, *J*=12.8 Hz, HC=CH), 6.40 (1H, d, *J*=12.8 Hz, HC=CH), 7.42 (1H, s, -NH-).

***N*-*n*-Hexylmaleimide.** *N*-*n*-Hexylmaleamic acid (10.3 g, 51.7 mmol) in dry benzene (250 ml) was heated to 65 °C, and then ZnCl<sub>2</sub> (7.03 g, 51.7 mmol) was added in one portion. The mixture was heated to 90 °C. 1,1,1,3,3,3-Hexamethyldisilazane (21.8 ml) was slowly added dropwise to the suspension with vigorous stirring. The reaction mixture was refluxed for 10 h. The solution was cooled to room temperature, and the precipitated solid was filtered. The residue was washed with methanol, and the resulting filtrate was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (100 ml), and then the organic layer was washed with 2*N* HCl (50 ml×2), distilled water (50 ml×2) and saturated NaCl<sub>aq</sub> (50 ml×3), and was dried over anhydrous magnesium sulfate. The organic solution was concentrated using an evaporator under reduced pressure. Crude *N*-*n*-hexylmaleimide (*n*-HMI) was purified by column chromatography on silica gel using (*n*-hexane/ethyl acetate 8/1 (v/v; R<sub>F</sub> 0.21)) to afford *n*-HMI (8.54 g 47.1 mmol, 91 %) as a pale yellow solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.86 (3H, t, *J*=6.6 Hz, -CH<sub>3</sub>), 1.23–1.29 (6H, m, hexyl), 1.55–1.60 (2H, m, hexyl), 3.51 (2H, t, *J*=7.3 Hz, -CH<sub>2</sub>-), 6.69 (2H, s, HC=CH).

***N*-*n*-Hexyl-2-bromomaleimide.** *N*-*n*-Hexyl-2-bromomaleimide (4.83 g, 18.6 mmol) was obtained as a pale yellow oil at an 83% yield from *n*-HMI (4.07 g, 22.5 mmol) with bromine (2.0 ml, 32.7 mmol), according to the procedure describing BrPhMI.

R<sub>F</sub> 0.22 (*n*-hexane/ethyl acetate 20/1 v/v); <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.88 (3H, t, *J*=6.6 Hz, -CH<sub>3</sub>), 1.25–1.29 (6H, m, hexyl), 1.56–1.61 (2H, m, hexyl), 3.55 (2H, t, *J*=7.3 Hz, -CH<sub>2</sub>-), 6.86 (1H, s, HC=CBr).

***N*-*n*-Hexyl-2,3-dibromomaleimide.** *N*-*n*-Hexyl-2,3-dibromomaleimide (0.88 g, 2.60 mmol) was obtained as a pale yellow solid at an 85% yield from *N*-*n*-hexyl-2-bromomaleimide (0.79 g, 2.94 mmol) with bromine (0.30 ml, 4.91 mmol), according to the procedure describing DBrPhMI.

R<sub>F</sub> 0.36 (*n*-hexane/ethyl acetate 20/1 v/v); m.p. 32–33 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.88 (3H, t, *J*=6.6 Hz, -CH<sub>3</sub>), 1.26–1.30 (6H, m, hexyl), 1.58–1.63 (2H, m, hexyl), 3.56 (2H, t, *J*=7.3 Hz, -CH<sub>2</sub>-).

Anal. Calcd. for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub>Br<sub>2</sub>: C, 35.43; H, 3.86; N, 4.13. Found: C, 35.19; H, 3.77; N, 4.20.

***N*-*n*-Dodecylmaleamic acid.** *N*-*n*-Dodecylmaleamic acid (12.8 g, 45.0 mmol) was obtained as a colorless solid at an 87% yield from *n*-dodecylamine (8.01 g, 43.2 mmol) with maleic anhydride (5.09 g, 51.8 mmol), according to the procedure describing *N*-*n*-hexylmaleamic acid.

M.p. 85–86 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.88 (3H, t, *J*=6.6 Hz, -CH<sub>3</sub>), 1.26–1.31 (18H, m, dodecyl), 1.57–1.60 (2H, m, dodecyl), 3.40–3.48 (2H, m, -CH<sub>2</sub>-), 6.26 (1H, d, *J*=12.8 Hz, HC=CH), 6.43 (1H, d, *J*=12.8 Hz, HC=CH), 6.70 (1H, s, -NH-).

***N*-*n*-Dodecylmaleimide.** *N*-*n*-Dodecylmaleimide (10.5 g, 39.6 mmol) was obtained as a colorless solid at an 88% yield from *N*-*n*-dodecylmaleamic acid (12.8 g, 45.0 mmol), according to the procedure describing *n*-HMI.

R<sub>F</sub> 0.50 (*n*-hexane/ethyl acetate 5/1 v/v); m.p. 52–53 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.88 (3H, t, *J*=6.7 Hz, -CH<sub>3</sub>), 1.25–1.29 (18H, m, dodecyl), 1.55–1.60 (2H, m, dodecyl), 3.50 (2H, t, *J*=7.3 Hz, -CH<sub>2</sub>-), 6.68 (2H, s, HC=CH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 14.07, 22.63, 26.69, 28.50, 29.29, 29.56, 31.86, 37.88, 133.97, 170.83.

***N*-*n*-Dodecyl-2-bromomaleimide.** *N*-*n*-Dodecyl-2-bromomaleimide (BrDMI) (5.45 g, 15.8 mmol) was obtained as a pale yellow solid at 71% yield from *N*-*n*-dodecylmaleimide (5.96 g, 22.5 mmol) with bromine (2.0 ml, 32.7 mmol), according to the procedure describing BrPhMI.

R<sub>F</sub> 0.30 (*n*-hexane/ethyl acetate 20/1 v/v); m.p. 45–47 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 0.88 (3H, t, *J*=6.5 Hz, -CH<sub>3</sub>), 1.23–1.29 (18H, m, dodecyl), 1.55–1.61 (2H, m, dodecyl), 3.55 (2H, t, *J*=7.3 Hz, -CH<sub>2</sub>-), 6.85 (1H, s, HC=CBr); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 14.09, 22.64, 26.62, 28.41, 29.04, 29.29, 29.41, 29.49, 29.56, 31.86, 38.87, 131.23, 131.70, 165.32, 168.60.

***N*-*n*-Dodecyl-2,3-dibromomaleimide.** DBrDMI (1.21 g, 2.86 mmol) was obtained as a pale yellow solid at a 97% yield from BrDMI (1.02 g, 2.94 mmol) with bromine (0.30 ml, 4.91 mmol), according to the procedure describing DBrPhMI.

$R_F$  0.44 (*n*-hexane/ethyl acetate 20/1 v/v); m.p. 47–47 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 0.88 (3H, t,  $J=6.6$  Hz,  $-\text{CH}_3$ ), 1.23–1.29 (18H, m, dodecyl), 1.57–1.63 (2H, m, dodecyl), 3.60 (2H, t,  $J=7.3$  Hz,  $-\text{CH}_2-$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm from TMS): 14.10, 22.65, 26.57, 28.39, 29.02, 29.30, 29.38, 29.50, 29.56, 31.87, 39.78, 129.24, 163.91.

Anal. Calcd. for  $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{Br}_2$ : C, 45.41; H, 5.95; N, 3.31. Found: C, 45.06; H, 5.67; N, 3.29.

### Polymerization

All moisture-sensitive synthetic manipulations were carried out under an inert nitrogen atmosphere using Schlenk glass tubes.

**Suzuki–Miyaura cross-coupling of DBrRMI with boronic acid derivatives by palladium catalyst.**<sup>10</sup> Schlenk reaction tubes were used to contain mixtures of DBrRMI (1.00 mmol), benzene-1,4-diboronic acid or 2,5-thiophenediboronic acid (1.00 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.010 mmol), toluene (5 ml) and aqueous potassium carbonate (2 M, 5 ml) under nitrogen atmosphere. The mixture was vigorously stirred at 90 °C for several polymerization times. After cooling to room temperature, the mixture was distilled with  $\text{CH}_2\text{Cl}_2$  (30 ml) and then washed with  $\text{H}_2\text{O}$  (30 ml). After drying over anhydrous sodium sulfate, the filtrate was concentrated *in vacuo*. The residue distilled with THF (0.5 ml) was slowly added dropwise into a large amount of *n*-hexane (100 ml). The precipitated polymer was separated by suction filtration, washed with *n*-hexane and dried. Purification of the polymer was performed with reprecipitation from a THF-*n*-hexane system three times and drying under vacuum at room temperature for 2 days.

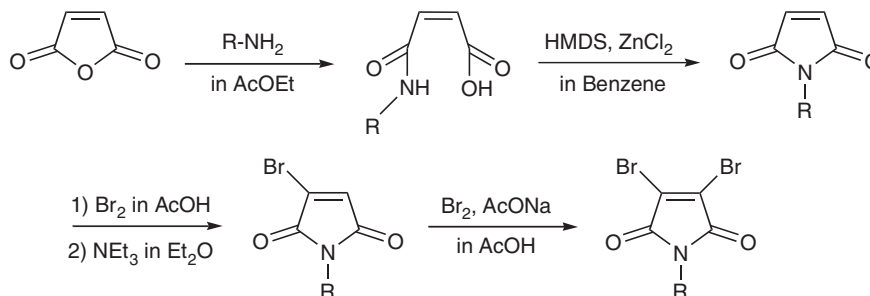
**Yamamoto coupling reaction of DBrRMI with aryl halide compounds using bis(1,5-cyclooctadiene)nickel ( $\text{Ni}(\text{COD})_2$ ).**<sup>9</sup> Schlenk reaction tubes were used

to contain mixtures of DBrRMI (0.40 mmol), 1,5-cyclooctadiene (0.90 mmol), 2,2'-bipyridyl (0.90 mmol) and 1,4-diiodobenzene or 2,5-dibromothiophene (0.40 mmol). The mixture was supplemented with  $\text{Ni}(\text{COD})_2$  (1.2 mmol), toluene (3 ml) and *N,N*-dimethylformamide (3 ml), and then replaced with  $\text{N}_2$ . It was stirred at 80 °C for several polymerization times, then poured into 5% acidic methanol (with HCl) and the appearing precipitates were collected by filtration. Precipitates were washed with 5% acidic methanol (with HCl) and an  $\text{H}_2\text{O}$ -acetone mixture) and then were dried under vacuum. The polymer distilled with THF (0.5 ml) was slowly added dropwise into a large amount of methanol (100 ml). Purification of the polymer was performed with reprecipitation from a THF-methanol system three times and drying under vacuum at room temperature for 2 days.

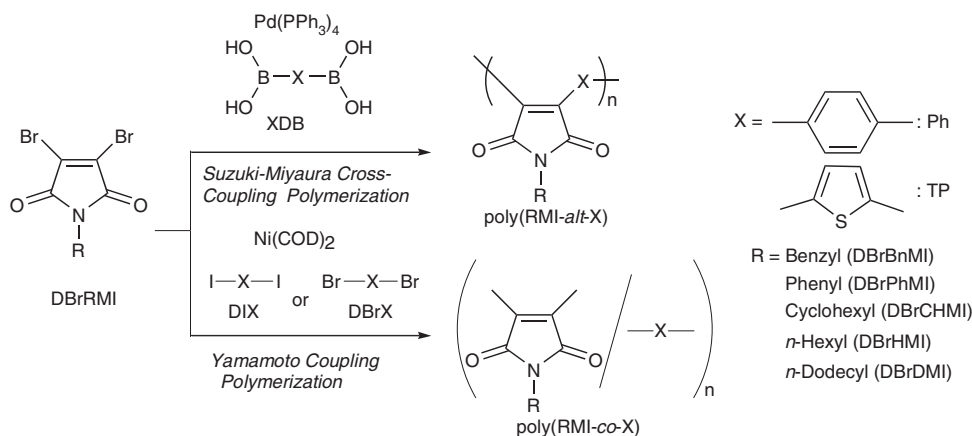
## RESULTS AND DISCUSSION

### Synthesis and characterization

**Suzuki–Miyaura cross-coupling polymerization of DBrRMI with benzene-1,4-diboronic acid or thiophene-2,5-diboronic acid.** The key five *N*-substituted 2,3-dibromomaleimide monomers (DBrRMI) were prepared in two steps from *N*-substituted maleimide and bromine according to the procedure described in the study by Adams *et al.* (Scheme 1).<sup>20</sup> Palladium(0)-catalyzed carbon–carbon coupling reactions with alkenyl dihalide and diboronic acid derivatives, known as the Suzuki–Miyaura cross-coupling reaction, were used to afford alternating copolymers consisting of RMI and 1,4-phenylene or 2,5-thiophenylene moieties (Scheme 2). The results of the cross-coupling polymerizations of DBrRMI with benzene-1,4-diboronic acid or 2,5-thiophene diboronic acid at 90 °C using  $\text{Pd}(\text{Ph}_3)_4$  as catalyst are summarized in Table 1. The polymerizations of maleimide monomers having benzyl, phenyl and cyclohexyl groups as an *N*-substituent on the maleimide ring were of low yield (runs 1–5). The polymerization of DBrPhMI with benzene-1,4-diboronic acid furnished THF-soluble



**Scheme 1** Synthesis of 2,3-dibromo-*N*-substituted maleimide.



**Scheme 2** Coupling polymerizations of 2,3-dibromo-*N*-substituted maleimide.

**Table 1** Suzuki–Miyaura cross-coupling polymerizations of DBrMI with benzene-1,4-diboric acid (PhDB)<sup>a</sup>

Run	R	Time (h)	Yield <sup>b</sup> (%)	$M_n^c \times 10^{-3}$	$M_w/M_n^c$
1		24	22.7	0.77 (1.01, 0.53)	1.20 (1.12, 1.01)
2	Bn	48	37.0	0.91	1.31
3		72	22.1	0.82 (1.26, 0.55)	1.07 (1.13, 1.05)
4	Ph	48	11.1 <sup>d</sup> /41.9 <sup>e</sup>	0.68 (0.86, 0.45)	1.20 (1.11, 1.02)
5	CH	48	17.0	0.95	1.41
6	H	48	Quant <sup>f</sup>	0.92	1.17
7	D	48	90.0 <sup>f</sup>	1.27	1.34

<sup>a</sup>DBrMI, 1.0 mmol; PhDB, 1.0 mmol; conditions: temperature, 90 °C; solvents, toluene and K<sub>2</sub>CO<sub>3</sub> aq.

<sup>b</sup>*n*-Hexane insoluble part.

<sup>c</sup>By gel permeation chromatography with poly(styrene) standard.

<sup>d</sup>Tetrahydrofuran (THF) soluble part.

<sup>e</sup>THF insoluble part.

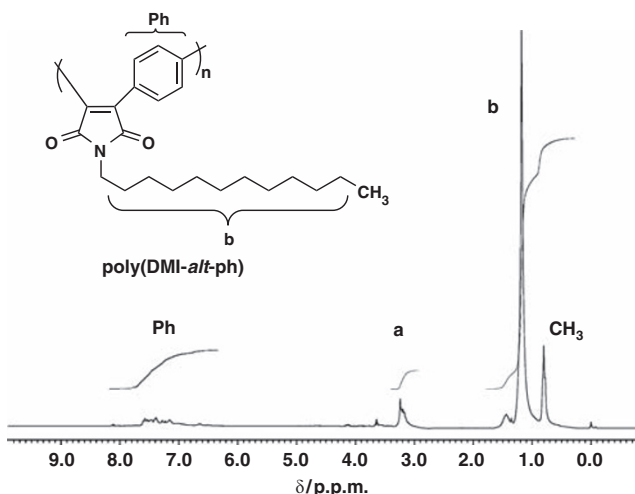
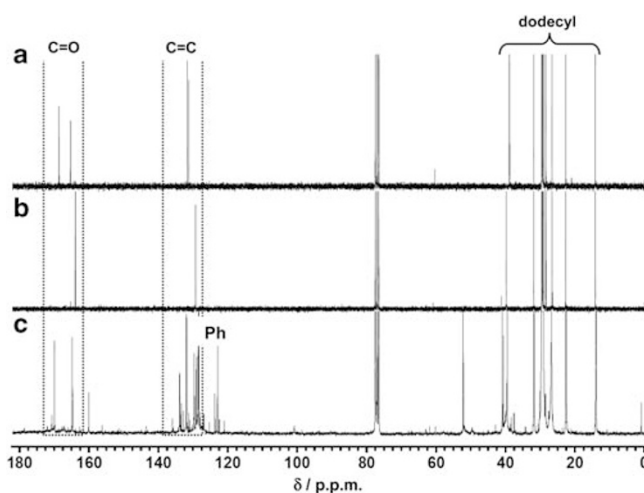
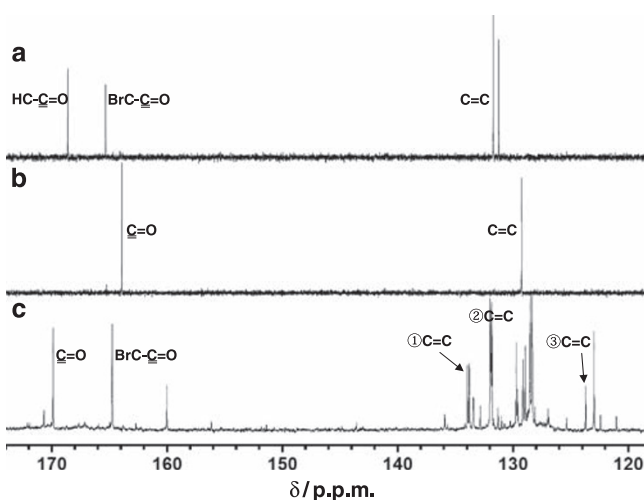
<sup>f</sup>*n*-Hexane soluble part.

and THF-insoluble polymers at 11.1 and 41.9% yields, respectively. Polymers obtained from *N*-*n*-hexyl-2,3-dibromomaleimide or DBrDMI were dissolved in *n*-hexane. The number-average molecular weights ( $M_n$ ) of poly(RMI-*alt*-Ph) obtained with benzene-1,4-boronic acid were 680–1270 (PD; 3–4 mer) by gel permeation chromatography analyses using a polystyrene standard. Gel permeation chromatography chromatographs in the range of the low-molecular-weight part showed a shoulder curve (runs 1, 3 and 4 in Table 1). The Suzuki–Miyaura cross-coupling polymerizations proceeded in a biphasic solvent (toluene–aqueous K<sub>2</sub>CO<sub>3</sub>). Polymers were precipitated from the biphasic solutions because of the low solubility of substituents such as the benzyl and phenyl groups. For these reasons, the polymers obtained by the Suzuki–Miyaura cross-coupling polymerizations exhibited low yields and  $M_n$ .

Figure 1 shows a representative <sup>1</sup>H NMR spectrum of poly(DMI-*alt*-Ph) in CDCl<sub>3</sub>. The signals at 0.7–1.6 and 3.2 p.p.m. are assigned to protons on the *n*-dodecyl substituent chains. The peaks that appear at 6.9–7.6 p.p.m. are due to phenylene protons. The numbers of aliphatic and aromatic protons estimated from peak integration are in good agreement with the molecular structures of the alternating copolymers.

Figures 2 and 3 show <sup>13</sup>C NMR spectra of BrDMI (a), DBrDMI (b) and poly(DMI-*alt*-Ph) (c), as well as expanded spectra between 120 and 175 p.p.m. The peaks due to the C=C double bond at BrDMI appear at 131.23 and 131.70 p.p.m. A single peak of DBrDMI appears at 129.24 p.p.m. Carbon peaks due to the main chain of poly(DMI-*alt*-Ph) are found at 134 and 132 p.p.m. The peak at 134 p.p.m. is based on the C=C bond at the maleimide ring, formed by the carbon–carbon coupling reaction. The peak at 132 p.p.m. is due to C=C–Br at the terminal maleimide groups. The peak at 124 p.p.m. is assigned to C=C–H at the terminal polymer. According to the <sup>13</sup>C NMR spectra of *N*-methyl-2-phenylmaleimide as model compounds,<sup>46</sup> the peak at 124 p.p.m. is assigned to C=C with a substitution of a bromine atom for a hydrogen atom. By contrast, BrDMI exhibits peaks due to C=O at around 165.32 and 168.60 p.p.m., and DBrDMI exhibits peaks due to C=O at around 163.91 p.p.m. The peaks at 165 and 170 p.p.m. are assigned to C=O having bromine at the terminal polymer and C=O-bonded phenyl groups at the 2,3-positions of the maleimide, respectively.

Polymerizations of DBrMI with thiophene-2,5-diboronic acid proceeded in a manner similar to poly(RMI-*alt*-Ph) at a low yield, as shown in Table 2. Poly(DMI-*alt*-TP)s were completely soluble in


**Figure 1** <sup>1</sup>H NMR spectrum of poly(DMI-*alt*-Ph) (run 7 in Table 1) ( $R=C_{12}H_{25}$ ) in CDCl<sub>3</sub>.

**Figure 2** <sup>13</sup>C NMR spectra of (a) BrDMI, (b) DBrDMI and (c) poly(DMI-*alt*-Ph) (run 7 in Table 1) ( $R=C_{12}H_{25}$ ) in CDCl<sub>3</sub>.

**Figure 3** Expanded <sup>13</sup>C NMR spectra of (a) BrDMI, (b) DBrDMI and (c) poly(DMI-*alt*-Ph) (run 7 in Table 1) ( $R=C_{12}H_{25}$ ) at 120–175 p.p.m. in CDCl<sub>3</sub>.



**Table 2** Suzuki–Miyaura cross-coupling polymerizations of DBrRMI with 2,5-thiophendiboronic acid (TPDB)<sup>a</sup>

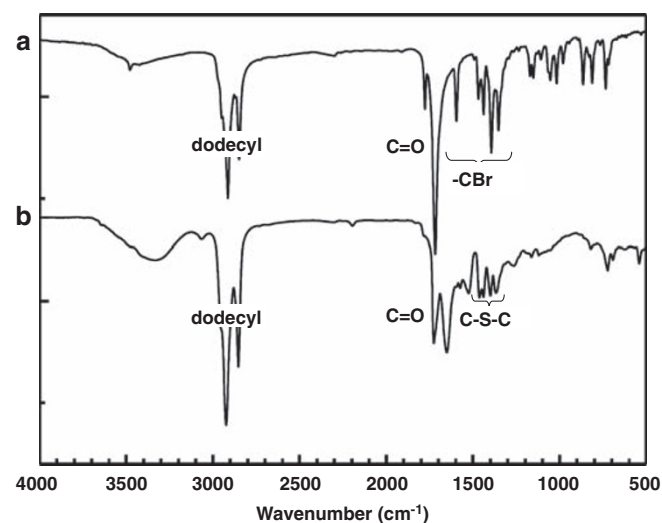
Run	R	Time (h)	Yield (%) <sup>b</sup>	$M_n^c \times 10^{-3}$	$M_w/M_n^c$
1	Bn	48	21.4	0.82 (1.13, 0.57)	1.22 (1.12, 1.02)
2	Ph	48	9.8	0.71 (1.22, 0.74)	1.29 (1.03, 1.02)
3	CH	48	6.7	0.98 (1.38, 0.61)	1.36 (1.21, 1.03)
4	H	48	68.5 <sup>d</sup>	0.87 (1.33, 0.47)	1.58 (1.31, 1.01)
5	D	48	79.2 <sup>d</sup>	1.46 (2.29, 0.80)	1.60 (1.31, 1.02)

<sup>a</sup>DBrRMI, 1.0 mmol; TPDB, 1.0 mmol; conditions: temperature, 90 °C; solvents, toluene and K<sub>2</sub>CO<sub>3</sub> aq.

<sup>b</sup>*n*-Hexane insoluble part.

<sup>c</sup>By gel permeation chromatographic analysis with poly(styrene) standard.

<sup>d</sup>*n*-Hexane soluble part.

**Figure 4** IR spectra of (a) DBrDMI and (b) poly(DMI-*alt*-TP) (run 5 in Table 2).**Table 3** Yamamoto coupling polymerizations of DBrRMI with 1,4-diiodobenzene (DIPh)<sup>a</sup>

Run	R	Time (h)	Yield (%) <sup>b</sup>	$M_n^c \times 10^{-3}$	$M_w/M_n^c$	RMI:Ph in copolymer (mol ratio) <sup>d</sup>
1	Bn	48	52.3	1.27 (1.93, 0.65)	1.57 (1.28, 1.02)	Not determined
2	Ph	48	86.3	1.34 (1.68, 0.64)	1.45 (1.29, 1.01)	Not determined
3	CH	48	55.3	1.46 (1.97, 0.66)	1.58 (1.35, 1.01)	Not determined
4	H	48	97.0	2.28	1.51	35:65
5	D	48	75.9	2.89	1.52	35:65

<sup>a</sup>DBrRMI, 0.40 mmol; DIPh, 0.40 mmol; conditions: temperature, 80 °C; solvents, toluene and *N,N*-dimethylformamide.

<sup>b</sup>MeOH insoluble part.

<sup>c</sup>By gel permeation chromatographic analysis with poly(styrene) standard.

<sup>d</sup>Calculated by <sup>1</sup>H nuclear magnetic resonance.

methanol. The polymers were isolated by reprecipitation at THF-*n*-hexane, and then they were filtered off to obtain the *n*-hexane-insoluble part (runs 1–3). However, the polymers (of runs 4 and 5) were completely soluble in *n*-hexane, because of a longer alkyl side chain than that shown in runs 1–3.  $M_n$ s were determined to be 710–1460 by gel permeation chromatography. As shown in Figure 4, the IR spectra of poly(DMI-*alt*-TP) show the characteristic imide group

**Table 4** Yamamoto coupling polymerizations of DBrRMI with 2,5-dibromothiophene (DBrTP)<sup>a</sup>

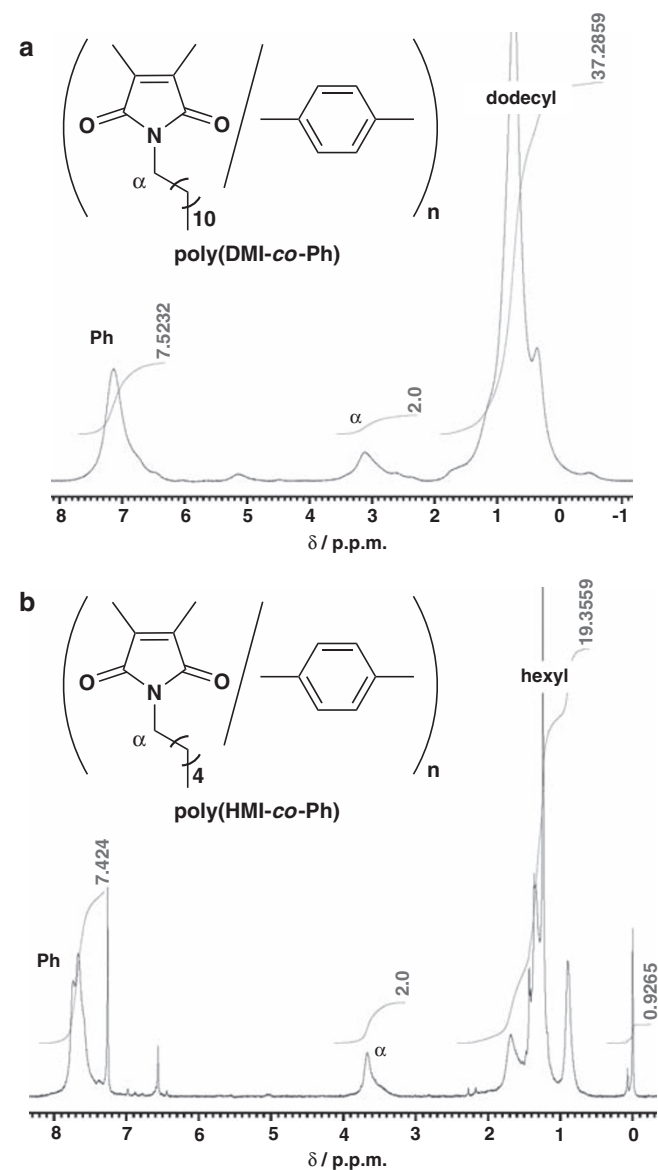
Run	R	Time (h)	Yield <sup>b</sup> (%)	$M_n^c \times 10^{-3}$	$M_w/M_n^c$	RMI:TP in copolymer (mol ratio) <sup>d</sup>
1	Bn	48	44.6	0.95	1.40	Not determined
2	Ph	48	48.6	1.02	1.24	Not determined
3	CH	48	57.2	1.32	1.78	Not determined
4	H	48	44.5	2.33	2.07	48:52
5	D	48	73.9	4.00	4.18	45:55

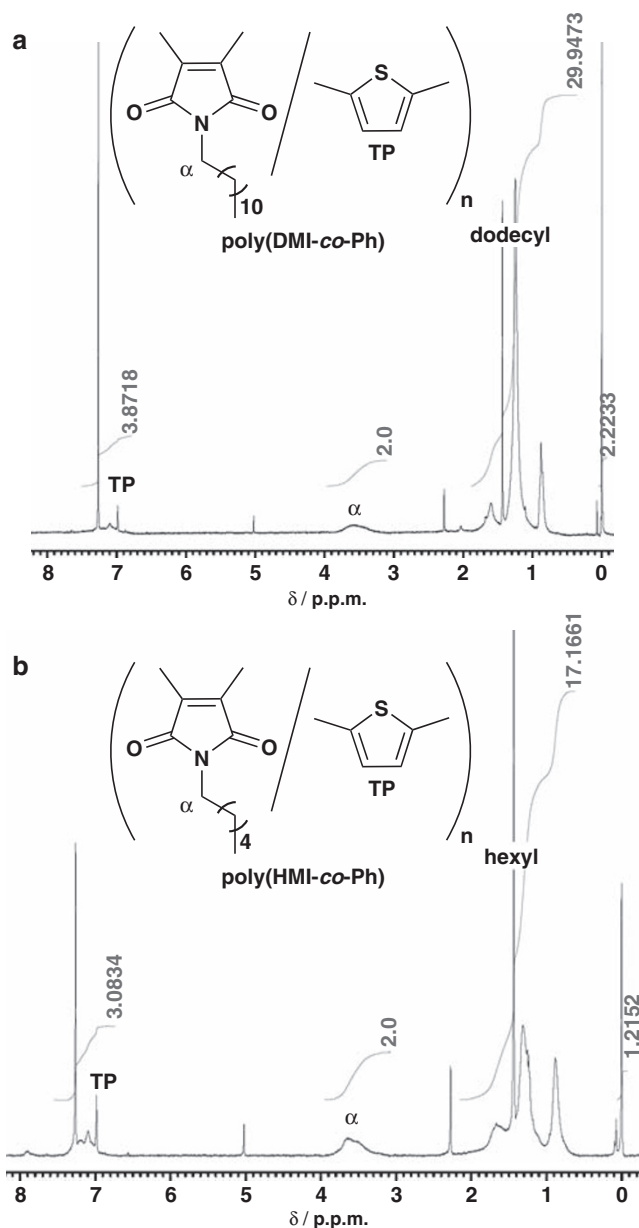
<sup>a</sup>DBrRMI, 0.40 mmol; DBrTP, 0.40 mmol; conditions: temperature, 80 °C; solvents, toluene and *N,N*-dimethylformamide.

<sup>b</sup>MeOH insoluble part.

<sup>c</sup>By gel permeation chromatographic analysis with poly(styrene) standard.

<sup>d</sup>Calculated by <sup>1</sup>H nuclear magnetic resonance.

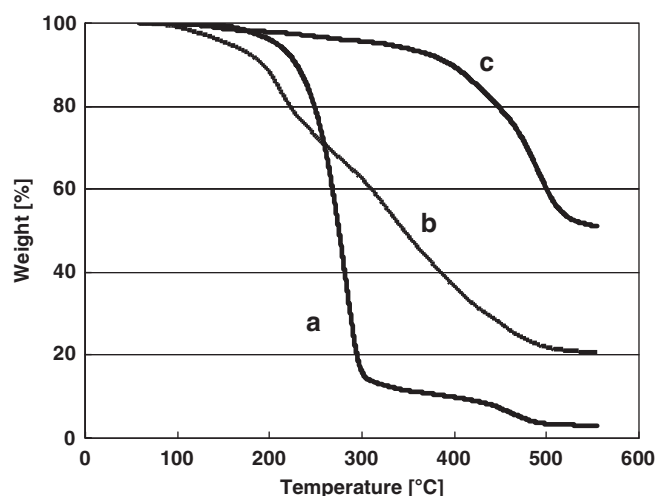
**Figure 5** <sup>1</sup>H NMR spectra of (a) poly(DMI-*co*-Ph) (run 5 in Table 3) and (b) poly(HMI-*co*-Ph) (run 4 in Table 3) in CDCl<sub>3</sub>.



**Figure 6** <sup>1</sup>H NMR spectra of (a) poly(DMI-co-TP) (run 5 in Table 4) and (b) poly(HMI-co-TP) (run 4 in Table 4) in CDCl<sub>3</sub>.

vibration band of C=O at 1730 cm<sup>-1</sup>, which is similar to that of DBrDMI. The characteristic stretching band of C-Br at 1350–1600 cm<sup>-1</sup>, shown in Figure 4a, is diminished in the spectrum of poly(DMI-*alt*-TP). The C-S-C absorption bands in thiophene at 1360–1460 cm<sup>-1</sup> appear in poly(DMI-*alt*-TP). The results derived from IR and NMR spectra indicate that polymerization was successfully carried out.

*Yamamoto coupling polymerization of DBrRMI with 1,4-diiodobenzene or 2,5-dibromothiophene.* We prepared random copolymers consisting of RMI and 1,4-phenylene or 2,5-thiophenylene segments by the Yamamoto coupling reaction using Ni(COD)<sub>2</sub> and 2,2'-bipyridyl as catalyst. As shown in Tables 3 and 4, poly(RMI-co-Ph)s have *M<sub>n</sub>* values of 1270–2890 with polydispersity indices (*M<sub>w</sub>*/*M<sub>n</sub>*) of 1.45–1.58. The <sup>1</sup>H NMR spectra of poly(DMI-co-Ph) and poly(HMI-co-Ph)



**Figure 7** Thermogravimetric curves of (a) DBrDMI, (b) poly(DMI-*alt*-Ph) and (c) poly(DMI-co-Ph) at a heating rate of 10 °C min<sup>-1</sup> in nitrogen.

**Table 5** UV-visual absorption maxima and photoluminescence emission of copolymers<sup>a</sup>

R	poly(RMI- <i>alt</i> -Ph)		poly(RMI- <i>alt</i> -TP)		poly(RMI-co-Ph)		poly(RMI-co-TP)				
	<i>A<sub>max</sub></i> (nm)	<i>λ<sub>max</sub></i> (nm)	<i>A<sub>max</sub></i> (nm)	<i>λ<sub>max</sub></i> (nm)	<i>A<sub>max</sub></i> (nm)	<i>λ<sub>max</sub></i> (nm)	<i>A<sub>max</sub></i> (nm)	<i>λ<sub>max</sub></i> (nm)			
Bn	295.0	389.5	542	293.5	502	334.5	385.5	547	289.5	461.0	587.5
Ph	295.5	541	292.5	501	315.0	548	293.5	445.5	593.5		
CH	298.5	543	293.0	517	313.5	546	292.0	467.0	591.0		
H	291.5	354.5	507	295.5	483	337.5	407.0	546	291.0	455.5	589.5
D	293.5	503	295.0	483	307.0	388.5	546	291.0	458.0	590.0	

<sup>a</sup>0.5 mmol l<sup>-1</sup> in tetrahydrofuran.

are shown in Figure 5. Aliphatic methylene peaks (α) at the side chain appear between 2.39 and 3.70 p.p.m. Aromatic proton peaks at phenyl groups in the main chain, formed by the carbon–carbon coupling reaction, appear between 6.4 and 7.7 p.p.m. From the integration values of proton peaks (Figures 5 and 6), we could estimate that the ratios of RMI to 1,4-phenylene and 2,5-thiophenylene units are 35:65 and 45:55, respectively. In the same manner, the ratios of the RMI unit in copolymers were determined by <sup>1</sup>H NMR, and are shown in Tables 3 and 4.

### Thermal properties

Figure 7 indicates the thermogravimetric analyses thermograms of DBrDMI, poly(DMI-*alt*-Ph) and poly(DMI-co-Ph) as indicated. The temperatures at 10% weight loss of DBrDMI, poly(DMI-*alt*-Ph) and poly(DMI-co-Ph) are 229, 190 and 397 °C, respectively. The thermal stability of poly(DMI-co-Ph) was better than that of DBrDMI and poly(DMI-*alt*-Ph). The slight amount of weight loss in poly(DMI-*alt*-Ph) is probably attributed to the existence of low-molecular-weight oligomers. Poly(DMI-co-Ph) shows very good thermal stability up to ~400 °C under N<sub>2</sub> atmosphere. The thermal stability of poly(DMI-co-Ph) is better than that of the poly(phenylenevinylene) derivatives (ca. 300–350 °C)<sup>47–50</sup> and poly(biphenylenevinylene) derivatives (~300 °C)<sup>51,52</sup> reported by other groups. The results were

ascribed not only to the maleimide ring but also to an increase of the phenylene unit.

### UV absorption and PL properties

The UV-visual and fluorescence spectra of copolymers in the THF solution are summarized in Table 5. The polymers emitted strong fluorescence under UV irradiation. Poly(RMI-*alt*-Ph) and poly(RMI-*alt*-TP) displayed absorption maxima spectra at around 295 nm in the UV range, and these were assigned to the  $\pi$ - $\pi^*$  transition. However, poly(RMI-*co*-Ph) and poly(RMI-*co*-TP) showed slightly red-shifted absorption maxima spectra. This result was attributable to the elongation of the conjugated main chain. Alternating copolymers bearing bulky substituents such as a phenyl, benzyl or cyclohexyl group are observed in the photoluminescence spectra (542 nm). The maximum emission spectra ( $\lambda_{\text{max}}$ ) of alternating copolymers bearing linear substituents were blue-shifted about 35 nm relative to those of the alternating copolymers obtained with DBrRMI (R=Ph, Bn, CH). By contrast, the random copolymers had similar emission spectra. Judging from the results of absorption and emission spectra, the photophysical properties of copolymers are influenced by *N*-substituents, the kinds of comonomer units and monomer sequences.

### CONCLUSIONS

We have successfully prepared alternating and random copolymers containing RMI through Suzuki–Miyaura cross coupling and Yamamoto coupling polymerizations. The polymers showed high solubilities in common organic solvents. The polymers also exhibited good thermal stability, with 10% weight loss at temperatures above 400 °C. The alternating copolymers showed strong photoluminescence from yellow to light blue in THF.

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