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Thermotropic liquid crystalline polymers containing five-membered heterocyclic groups

IX. Synthesis and optical properties of liquid crystalline semi-rigid polyesters composed of a quinquephenyl analogue containing 1,3,4-thiadiazole and aliphatic chains†

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Novel semi-rigid polyesters containing a quinquephenyl analogue containing 1,3,4-thiadiazole and a central 1,3-phenylene unit in the main chain were synthesized by high temperature solution polycondensation of a dimethyl ester derivative of 1,3-bis(5-phenyl-1,3,4-thiadiazol-2-yl)benzene with an aliphatic (octa-, deca- and dodecamethylene) diol. The proposed structures were confirmed using FTIR and ^{1}H NMR spectroscopies, and elemental analyses; their liquid crystalline and photoluminescent (PL) properties were examined by means of differential scanning calorimetry, optical texture observations using polarizing microscopy, powder X-ray diffraction, and UV-vis and PL spectra measurements. These measurements showed that the polymers not only show a monotropic solid smectic or disordered crystal phase, but also PL properties with blue emission in HFIP solutions and in the solid phase, Stokes shifts of 116.5–119 nm being observed.

1. Introduction

1,3,4-Thiadiazoles are five-membered heterocycles containing sulphur and nitrogen atoms, and are analogous to the corresponding 1,3,4-oxadiazoles. Mesogens based on 1,3,4-oxadiazoles have low mesomorphic tendencies because of their bent molecular structures [1, 2], whereas 1,3,4-thiadiazoles are good calamitic mesogens and form stable thermotropic liquid crystalline (LC) mesophases [3–6]. Dimitrova *et al.* found that biphenyl, terphenyl and quaterphenyl analogues containing 1,3,4-thiadiazole show thermotropic nematic and smectic LC phases [5]. We reported that twin terphenyl analogues containing 1,3,4-thiadiazole having a central octamethylene spacer form more stable thermotropic LC phases than the corresponding 1,3,4-oxadiazole derivatives [6].

Light-emitting and/or charge-transporting compounds and conjugated and non-conjugated polymers containing heterocycles such as 1,3,4-oxadiazoles and thiophenes, and aromatic rings and/or aliphatic chains, have attracted much attention as materials for organic electroluminescent (EL) devices, organic semiconductors and plastic lasers [7–16]. In recent years, low molar mass compounds and polymers which show not only thermotropic LC properties, but also photoluminescent (PL) and EL properties have been reported [17–24]. For example, a quaterphenyl analogue containing 1,3,4-oxadiazole, 2-(4-hexyloxy-4-biphenylyl)-5-(4-hexyloxyphenyl)-1,3,4-oxadiazole, having a high electron mobility and polarized EL behaviour, also showed smectic LC phases [17]. Pshirer *et al.* reported LC poly(*p*-phenyleneethynylene)s displaying blue fluorescence in the solid state [18]. We have prepared low molar mass 1,3,4-thiadiazole derivatives [19] and a series of semi-rigid polyesters containing terphenyl [20], quaterphenyl [21] and distyrylbenzene analogues [22] containing 1,3,4-thiadiazole in the main chain, and discovered that some of these not only form thermotropic nematic and/or smectic LC phases, but also emit PL and EL light. Polyesters having the distyrylbenzene analogue containing 1,3,4-thiadiazole formed both thermotropic smectic C and lyotropic LC phases [22]. Quaterphenyl analogues containing 2,2′-bis(1,3,4-thiadiazole) showed EL behaviour in addition to LC formation and PL properties with blue and green

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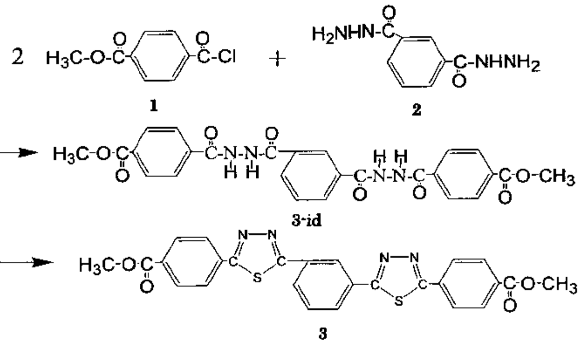
emission [19]. These are expected to be candidate materials for organic EL devices.

This paper describes the preparation of new semi-rigid polyesters **5a–c** composed of a quinquephenyl analogue containing 1,3,4-thiadiazole with a central 1,3-phenylene unit, i.e. 1,3-bis(5-phenyl-1,3,4-thiadiazol-2-yl)benzene and aliphatic chains, by the high temperature solution polycondensation of the dimethyl ester monomer **3**, 1,3-bis[5-(4-methoxycarbonylphenyl)-1,3,4-thiadiazol-2-yl]benzene, with three aliphatic diols **4a–c** (**4a**; $m = 8$, **4b**; $m = 10$, **4c**; $m = 12$) (see Schemes 1 and 2), The LC and light-emitting properties of these polymers are also described. The polyesters **5a–c** not only form thermotropic mesomorphic phases, but also show PL properties, and may be considered as candidate organic materials for EL devices.

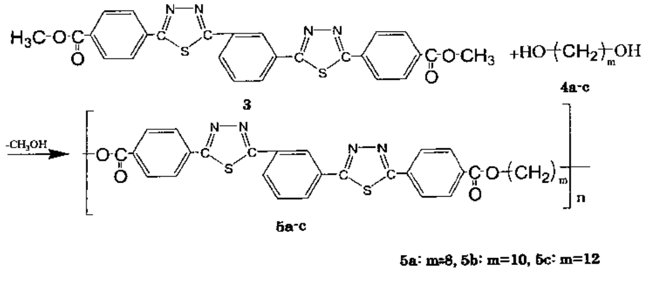
2. Experimental

2.1. *Characterization*

FTIR spectroscopy, UV-vis and PL spectrum measurements, differential scanning calorimetry (DSC), optical texture observations using a polarizing microscope equipped with a hot stage and powder X-ray analysis were undertaken according to our published procedures [6, 19–24]. ^{1}H NMR spectra were measured in TFAA/$CDCl_3$ = 1/3 v/v or HFIP/$CDCl_3$ = 1/3 v/v. TG-DTA measurements were carried out using a Rigaku TG-DTA analyser TG-8120 at a heating rate of 10°C min^{-1} in air. Inherent viscosity measurements were conducted at a concentration of 0.1 g dl^{-1} in DCAA at 30°C using an Ostwald viscometer. Molecular lengths of the polymer repeating unit were estimated using Maruzen HGS Molecular Structure Model.



Scheme 1. Synthesis of monomer **3**.



Scheme 2. Synthesis of polymers **5a–c**.

2.2. *Materials*

Isophthalic dihydrazide **2**, terephthalic acid monomethyl ester chloride **1**, Lawesson's reagent, 1,4-dioxane (special grade) and di-*n*-butyltin dioxide were commercially available from Tokyo Chemical Industry Co., Ltd, and used as received. 1,8-Octanediol **4a**, 1,10-decanediol **4b** and 1,12-dodecanediol **4c** (Tokyo Chemical Industry Co., Ltd.) were recrystallized from methanol and used after drying under vacuum. Pyridine, *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), 1-chloronaphthalene, trifluoroacetic acid (TFAA), dichloroacetic acid (DCAA) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Tokyo Chemical Industry Co., Ltd. and Kishida Chemicals Co., Ltd) were purified by vacuum distillation.

2.3. *Synthesis of monomer 1,3-bis[5-(4-methoxycarbonylphenyl)-1,3,4-thiadiazol-2-yl]benzene, 3*

Isophthalic dihydrazide **2** (0.02 mol, 3.91 g) and terephthalic acid monomethyl ester chloride **1** (0.04 mol, 7.99 g) were stirred in DMAc (30 ml) in the presence of pyridine (0.04 mol) for 30 min in an ice–water bath, and then for 48 h at room temperature. The reaction solution was poured into water to precipitate the intermediate dihydrazide compound **3-id**. The precipitate was collected by filtration, washed thoroughly with water and dried at 60°C in vacuum for one day. The intermediate **3-id** (0.02 mol, 10.37 g) was then heated under reflux with stirring in 1,4-dioxane (90 ml) containing Lawesson's reagent (0.05 mol, 21.25 g) for 3 h. After the reaction was complete, the reaction mixture was poured into 1M NaOH aqueous solution including ice. After standing overnight, the resulting solid was filtered off and washed thoroughly with water and ethanol. Two recrystallizations from DMF and drying at 60°C under vacuum for 24 h gave the product **3** in a yield of 71%; m.p. 361–363°C. FTIR (KBr): $\nu = 2920$, 2850 (CH stretching), 1725 (ester C–O), 1607 (C–C), 1405 (thiadiazole), 1278 cm^{-1} (C–O–C). ^{1}H NMR (270 MHz, TFAA/$CDCl_3$ = 1/3 v/v): $\delta = 8.65$ (s, 1H, ar C–H), 8.26 (t, 6H, ar C–H), 8.12 (d, 4H, ar C–H), 7.87 (t, 1H, ar C–H), 4.07 ppm (s, 6H, CH_3). $C_{26}H_{18}N_4O_4S_2$ (514.6): calcd C 60.68, H 3.53, N 10.89; found C 60.60, H 3.60, N 10.73%.

2.4. *Polymer synthesis*

A typical method for polymer **5a** is described. The monomer **3** (0.75 mmol, 0.386 g) and the diol **4a** (0.75 mmol, 0.110 g) were stirred at 180–190°C for 9 h in 1-chloronaphthalene (2.5 ml) in the presence of di-*n*-butyltin oxide (5 mg) under nitrogen. The byproduct, methanol, was removed every 1 h. After polycondensation, the reaction mixture was dissolved in HFIP and the solution poured into methanol. The precipitated solid was filtered off and washed thoroughly with water and refluxing ethanol three times. The resulting polymer **5a** was dried at 60°C for one day in vacuum: yield 88%, $\eta_{\mathrm{inh}} = 0.18\,\mathrm{dl\,g^{-1}}$ in DCAA at 30°C ($c = 0.1\,\mathrm{g\,dl^{-1}}$). FTIR (KBr): $\nu = 2928$, 2855 (CH stretching), 1716 (ester C–O), 1608 (C=C), 1401 (thiadiazole), $1276\,\mathrm{cm^{-1}}$ (C–O–C). ^{1}H NMR (270 MHz, HFIP/$CDCl_3$ = 1/3 v/v): $\delta = 8.59$ (s, 1H, ar C–H), 8.21 (t, 6H, ar C–H), 8.11 (d, 4H, ar C–H), 7.76 (t,1H, ar C–H), 4.42 (t, 4H, OCH_2), 4.02 (s, CH_3), 1.83 (t, 4H, CH_2), 1.47, 1.40 ppm (8H, CH_2). $(C_{32}H_{28}N_4O_4S_2)_n$ $(596.7)_n$: calcd C 64.41, H 4.73, N 9.39; found C 63.19, H 4.95, N 9.11%.

5b: yield 90%, $\eta_{\mathrm{inh}} = 0.37\,\mathrm{dl\,g^{-1}}$ in DCAA at 30°C ($c = 0.1\,\mathrm{g\,dl^{-1}}$). FTIR (KBr): $\nu = 2925$, 2853 (CH stretching), 1717 (ester C–O), 1608 (C=C), 1401 (thiadiazole), $1276\,\mathrm{cm^{-1}}$ (C–O–C). ^{1}H NMR (270 MHz, TFAA/$CDCl_3$ = 1/3 v/v): $\delta = 8.65$ (s, 1H, ar C–H), 8.26 (t, 6H, ar C–H), 8.11, 8.08 (d, 4H, ar C–H), 7.86 (t, 1H, ar C–H), 4.45 (t, 4H, OCH_2), 4.07 (s, CH_3), 1.86 (t, 4H, CH_2), 1.38 ppm (s, 12H, CH_2). $(C_{34}H_{32}N_4O_4S_2)_n$ $(624.8)_n$: calcd C 65.36, H 5.16, N 8.97; found C 64.63, H 5.38, N 8.75%.

5c; yield 87%, $\eta_{\mathrm{inh}} = 0.35\,\mathrm{dl\,g^{-1}}$ in DCAA at 30°C ($c = 0.1\,\mathrm{g\,dl^{-1}}$). FTIR (KBr): $\nu = 2925$, 2852 (CH stretching), 1717 (ester C–O), 1608 (C=C), 1401 (thiadiazole), $1276\,\mathrm{cm^{-1}}$ (C–O–C). ^{1}H NMR (270 MHz, TFAA/$CDCl_3$ = 1/3 v/v): $\delta = 8.62$ (s, 1H, ar C–H), 8.24 (t, 6H, ar C–H), 8.11, 8.08 (d, 4H, ar C–H), 7.84 (t, 1H, ar C–H), 4.43 (t, 4H, OCH_2), 4.06 (s, CH_3), 1.85 (t, 4H, CH_2), 1.34 ppm (s, 16H, CH_2). $(C_{36}H_{36}N_4O_4S_2)_n$ $(652.8)_n$: calcd C 66.23, H 5.64, N 8.58; found C 65.11, H 5.42, N 8.51%.

3. Results and discussion

3.1. *Preparation of monomer 3 and polymers 5a–c*

The new semi-rigid polyesters **5a–c** comprising a quinquephenyl analogue containing 1,3,4-thiadiazole with a central 1,3-phenylene unit, i.e. 1,3-bis(5-phenyl-1,3,4-thiadiazol-2-yl)benzene, and aliphatic chains ($m = 8$, 10 and 12) were prepared in yields of 87–90% by the high temperature solution polycondensation of monomer **3** with the aliphatic diols **4a–c** (**4a**: 1,8-octanediol, **4b**: 1,10-decanediol, **4c**; 1,12-dodecanediol) in 1-chloronaphthalene in the presence of di-*n*-butyltin oxide as catalyst. The inherent viscosities of the polymers were 0.18–$0.37\,\mathrm{dl\,g^{-1}}$ at 30°C in DCAA. The resulting polymers **5a–c** were soluble in HFIP and TFAA at room temperature and in DCAA on heating, but insoluble in methanol, chloroform, DMF and DMAc. The dimethyl ester monomer **3** used in the preparation of the polyesters **5a–c** was obtained in a yield of 71% by the intramolecular dehydration of the corresponding intermediate dihydrazide **3-id**, which was prepared from isophthalic dihydrazide, **2**, and terephthalic acid monomethyl ester chloride, **1**, in the presence of pyridine in DMAc, using Lawesson's reagent in 1,4-dioxane.

The structures of monomer **3** and polymers **5a–c** were identified by FTIR and ^{1}H NMR spectroscopies, and elemental analyses. The characterization data for diester **3** are listed in §2. In the FTIR spectra of polymers **5a–c**, characteristic absorption bands associated with CH stretching at 2925–2928 and 2852–$2855\,\mathrm{cm^{-1}}$, ester C–O at around $1717\,\mathrm{cm^{-1}}$, thiadiazole at $1401\,\mathrm{cm^{-1}}$, C=C of the benzene rings at $1608\,\mathrm{cm^{-1}}$ and C–O–C at $1276\,\mathrm{cm^{-1}}$ were observed. The ^{1}H NMR spectra of polymers **5a–c** in TFAA/$CDCl_3$ = 1/3 v/v or HFIP/$CDCl_3$ = 1/3 v/v showed proton signals associated with the benzene rings at 7.76–8.59 ppm, –C(O)OCH_2– at 4.42 ppm and alkylene chains at 1.40–1.83 ppm. The elemental analysis data for polymers **5a–c** were in agreement with the calculated values for the polymer repeating units.

3.2. *Mesogenic properties of polyesters 5a–c*

The thermal and mesomorphic properties of polyesters **5a–c** were examined by means of TG-DTA and DSC, optical texture observations using a polarizing microscope and powder X-ray diffraction.

In the DSC curves of polymers **5a–c**, only endothermic peaks associated with melting (T_m) (**5a**: 356°C, **5b**: 342°C, **5c**: 327°C) were observed in the first heating scans, but two exotherms due to an isotropic–LC phase (T_i) transition (**5a**: 311°C, **5b**: 285°C, **5c**: 264°C) and a LC–solid (T_c) transition (**5a**: 287°C, **5b**: 235°C, **5c**: 207°C) were detected in the first cooling runs. The DSC curves for polymer **5b** for the first heating and cooling scans are shown in figure 1. Glass transitions (T_g) are detected only with difficulty. Polarizing microscope observations indicated that polymers **5a–c** show monotropic mesophases (fine texture) between T_i and T_c on the first cooling. For the second heating runs, clear DSC curves were not obtained because of the partial decomposition of polymers **5a–c** after isotropization in the first heating. The polymers **5a–c** were seen to decompose by polarizing microscopy. This finding was supported by TG-DTA measurements, which

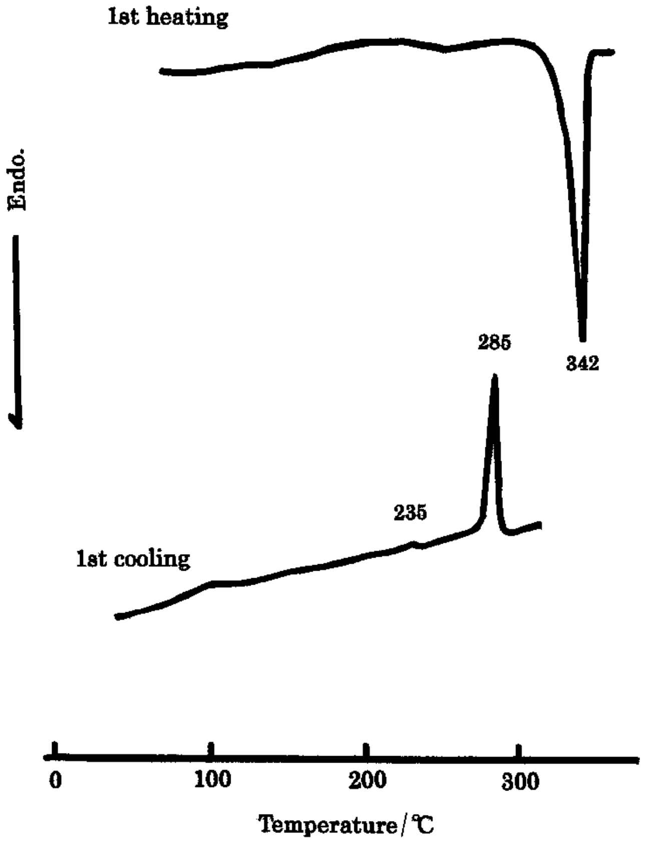


Figure 1. DSC curves of polyester **5b** for the first heating and cooling runs.

showed that polymers **5a–c** begin to lose weight at around 250°C and rapidly decompose between 350 and 400°C (T_d **5a** 367°C, **5b** 373°C, **5c** 372°C) and in the range 550–600°C in air in two steps. The TG-DTA curves of polymer **5b** are shown in figure 2. The thermal analysis data for the polymers **5a–c** are listed in Table 1.

The mesophases were characterized by powder X-ray analyses. The *d*-spacings estimated from the X-ray data are 28.8 Å (**5a**), 30.7 Å (**5b**) and 31.5 Å (**5c**), and shorter than molecular lengths (**5a**: 35.4 Å, **5b**: 37.7 Å, **5c**: 40.0 Å) for the repeat unit of the polymers **5a–c** estimated using the Molecular Structure Model, see table 2. The *d*-spacings increase on increasing the length of the aliphatic chains. In the X-ray patterns of polymers **5a–c** quenched from the mesophase, sharp reflections at small angles (**5a**: 3.06°, **5b**: 2.87°, **5c**: 2.80°), broad reflections around 23° together with two reflections at 15°–30° (17.2°–17.6° and 26.1°–26.5°) are found, although the polymers partially decompose as discussed (figure 3). It is suggested that the reflections at 15°–30° indicate a higher ordered smectic or crystal phase (solid mesophase: B, E, H or F/G) [25].

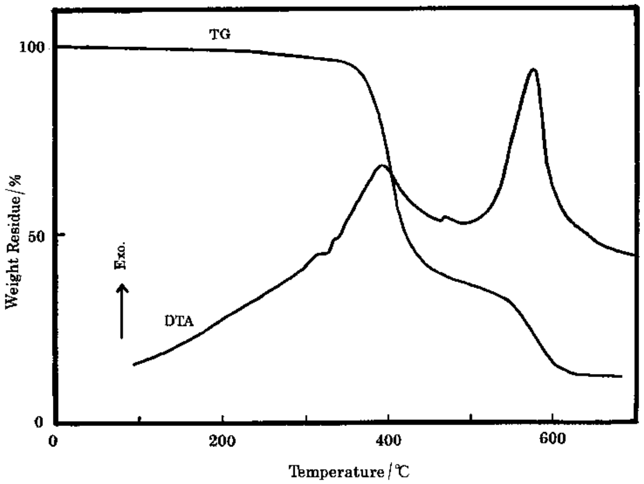


Figure 2. TG-DTA curves of polyester **5b** at a heating rate of 10°C min^{-1} in air.

Table 1. Transition and decomposition temperatures of polyesters **5a–c**. Cooling scan results are in brackets.

Polymer	T_c^{b} °C	T_m^{a} °C	T_i^{b} °C	ΔT^{b} °C	T_d^{c} °C
5a		356			367
	(287)		(311)	(24)	
5b		342			373
	(235)		(285)	(50)	
5c		327			372
	(207)		(264)	(57)	

[a] Observed on the first heating scans: T_m = melting temperature.

[b] Observed on the first cooling scans: T_c = LC – solid transition temperature; T_i = isotropic – LC transition temperature, $\Delta T = T_i - T_c$ is the LC temperature range.

[c] T_d = temperature for 10% weight loss.

Table 2. X-ray data for polyesters **5a–c**.

Polymer	Small angle 2 θ/°	Small angle *d*-spacing/Å	Molecular length^a/Å	Wide angle 2 θ/°
5a	3.06	28.8	35.4	17.5, 26.1
5b	2.87	30.7	37.7	17.6, 26.4
5c	2.80	31.5	40.0	17.2, 26.5

[a] Length of polymer repeating unit.

Generally, in LC main chain polymers sharp reflections at small angles and reflections at wide angles arising from the higher ordered smectic phases are observed in the solid states (solid mesophases) [26]. The wide angle reflections are broad in a frozen smectic C or A phase [25]. Thus, the X-ray data for polyesters **5a–c** showing sharp reflections at small angles together with two reflections at wide angles (17.2°–17.6° and 26.1°–26.5°) (figure 3) suggest that the polyesters show monotropic solid smectic/disordered crystal phases.

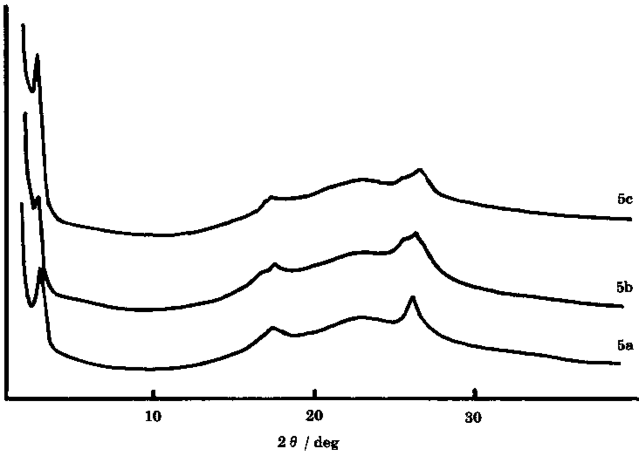


Figure 3. X-ray diffraction patterns for polyesters **5a–c**.

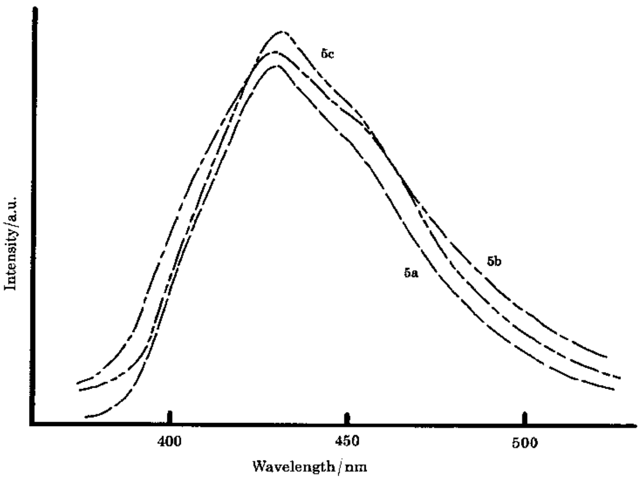


Figure 4. Solid state PL spectra of polyesters **5a–c**.

3.3. *Optical properties of polyesters 5a–c*

UV-vis and PL spectra of polyesters **5a–c** were measured in HFIP solution and in the solid state. The UV-vis spectra of polymers **5a–c** in HFIP solution were normalized to the absorption peak maxima (**5a**: 303.5 nm, **5b**: 304.5 nm, **5c**: 304.5 nm) associated with the π–π* electron transition of the quinquephenyl analogue containing of 1,3,4-thiadiazole. The PL spectra in HFIP solution showed blue-emitting maxima (**5a**: 377 nm, **5b**: 376.5 nm, **5c**: 376 nm) when excited at 304 nm, which were Stokes-shifted by 71.5–73.4 nm. The solid state UV-vis spectra exhibited similar absorbance maxima (**5a**: 310 nm, **5b**: 312 nm, **5c**: 312.5 nm).

The band gap energies (E_g) of polymers **5a–c** calculated from extrapolated absorption edges in the solid state (**5a**: 3.23 eV, **5b**: 3.22 eV, **5c**: 3.20 eV) are higher than those of the analogous semi-rigid polyesters described in our previous papers [20, 21]. In the solid state PL spectra, on excitation at 310–312.5 nm polymers **5a–c** display peak maxima (**5a**: 429 nm, **5b**: 428.5 nm, **5c**: 429.5 nm) with blue emission, the Stokes shifts being 116.5–119 nm, see figure 4. Their band edges extend beyond 500 nm. The solid state PL spectra were shifted to lower energies than the solution PL spectra, which might be due to intermolecular aggregation effects [27]. The UV-vis and PL spectral data for polymers **5a–c** in HFIP solution and in the solid phase are listed in table 3. These data suggest that the polyesters display solid state fluorescence at shorter wave lengths than some of the semi-rigid polyesters incorporating the terphenyl, quaterphenyl and distyrylbenzene analogues containing 1,3,4-thiadiazole and aliphatic chains [20–22]. This is probably because the conjugation in the quinquephenyl analogue containing 1,3,4-thiadiazole is disrupted by the central 1,3-phenylene ring. These polymers **5a–c** have potential application as blue-emitting materials in organic EL devices.

Table 3. UV-vis and PL spectral data of polyesters **5a–c**.

	Solution in HFIP		Solid state		
Polymer	$\lambda_{\mathrm{max,abs}}$/nm	$\lambda_{\mathrm{max,PL}}$/nm	$\lambda_{\mathrm{max,abs}}$/nm	$\lambda_{\mathrm{max,PL}}$/nm	$E_g{}^a$/eV
5a	303.5	377	310	429	3.23
5b	304.5	376.5	312	428.5	3.22
5c	304.5	376	312.5	429.5	3.20

^{a}Band gap energy for polymers **5a–c** in the solid.

4. Conclusion

The semi-rigid polyesters **5a–c** comprising the quinquephenyl analogue containing 1,3,4-thiadiazole and aliphatic chains (octa-, deca- and dodecamethylene) in the main chain were synthesized by high temperature solution polycondensation and found to show not only a monotropic highly ordered smectic or disordered crystal phase in the solid state, but also PL properties with blue emission in HFIP solution and in the solid state as expected.

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