

Preparation, Thermotropic Liquid-Crystalline and Fluorescent Properties of Semi-Rigid Homo- and Copoly(ester-imide)s Composed of 3,3'',4,4''-*p*-Terphenyltetracarboxdiimide and 3,3',4,4'-Biphenyltetracarboxdiimide

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(Received February 25, 2002; Accepted June 14, 2002)

ABSTRACT: Semi-rigid homo- and copoly(ester-imide)s were prepared from bismethyl ester of 3,3'',4,4''-*p*-terphenyltetracarboxdiimide and bisalcohols of 3,3',4,4'-biphenyltetracarboxdiimide by melt polycondensation and their thermotropic liquid-crystalline, photo- (PL) and electroluminescent (EL) properties were investigated. Differential scanning calorimetry (DSC) measurements, polarizing microscope observations of textures and powder X-Ray analyses suggested that homopolymer having hexamethylene chain form monotropic smectic C or A phase and most of copolymers enantiotropic nematic phase. PL spectra showed that the polymers emit blue light in the chloroform solutions and in the films. EL spectra of polymers in double-layer devices (ITO/poly(3,4-ethylene dioxathiophene) (PE DOT)/polymer/LiF or Ca/Al), with blue emission, were almost identical to the PL spectra, although luminances were very low. The poly(ester-imide)s can be used as blue light-emitting and/or electron-transporting materials for organic EL devices.

KEY WORDS Semi-Rigid Poly(ester-imide) / Photoluminescent Property / Electroluminescent Property / 3,3'',4,4''-*p*-Terphenyltetracarboxdiimide / 3,3',4,4'-Biphenyltetracarboxdiimide / Powder X-Ray Analysis / Monotropic Smectic Phase / Blue Emission /

Semi-rigid polyimides have been known to form thermotropic liquid-crystalline (LC) phases.^{1–18} Kricheldorf *et al.* found that semi-rigid poly(ester-imide)s derived from *N,N'*-bisphenol¹ or *N,N'*-bisester² derivative of 3,3',4,4'-biphenyltetracarboxdiimide with benzene ring next to the imide unit form enantiotropic smectic phases and aliphatic chains having odd numbers favor LC formation of polymers. We have prepared a series of semi-rigid poly(ester-imide)s and poly(imide-carbonate)s^{5–18} and found that the 3,3'',4,4''-*p*-terphenyltetracarboxdiimide has good mesogenic property, but that of 3,3',4,4'-biphenyltetracarboxdiimide is low.^{8,9,18} Aliphatic chains next to the imide ring play an important role on LC formation of polymers. Among the above-mentioned semi-rigid poly(ester-imide)s having the 3,3',4,4'-biphenyltetracarboxdiimide, homopolymers containing decamethylene chain and decamethylene chain-rich copolymers formed nematic phase, although its texture was not clear.¹⁸ Introduction of 3,3'',4,4''-*p*-terphenyltetracarboxdiimide, which has higher mesogenic character than the 3,3',4,4'-biphenyltetracarboxdiimide,^{16,17} into the backbones of semi-rigid poly(ester-imide)s would be likely to enhance potential of emergence of LC phases and to

promote the formation of clearer LC textures.

On the other hand, it has been reported that aromatic polyimides being heat-resistant polymeric materials display photoluminescent (PL) and LC properties, because they are made up of electron-donating and electron-withdrawing well-defined conjugation units.^{19–21} They have a potential as light-emitting and electron- or hole-transporting materials for electroluminescent (EL) devices. Pyo *et al.*¹⁹ developed blue light emitting polypyromellitimide composed of quarterphenyl analogue of 2,2'-bifuryl, showing a peak maximum at 442 nm in a high quantum yield. Polyimides made up of *p*-terphenyl, 1,3,5-triphenylbenzene or triphenylmethane moieties displayed outstanding thermal stabilities and PL properties with blue emission.^{20,21} It was reported that polyimides containing *N*-phenyl-1,8-naphthalimide ring, which acts as laser media, in the main chain show EL properties with green and yellow emission in film.²² We found that semi-rigid poly(ester-imide)s having 3,3',4,4'-biphenyltetracarboxdiimide ring not only show LC properties, but also emit blue light in solutions and in films.¹⁸

The purpose of this work is to prepare thermotropic liquid-crystalline semi-rigid poly(ester-

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imide)s (6) composed of well-defined 3,3'',4,4''-*p*-terphenyltetracarboxdiimide and/or 3,3',4,4'-biphenyltetracarboxdiimide and aliphatic (decamethylene and hexa- or pentamethylene) chains and to investigate their fluorescent properties. Length and combination of the aliphatic (hexa- and pentamethylene) chains next to the imide ring are supposed to affect the LC properties of these poly(ester-imide)s (6). It is also considered that these polymers (6) show not only LC properties, but also PL and EL properties, because the 3,3'',4,4''-*p*-terphenyltetracarboxdiimide is a good mesogen as well as well-defined conjugation unit and an electron-withdrawing group.

EXPERIMENTAL

Materials

11-Aminoundecanoic acid (2) was commercially available and used after recrystallization from water/ethanol. Pyridine was purified by distillation under reduced pressure. *N,N*-dimethylformamide (DMF) and 1,4-dioxane were dried over molecular sieve (4 Å). *N,N'*-bis(6-hydroxyhexyl)-3,3',4,4'-biphenyltetracarboxdiimide (5a) and *N,N'*-bis(5-hydroxypentyl)-3,3',4,4'-biphenyltetracarboxdiimide (5b) were synthesized according to our previously-described procedures.^{7, 17}

Preparation of Monomer (4)

N,N'-Bis(10-methoxycarbonyldecyl)-3,3',4,4''-*p*-terphenyltetracarboxdiimide (4). 3,3'',4,4''-*p*-Terphenyltetracarboxylic dianhydride (1) (0.01 mol, 3.70 g) and the compound (2) (0.02 mol, 4.03 g) were refluxed in DMF (20 mL) for 6 h. Acetic anhydride (9.5 mL) was added into the reaction mixture and refluxed further 2 h. The reaction solution was cooled and poured into an excess of water to precipitate the biscarboxylic acid derivative (3). The precipitated was collected by filtration, washed thoroughly with water and recrystallized from DMF. Subsequently, the biscarboxylic acid derivative (3) (6.79 mmol, 5.00 g) was refluxed in a mixture of 1,4-dioxane (14 mL) and methanol (40 mL) for one day in the presence of a trace of sulfuric acid as catalyst. Then the reaction solution was cooled and the separated product (4) was filtered off and recrystallized from 1,4-dioxane/methanol = 1/3(v/v) twice. Yield; 44%. mp: 139.2–143.8°C.

(C₄₄H₅₂N₂O₈) (764.9) Calc. C 72.22 H 7.38 N 3.66
Found C 72.26 H 7.46 N 3.65.

FT-IR (KBr): ν = 2930, 2850 (m, CH stretching), 1730 (s, ester C=O), 1770, 1710 (s, imide C=O), 1620 (w, C=C), 1393, 1360 (m, imide), 1170 (m, C–O–C), 740 cm⁻¹ (m, imide ring).

¹³C NMR (CDCl₃): δ = 174.3 (ester C=O), 168.2 (imide C=O), 146.2, 139.5, 133.2, 132.3, 131.0, 128.1, 123.7, 121.7 (benzene ring), 51.4 (CH₃), 38.2 (>NCH₂-), 34.1 (-CH₂C(O)O), 29.2, 29.14, 29.11, 28.6, 26.9, 24.9 ppm (-CH₂-).

Synthesis of Polymers (6)

Homopolymers (6a) and (6f). A typical example for the polymer (6a) is described. A mixture of monomer (4) (0.4 mmol, 0.306 g) and compound (5a) (0.4 mmol, 0.197 g) was stirred at 180–185°C for 2 h in the presence of tetraisopropyl orthotitanate in nitrogen. Then the mixture was heated at 190–195°C for 1 h at a pressure of 2.27 × 10³–2.40 × 10³ Pa (17–18 Torr) and finally at 200–205°C for 1 h at 2.67 × 10² Pa (2 Torr). After the polymerization, the obtained polymer (6a) was dissolved in trifluoroacetic acid (TFAA) or chloroform and the solution was poured into methanol to reprecipitate the polymer. The product was collected by filtration, washed with water and refluxing methanol three times, and dried at 60°C in a reduced pressure for 24 h. Yield; 94%.

(C₇₂H₈₀N₄O₁₂)_n (1193.4)_n Calc. C 72.46 H 6.76 N 4.70
Found C 71.95 H 6.67 N 4.70.

Copolymers (6b) and (6e)

The copolymers were synthesized by the same procedure as that for the homopolymer (6a).

Copolymer (6c):

(C_{71.2}H_{78.4}N₄O₁₂)_n (1182.2)_n Calc. C 72.33 H 6.68 N 4.74
Found C 72.20 H 6.62 N 4.75.

Measurements

Differential scanning calorimetry (DSC), optical texture observations, X-Ray analyses and size exclusion chromatography (SEC), FT-IR and ¹³C NMR spectroscopy were carried out according to our published methods.^{5–18} UV-vis and PL spectra were recorded on a Jasco V-560 UV/VIS spectrophotometer or Shimadzu UV-vis 3100 spectrophotometer and on a Hitachi 850 fluorescence spectrophotometer, respectively. Two types of double-layer EL devices were fabricated using Ca and Al as cathode or LiF and Al as cathode. The polymers were spin-coated from the chloroform solutions on poly(3,4-ethylene dioxythiophene) (PEDOT) spun onto indium tin oxide (ITO) coated glass substrate and then LiF or Ca and aluminum electrode were deposited on the top of device; (ITO (130 nm)/PEDOT (60 nm)/polymer (100 nm)/LiF (0.5 nm)/Al (100 nm)) and (ITO (130 nm)/PEDOT (60 nm)/polymer (100 nm)/Ca (20 nm)/Al (100 nm)).

Table I. Yields, \overline{M}_n and $\overline{M}_w/\overline{M}_n$ of polymers (6a)–(6f)

Polym. No.	x	y	Yield %	\overline{M}_n^a	$\overline{M}_w/\overline{M}_n^b$	Solubility ^c	
						CHCl ₃	CH ₃ OH
6a	1.0	0	94	18600	1.77	++	–
6b	0.8	0.2	83	21100	2.37	++	–
6c	0.6	0.4	85	21900	2.33	++	–
6d	0.4	0.6	87	20700	1.83	++	–
6e	0.2	0.8	85	20800	1.75	++	–
6f	0	1.0	94	37300	1.42	++	–

^a \overline{M}_n : number-average molecular weight estimated by SEC using chloroform as solvent and polystyrene as standard. ^b $\overline{M}_w/\overline{M}_n$: molecular-weight distribution. ^c+: soluble at room temperature, –: insoluble.

RESULTS AND DISCUSSION

Synthesis of Polymers (6)

Semi-rigid homo- and copoly(ester-imide)s (6a)–(6f) having both 3,3'',4,4''-*p*-terphenyltetracarboxdiimide and 3,3',4,4'-biphenyltetracarboxdiimide together with aliphatic (decamethylene and hexa- or pentamethylene) chains in the repeating unit were prepared by melt polycondensation from a mixture of *N,N'*-bismethyl ester derivative (4) of the 3,3'',4,4''-*p*-terphenyltetracarboxdiimide and *N,N'*-bisalcohols (5a) and (5b) of the 3,3',4,4'-biphenyltetracarboxdiimide taken in a definite mole ratio in the presence of tetraisopropyl orthotitanate under polymerization conditions described in the experimental part according to our previously-described methods.^{9,18} The monomer (4) (*N,N'*-bismethyl ester derivative) was synthesized by esterification of corresponding biscarboxylic acid derivative (3) of 3,3'',4,4''-*p*-terphenyltetracarboxdiimide derived from 3,3'',4,4''-*p*-terphenyltetracarboxylic dianhydride (1) and 11-aminoundecanoic acid (2) in the presence of sulfuric acid as catalyst. Melt polycondensation proceeded readily and gave high molecular-weight polymers ($\overline{M}_n = 18600$ –37300, $\overline{M}_w/\overline{M}_n = 1.42$ –2.37) in high yields of 83–94%. They had good solubilities in organic solvents such as chloroform, TFAA and dichloroacetic acid. Flexible films could be cast from the chloroform solutions of polymers (6a)–(6f). Data of synthetic results for polymers (6a)–(6f) are listed in Table I.

Assigned structures of polymers (6a)–(6f) were characterized from ¹³C NMR, FT-IR spectra and elemental analyses. The ¹³C NMR spectra of polymers (6) in CDCl₃ displayed carbon signals of ester C=O at 173.8 ppm, imide C=O at 168.1 ppm, carbon atoms of benzene ring at 122–146 ppm, –C(O)OCH₂– at 63.9 ppm, >NCH₂ at 38.1 ppm, –OC(O)CH₂– at 34.3 ppm and aliphatic chains at 23.3–

29.4 ppm. The FT-IR spectra exhibited characteristic absorption bands of imide C=O at 1707–1710 and 1770 cm⁻¹, imide around 1393–1395 and 745 cm⁻¹, ester C=O at 1730 cm⁻¹ (shoulder), C–O–C at 1167–1170 cm⁻¹ and so on. Elemental analysis values were in good agreement with the calculated ones. These data suggest the production of expected polymers (6).

Thermal and Liquid-Crystalline (LC) Properties of Polymers (6)

Thermal and LC properties of polymers (6) were investigated by DSC measurements, polarizing microscope observation and powder X-Ray analyses. These measurements indicated that homopolymer (6a) from *N,N'*-bis(hexanol) derivative (5a) forms monotropic smectic phase and the copolymers (6b)–(6d) enantiotropic nematic phase. In the DSC curves of polymer (6a) two endotherms were observed together with glass transition step (*T*_g) at 48°C on the first heating run. No LC phases were observed between the temperatures (104°C and 168°C). On the first cooling run, the corresponding two exotherms were observed at 149°C (isotropization-to-LC phase: *T*_i) and 78°C (LC phase-to-solid: *T*_c) and monotropic fine texture was observable. Two exothermal peaks and one endotherm were shown on the second heating scan. In the DSC curves of polymers (6b)–(6d) three or four endotherms were observed on the first heating runs. Two endothermal (*T*_m and *T*_i) or exothermal peaks (*T*_c and *T*_i) were detected on the first cooling or the second heating runs in addition to the *T*_g steps (Figure 1). Between these two peaks (*T*_m and *T*_i) enantiotropic nematic phase was recognized. Polarizing microscope observations of textures showed that the homopolymer (6a) forms fine texture and the copolymers (6b)–(6d) schlieren texture. Powder X-Ray analyses of polymers (6) quenched from the LC states suggested the emergence of smectic phase in the homopolymer (6a) and nematic phase in the copolymers (6b)–(6d). In the X-Ray pattern of the homopolymer (6a) illustrated in Figure 2, sharp re-

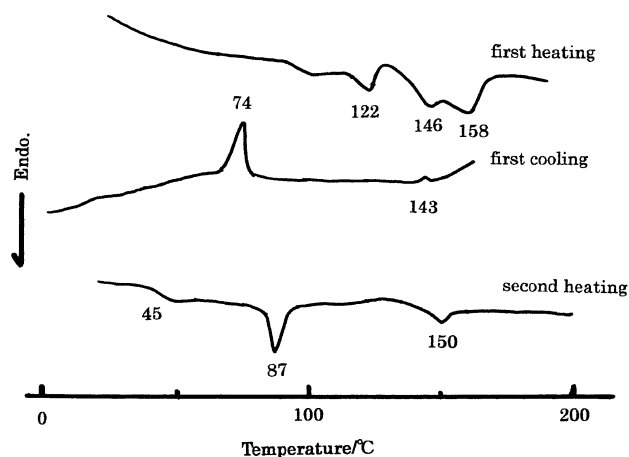


Figure 1. DSC curves of polymers (6b).

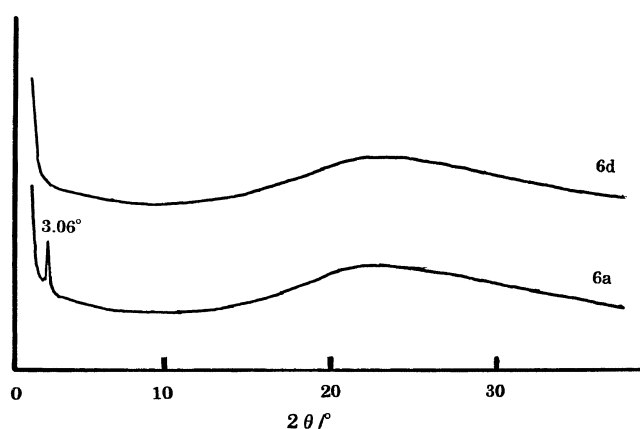


Figure 2. X-Ray diffraction patterns of polymers (6a) and (6d).

Table II. Phase transition temperatures of polymers (6a)–(6f)^a

Polym. No.	T_g °C	T_c °C	T_m °C	T_i °C	ΔT °C	Phase
6a	45	86, 128	168 (78) ^b	— (149) ^b	— (71) ^b	Smectic
6b	46	—	87	150	63	Nematic
6c	46	—	78	140 ^c	62	Nematic
6d	48	—	71	145 ^c	74	Nematic
6e	46	—	136 ^d	—	—	—
6f	41	—	140 ^d	—	—	—

^aData observed on the second heating runs. T_g : glass transition temperature; T_c : crystallization temperature; T_m : melting temperature; T_i : isotropization temperature; $\Delta T = T_i - T_m$: temperature range of LC phase. ^bOn first cooling. ^cObserved by polarizing microscope. ^dOn first heating.

flection at $\theta = 3.06^\circ$ (d spacing of 28.9 Å) and broad reflection around $\theta = 23^\circ$ are observable, respectively. This proves that the LC phase of polymer (6a) is smectic C or A. In the patterns of polymers (6b)–(6d), no reflections at small angles and broad reflections around $\theta = 23^\circ$ were detected, whose phase is nematic. The phase transition data are presented in Table II. Unfortunately the polymers (6e) and (6f) formed no LC phases.

From these results, it is found that in the ho-

mopolymer (6a) having two even (decamethylene and hexamethylene) spacers and total length ($10 + 6 = 16$) of aliphatic chains with even number between two diimide rings, the ordered structure of polymer is retained and the smectic phase appears owing to the good mesogenic character of the 3,3'',4,4''-*p*-terphenyltetracarboxdiimide unit in spite of coexistence of both the symmetric diimide rings in the backbone. The copolymers (6b)–(6d) having the spacer with odd number (pentamethylene) and total length of aliphatic chains ($10 + 5 = 15$) showed nematic phase, probably due to reduction of alignment of polymer chains by the presence of the pentamethylene chain.

Absorbing and Emitting Properties of Polymers (6)

Absorption and emission spectra of the polymers (6a)–(6f) in chloroform solutions and in films were investigated. In the UV-vis spectra in the solutions and in the films, absorption peak maxima were detected at 334–337 nm and 337–341 nm, respectively. Our previous papers described that UV-vis spectra of semi-rigid poly(imide-carbonate)s containing the 3,3'',4,4''-*p*-terphenyltetracarboxdiimide²³ and those of poly(ester-imide)s with the 3,3',4,4'-biphenyltetracarboxdiimide¹⁸ in the chloroform solutions show peak maxima around 343 nm and 325 nm, respectively. The peak maxima of polymers (6a)–(6f) in this work were observed between those for the two kinds of polyimides. The absorption maxima due to the 3,3',4,4'-biphenyltetracarboxdiimide unit overlapped with those of the 3,3'',4,4''-*p*-terphenyltetracarboxdiimide. HOMO-LUMO band gap energies (E_g) of these polymers (6a)–(6f) estimated from onset of the UV-vis spectra in the films were 3.12–3.14 eV. The PL spectra of polymers (6a)–(6f) in the chloroform solutions and in the films were normalized to peak maxima at 413–415 and 424–429 nm, respectively, with blue emission when excited at 334–337 nm in the solutions and at 337–341 nm in the films. The PL spectra were shifted to longer wave lengths by 78–79 nm in the solutions and by 87–88 nm in the films compared to the UV-vis spectra of polymers (6a)–(6f), probably due to intermolecular aggregation effects.²⁴ The UV-vis and PL spectra of polymers (6a)–(6f) in the films are shown in Figures 3 and 4. The data in the chloroform solutions and in the films are listed in Table III.

EL spectra of as-spin-coated and unordered (unheat-treated) polymers (6a) and (6f) in devices fabricated using the LiF and Al as the cathode (ITO/PEDOT/polymer/LiF/Al) display peak maxima around 422–423 nm with blue emission. The devices (ITO/PEDOT/polymer/Ca/Al) had the same EL spec-

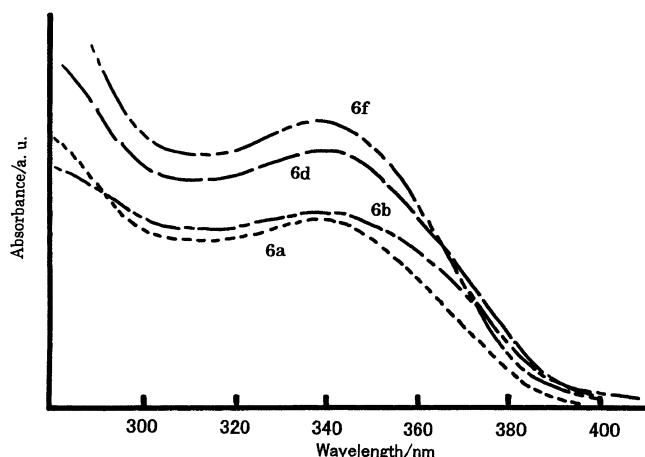


Figure 3. UV-vis spectra of polymers (6a), (6b), (6d), and (6f) in films.

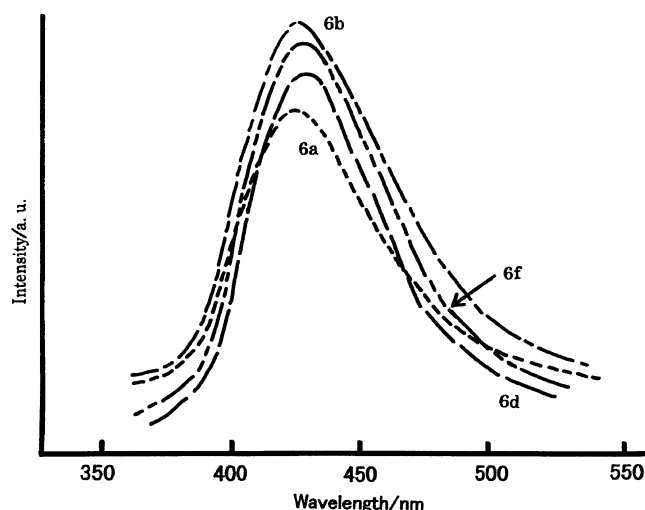


Figure 4. PL spectra of polymers (6a), (6b), (6d), and (6f) in films.

Table III. UV-vis and PL spectral data of polymers (6a)–(6f)

Polymer	UV-vis		PL	
	λ_{\max}/nm in solution	λ_{\max}/nm in film	λ_{\max}/nm in solution	λ_{\max}/nm in film
6a	337	337	415	424
6b	335	340	413	426
6c	334	339	414	426
6d	336	339	413	428
6e	337	341	413	425
6f	336	339	413	429

tra as those (ITO/PEDOT/polymer/LiF/Al), showing peak maxima around 422–423 nm with blue emission. As shown in Figure 5, the EL spectra of unordered polymers (6a) and (6f) in the two devices and the above-mentioned PL spectra in the films in Figure 4 were almost identical, indicating that the same excited state was involved in the two processes, which display peak maxima around 424 and 426 nm with blue emission. Maximum luminances for the devices (ITO/PEDOT/polymer/LiF/Al) of polymers (6a) and

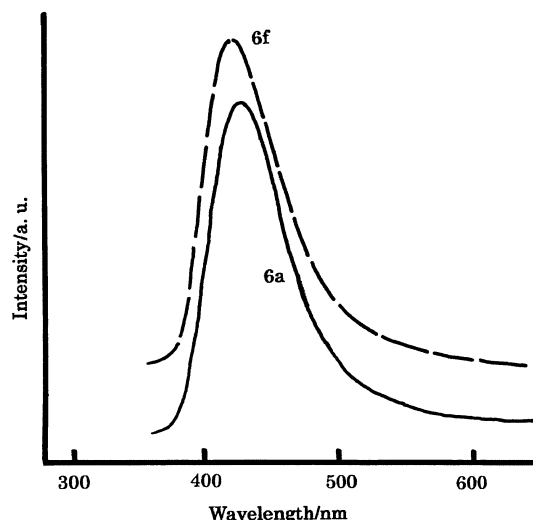


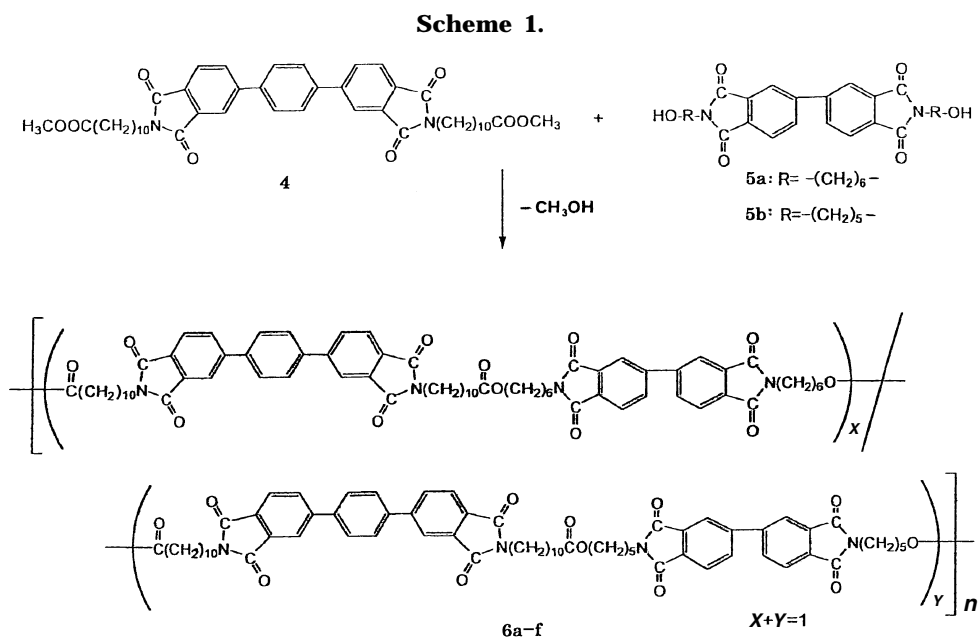
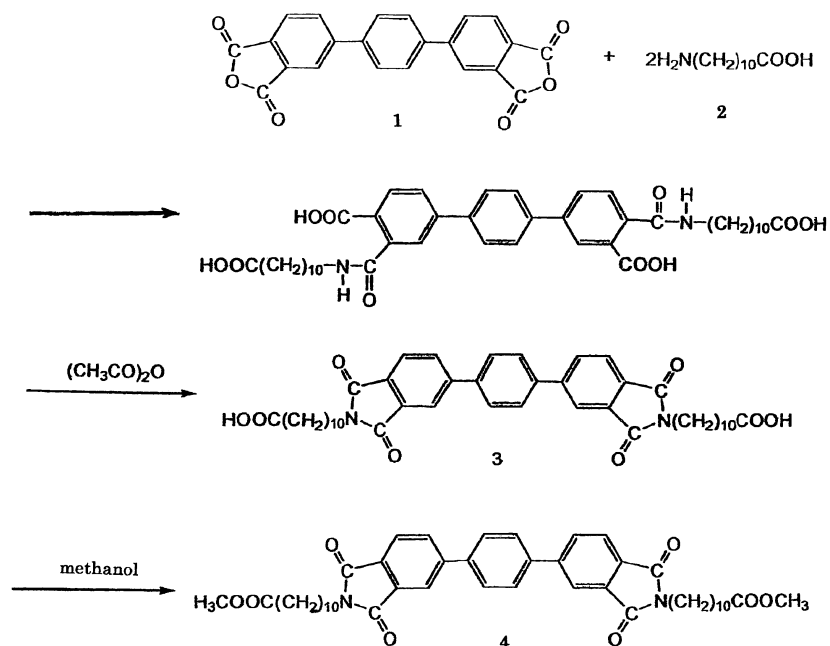
Figure 5. EL spectra of devices (ITO/PEDOT/polymer/LiF/Al) fabricated with polymers (6a) and (6f).

(6f) were 0.319 cd m^{-2} at the driving voltage of 14 V and 0.536 cd m^{-2} at 13 V, respectively. External quantum efficiencies of the devices were 0.002% at 12 V for the polymer (6a) and 0.004% at 11 V for the polymer (6f). The maximum luminance of the devices (ITO/PEDOT/polymer/Ca/Al) with the polymer (6a) was 0.124 cd m^{-2} at 14 V and that with the polymer (6f) 0.227 cd m^{-2} at 20 V. In addition, the external quantum efficiencies were 0.001% at 17 V in the polymer (6a) and 0.003% at 14 V in the polymer (6f), respectively. The luminances of polymers (6a) and (6f) were considerably low compared with already-reported 1,3,4-oxadiazole-containing polymers^{25–27} (for example, 38 cd m^{-2} at 10 V²⁵ and 25 cd m^{-2} at 12 V²⁷) and our previously-prepared semi-rigid poly(imide-carbonate)s²³ (1.65 cd m^{-2} at 12 V).

These data suggest that the LC semi-rigid poly(ester-imide)s (6) in this work can be used as blue light emitting and/or electron-transporting materials for the EL devices, although there are many problems to improve in the present time. A clear relationship between the LC character and the PL and the EL properties of these poly(ester-imide)s (6) is not found in this work.

CONCLUSIONS

Organic-soluble and high molecular-weight semi-rigid homo- and copoly(ester-imide)s composed of both 3,3',4,4'-*p*-terphenyltetracarboxdiimide and 3,3',4,4'-biphenyltetracarboxdiimide units without well-known mesogens in the backbone were synthesized in high yields. Homopolymer having hexamethylene chain formed monotropic smectic phase and most of copolymers enantiotropic nematic phase. Solution and solid state PL spectra of polymers fluoresced



blue light, which were shifted to longer wave lengths compared to the absorption spectra, and were almost identical to EL spectra of polymers in double-layer devices (ITO/PEDOT/polymer/LiF or Ca/Al) with blue emission. The polymers in this work are candidate materials for organic EL devices.

Acknowledgments. The authors would like to express their gratitude to Ms. Michiko Egawa for her help in obtaining elemental analysis data.

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