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Liquid Crystals

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Liquid crystalline semirigid polyesters based on phenylstilbene analogues of 1,3,4-thiadiazole

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Semirigid polyesters composed of phenylstilbene analogues of 1,3,4-thiadiazole, 2-(2-phenylethenyl)-5-phenyl-1,3,4-thiadiazole (PEPT), linking an octamethylene chain at different disubstituted (3,3'-, 3,4'-, 4,3'- and 4,4'-) positions, were prepared from four diphenols of the PEPT and sebacoyl chloride by interfacial polycondensation. The effect of polymer structure on thermotropic liquid crystalline (LC) and optical properties is discussed. Differential scanning calorimetry (DSC) measurements, optical texture observations and powder X-ray diffraction patterns showed that the polymer linking the octamethylene chain at the 4,4'-position (4,4'-PEPT) has a linear structure and forms an enantiotropic nematic LC phase. Polymers linking the octamethylene chains at the 4,3'- (4,3'-PEPT), the 3,4'- (3,4'-PEPT) and the 3,3'-positions (3,3'-PEPT) positions have a less linear structure and display monotropic smectic phase or no LC phase. Solution and solid-state UV-visible and emission spectra indicated that the polyesters exhibit absorption maxima due to the PEPT moieties and fluoresce blue light, but low or no quantum efficiencies were recognized. The polyesters emitted weak polarized fluorescent light at room temperature.

1. Introduction

Aromatic derivatives such as biphenyl, terphenyl and quaterphenyl analogues of 1,3,4-thiadiazole (TD), a five-membered heterocyclic ring containing one sulfur atom and two nitrogen atoms, are known to be good calamitic mesogens and to form thermotropic nematic and smectic liquid crystalline (LC) mesophases [1–5] despite having a bent molecular structure core angle (160°) [6, 7]. Side- and main-chain polymers having the aromatic TD derivatives also show thermotropic LC phases [8–18].

In recent years, low molar mass organic compounds and polymers having photoluminescent (PL) and electroluminescent (EL) properties as well as thermotropic LC properties have attracted much attention as functional materials [5, 19–23]. We disclosed that quaterphenyl analogues of TD exhibit PL and EL properties and emit blue or bluish green light in addition to formation of thermotropic LC phases [5]. Quaterphenyl analogues of 1,3,4-oxadiazole (OXD), which are similar five-membered aromatic derivatives to the TD compounds and are electron-transporting materials [19], and polymers having the quaterphenyl structures in the side chains also have been reported to

not only form thermotropic nematic or smectic phase, but also to show EL properties and be able to be used as the organic materials for the EL devices [20]. A series of polymers composed of terphenyl (2,5-diphenyl-1,3,4-thiadiazole (DPTD)) [9–12], quarterphenyl [13, 14], quinquephenyl [15] and distyrylbenzene analogues (2,5-bis(2-phenylethenyl)-1,3,4-thiadiazole (BPET)) [16, 17] of TD have been prepared and relationships between the polymer structures and the LC and optical (UV-visible spectrum, PL and EL) properties discussed. Among the polymers, the polyesters composed of the BPET and alkylene or oligoethylene oxide chains were found to form a smectic mesophase and to emit blue or bluish green fluorescent light [16, 17].

In this work, semirigid thermotropic LC polyesters (**7a–7d**) composed of phenylstilbene analogue of TD, 2-(2-phenylethenyl)-5-phenyl-1,3,4-thiadiazole (PEPT), were prepared by interfacial polycondensation of four diphenols (**5a–5d**) of the PEPT, linking dihydroxy groups at different disubstituted (3,3'- (**5a**), 3,4'- (**5b**), 4,3'- (**5c**) and 4,4'- (**5d**)) positions, with sebacoyl chloride (**6**) and their LC and PL properties were discussed. The polymers (**7a–7d**) are expected to emit blue light based on the PEPT unit, because its moiety in the polymer repeating unit has a shorter conjugated structure than the BPET.

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2. Results and discussion

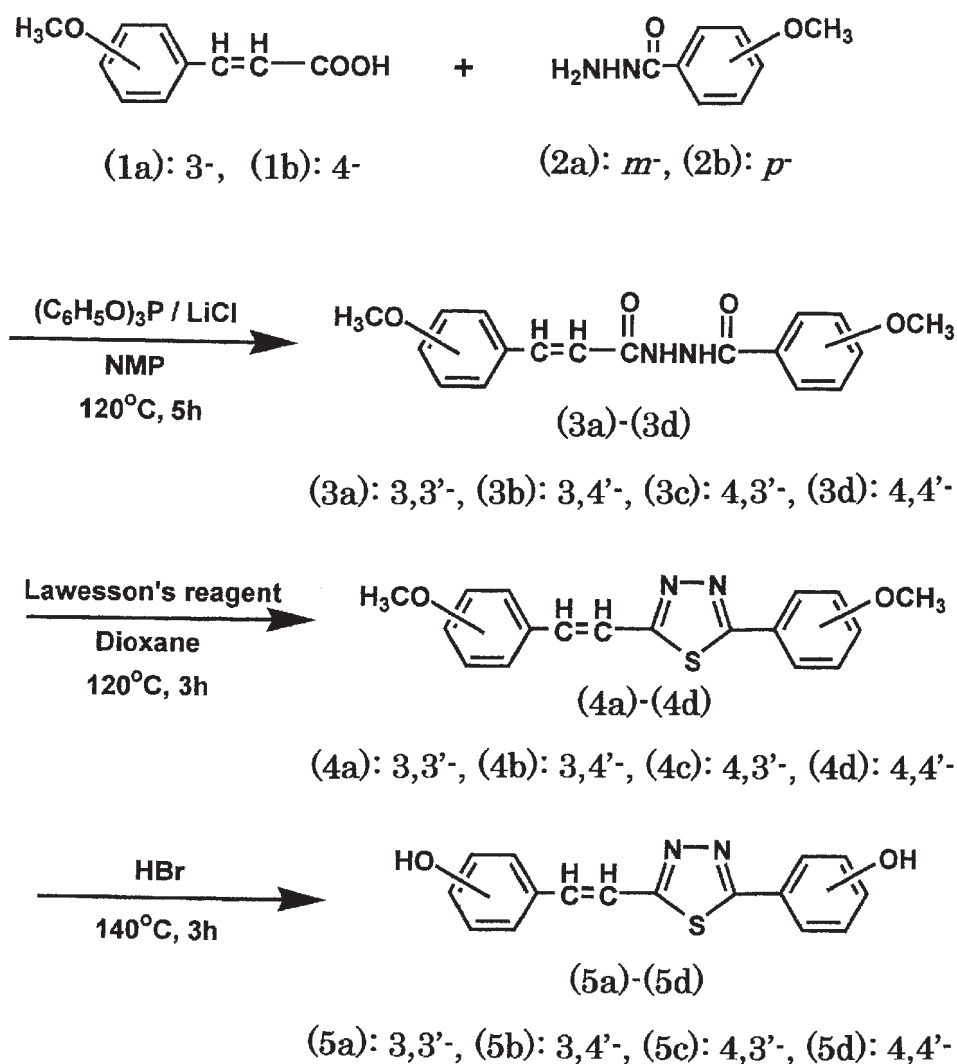
2.1. Monomer and polymer syntheses

Four monomers (**5a–5d**), diphenols of the PEPT linking the dihydroxy groups at different disubstituted (3,3'- (**5a**), 3,4'- (**5b**), 4,3'- (**5c**) and 4,4'- (**5d**)) positions, were synthesized by hydrolysis of the corresponding dimethoxy derivatives (**4a–4d**) of the PEPT in hydrobromic acid, which were prepared by intramolecular dehydration of intermediate hydrazides (**3a–3d**) of the PEPT by using Lawesson's reagent in 1,4-dioxane, as monomers for the polyester syntheses. The intermediate hydrazide derivatives (**3a–3d**) were derived from 3- and 4-methoxycinnamic acid (**1a** and **1b**) and *m*- and *p*-anisic hydrazide (**2a** and **2b**) using triphenyl phosphite as condensation reagent in *N*-methyl-2-pyrrolidone

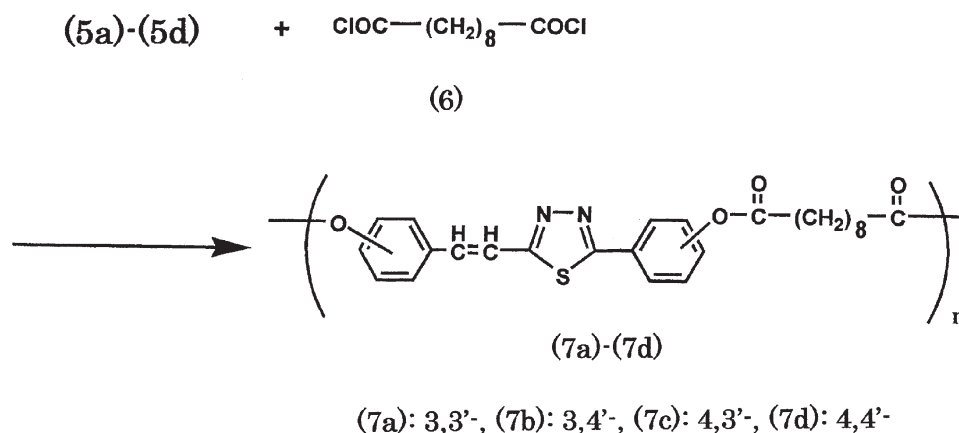
(NMP) including LiCl (see scheme 1). These compounds were identified by FTIR and ¹H NMR spectroscopies and elemental analyses. Their spectral and elemental analysis data were given in the experimental section.

Subsequently, semirigid polyesters (**7a–7d**) of PEPT linking the octamethylene chain at different disubstituted (3,3'- (**7a**), 3,4'- (**7b**), 4,3'- (**7c**) and 4,4'- (**7d**)) positions were prepared by interfacial polycondensation of the four diphenols (**5a–5d**) with sebacoyl chloride (**6**), as shown in scheme 2, with obtained yields of 71–96%.

All the polyesters (**7a–7d**) dissolved in organic acids, e.g. dichloroacetic acid (DCAA), trifluoroacetic acid (TFAA) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), at room temperature. In chloroform, the polyesters linking at 3,3'- (**7a**), 3,4'- (**7b**) and 4,3'- (**7c**) positions



Scheme 1. Synthesis of diphenol polyester precursors **5a–5d**.

Scheme 2. Synthesis of polyesters **7a-7d**.

were soluble, but the polyester (**7d**) with more linear PEPT structure linking the octamethylene chain at the 4,4'-position was insoluble. Number-average molecular weights (M_n) and molecular-weight distributions (M_w/M_n) for the polymers **7a-7c**, obtained by SEC measurements with chloroform as an eluent, were 4000–6300 and 1.38–1.70, respectively. The M_n for the polymer **7d** could not be measured by the SEC method using chloroform. The inherent viscosity (η_{inh}) for polymer **7d** was 0.31 dl g⁻¹ at a concentration of 0.2 g dl⁻¹ in DCAA at 30°C. The other polymers (**7a-7c**) had η_{inh} values of 0.29–0.44 dl g⁻¹. The synthetic data for polyesters **7a-7d** are listed in table 1.

The structures of the resulting polyesters (**7a-7d**) having the PEPT moieties were confirmed with FTIR and ¹H NMR spectroscopies and elemental analyses. The FTIR spectra of polymers **7a-7d** showed absorption bands of ester C=O at 1754 cm⁻¹, CH stretching at around 2926 and 2852 cm⁻¹, C=C at 1603 cm⁻¹ and C-O-C at 1135–1150 and 1209–1257 cm⁻¹ together with

the absorptions of thiadiazole at 1410–1414 cm⁻¹, whereas those of OH stretching at 3281–3443 cm⁻¹ for the monomers (**5a-5d**) disappeared. In the ¹H NMR spectra of polyesters **7a-7d** in CDCl₃ or in TFAA(v)/CDCl₃(v)=1/3, proton signals of trans CH=CH and aromatic rings at 6.97–8.02 ppm, –OC(O)CH₂ at 2.27–2.64 ppm and CH₂ chains at 1.22–1.44 ppm and 1.64–1.82 ppm were observed. The elemental analysis values of polyesters **7a-7d** were in agreement with the calculated ones, as shown in table 1. These results suggest production of the expected semirigid polyesters **7a-7d** composed of the PEPT and octamethylene chain.

2.2. LC properties

Thermal and mesogenic properties of polyesters **7a-7d** were examined by differential scanning calorimetry (DSC) measurements, polarizing microscope observations and powder X-ray analyses, because they are expected to form thermotropic LC phases owing to the

Table 1. Synthetic data for polyesters **7a-7d**.

Polymer	Yield/%	η_{inh}^a /dl g ⁻¹	M_n^b	M_w/M_n^b	Elem. Anal./%			
					C	H	N	
7a ^c	96	0.29	4100	1.38	Calc.	67.80	5.26	6.08
					Found	67.20	5.80	5.51
7b ^c	81	0.44	6300	1.65	Calc.	67.80	5.26	6.08
					Found	66.34	5.84	5.05
7c ^c	79	0.29	4000	1.70	Calc.	67.80	5.26	6.08
					Found	66.63	6.08	5.14
7d ^c	71	0.31			Calc.	67.80	5.26	6.08
					Found	66.09	5.95	5.18

^aInherent viscosity measured at a concentration of 0.2 g dl⁻¹ in DCAA at 30°C. ^bMeasured in chloroform with polystyrene as a standard; M_n =number-average molecular weight, M_w/M_n =molecular-weight distribution. ^c(C₂₆H₂₄N₂O₄S)_n [formula weight=(460.6)_n].

presence of rigid-rod PEPT moiety and flexible octamethylene chain in the repeating units, although the rigid-rod and conjugated PEPT unit is shorter than the BPET moiety.

The DSC curves on the first and the second heating runs indicated that the polymers (**7a–7c**) show one or two endothermic peaks due to a solid-to-solid transition (T_k) (148°C (**7b**) and 132°C (**7c**)) and melting (T_m) (158°C (**7a**), 168°C (**7b**) and 158°C (**7c**)), together with one exotherm for crystallization (T_c) (126°C (**7a**), 113°C (**7b**) and 102°C (**7c**)) and glass transition (T_g) (41°C (**7a**), 55°C (**7b**) and 37°C (**7c**)). On cooling, broad and ambiguous exotherms attributed to the isotropic-to-LC phase transition (T_i) (131°C (**7b**) and 119°C (**7c**)) and LC phase-to-solid transition (T_{LCS}) (105°C (**7b**) and 77°C (**7c**)) were observed in polymers **7b** and **7c**. Emergence of monotropic LC phase (fine texture) was confirmed between T_i and T_{LCS} for polymers **7b** and **7c** by polarizing microscope observations, but it was difficult to identify their mesophases. Therefore, the LC phases of polymers **7b** and **7c** between T_i and T_{LCS} were identified by X-ray diffraction analyses, as described subsequently. Their LC temperature ranges (ΔT) were 26°C (**7b**) and 42°C (**7c**). Polymer **7a** melted without showing a LC phase.

On the other hand, the DSC curve of polymer **7d** displayed an endothermic peak based on T_m at 218°C, but a T_i transition could not be detected up to 300°C on heating. On cooling, two exotherms due to the broad ($T_i=234^\circ\text{C}$) and sharp ($T_{LCS}=193^\circ\text{C}$) transitions were detectable. Polarizing microscope observations indicated that the polymer **7d** forms enantiotropic Schlieren texture above T_m (218°C) on heating and between T_i and T_{LCS} on cooling. The ΔT was over 82°C and the T_g step was at 30°C. The polarizing microphotograph for polymer (**7d**) at 240°C on heating is portrayed in figure 1. The phase transition and thermodynamic data are summarized in table 2.

In the powder X-ray diffraction patterns of polymers **7b–7d** in figure 2, which have LC phases retained on quenching, polymers **7b** and **7c** show sharp reflections at middle angles, $2\theta=3.48^\circ$ (**7b**) and 3.63° (**7c**), together

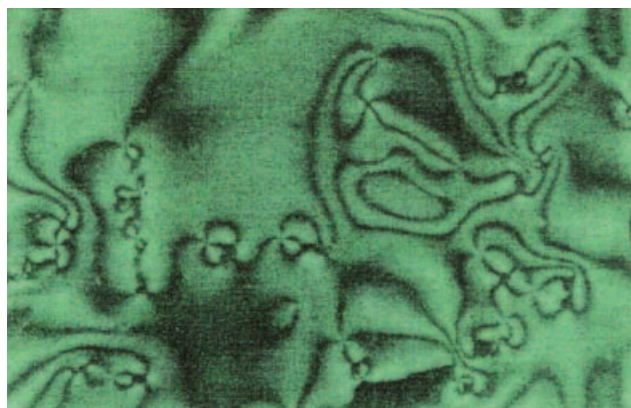


Figure 1. Polarizing microphotograph for polyester **7d** at 240°C on heating (magnification: $\times 200$).

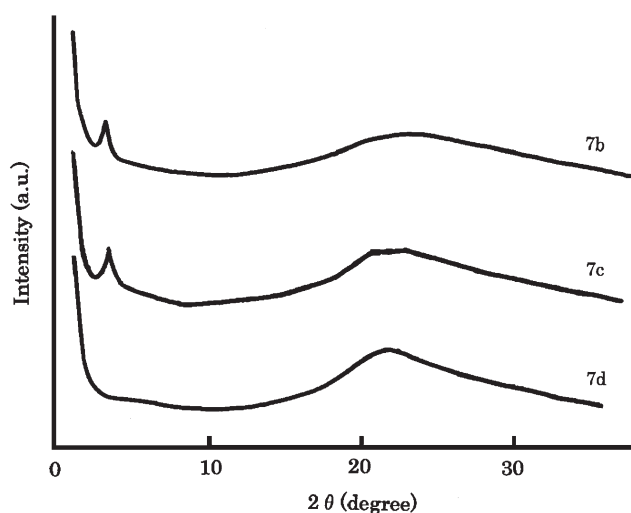


Figure 2. Powder X-ray diffraction patterns of polyesters **7b–7d**.

with broad reflections at wide angles around $2\theta=22\text{--}23^\circ$, although few reflections due to crystallization coexist in polymer **7c**. The d spacing values of the polymers **7b** and **7c**, calculated from the middle angles, are 25.4 Å and 24.3 Å, respectively, which are consistent

Table 2. Phase transition temperatures and thermodynamic data for polyesters **7a–7d** observed on the second heating scans. T_g =glass transition temperature, T_c =crystallization temperature on heating, T_{LCS} =LC phase-to-solid transition temperature on cooling, T_k =solid-to-solid transition temperature, T_m =melting temperature, T_i =isotropization temperature on heating or isotropization-to-LC phase transition temperature on cooling, $\Delta T=T_i-T_m$ or T_i-T_c (temperature range of mesophase).

Polymer	$T_g/^\circ\text{C}$	$T_c/^\circ\text{C}$	$T_{LCS}/^\circ\text{C}$	$T_k/^\circ\text{C}$	$T_m/^\circ\text{C}$	$\Delta H_m/\text{Jg}^{-1}$	$T_i/^\circ\text{C}$	$\Delta H_i/\text{Jg}^{-1}$	$\Delta T/^\circ\text{C}$
7a	41	126		126	158	10.0			
7b	55	113	(105) ^a	148	168	2.43	(131) ^a	(1.27) ^a	(26) ^a
7c	37	102	(77) ^a	132	158	8.62	(119) ^a	(7.96) ^a	(42) ^a
7d	30				218	7.18	>300		>82

^aObserved on the first cooling scans (monotropic smectic phase). ^bEnantiotropic nematic phase.

Table 3. X-ray data of polymers **7a–7d** quenched from the LC state between T_m and T_i .

Polymer	$2\theta/^\circ$	d Spacing/ \AA	Molecular length/ \AA	Mesophase
7a			27.6	No LC
7b	3.48	25.4	27.2	Frozen smectic
7c	3.63	24.3	27.2	Frozen smectic
7d			26.6	Frozen nematic

^aLength of polymer repeating unit.

with or shorter than the estimated molecular lengths (27.2 \AA) for repeating units of the polymers **7b** and **7c** (see table 3). The X-ray patterns for polymers **7b** and **7c** suggest that the mesophases are ordered LC phases (smectic A and C). Polymer **7d** exhibited no sharp reflections at the middle or small angles except for broad reflection at the wide angle near $2\theta=22^\circ$, which is a typical X-ray pattern for less ordered LC phase, showing the formation of nematic phase in the polymer **7d**.

Molecular alignments of the polymers (**7b–7d**) quenched from the LC state were evaluated from polarized absorption spectra. Table 4, which lists R_A (dichroic ratio) and S (order parameter) values for polymers **7b–7d**, indicates that the absorbances parallel to shearing direction (A_{\parallel}) is almost the same as that perpendicular to the shearing direction (A_{\perp}). The R_A and the S values are lower than those for LC polymers having side-chain OXD chromophores [20] and previously reported semirigid main-chain LC polyesters [10, 11]. This means that the PEPT groups are poorly aligned to the shearing direction in the LC state. It is probably due to the disturbed geometry of molecular long axis on the basis of the phenyl ring in the phenylstilbene unit.

From these results it is suggested that some semirigid polyesters composed of the PEPT moiety and octamethylene chain form thermotropic enantiotropic or monotropic LC phase (nematic or smectic), depending on the disubstituted positions of PEPT linking the octamethylene chain in the repeating units; polymer **7d**

Table 4. Dichroic ratios (R_A) and order parameters (S) estimated from absorbances, and dichroic ratios (R_I) from fluorescent intensities of polymers **7b–7d** quenched from the LC states. ($R_A=A_{\parallel}/A_{\perp}$, $S=(R_A-1)/(R_A+2)$, $R_I=I_{\parallel}/I_{\perp}$).

Polymer	R_A	S	R_I
7b	1.17	0.05	1.15
7c	1.07	0.02	1.17
7d	1.11	0.03	1.51

composed of the 4,4'-PEPT moiety having the most linear structure formed enantiotropic nematic LC phase. Polymers **7b** and **7c**, having a less linear molecular structures (3,4'- or 4,3'-PEPT moiety) showed a frozen monotropic smectic phase. Polymers **7a** composed of the 3,3'-PEPT unit with bent molecular structure had no LC melt. These facts indicate that liquid crystal formation in polymers **7a–7d** is consistent with those in the aforementioned semirigid polyesters containing the DPTD moieties, which decreased in the order of 4,4'-DPTD > 3,4'-DPTD > 3,3'-DPTD [10, 11]. In addition, polymers **7a–7d** tend to form less ordered LC phases and to exhibit low LC properties compared with the polymers made up of the BPET moieties, probably due to the asymmetric structures of the PEPT moieties [16, 17] and their poor alignment in the LC phases on the basis of the substituted phenyl group on the PEPT units, as shown in table 4.

2.3. Optical properties

The absorption and emission spectra of polymers **7a–7d** in solution and in the solid state were examined. UV-visible spectra of polymers in chloroform (**7a–7c**) and in a mixture of chloroform (90% (v)/(v)) and DCAA (10%(v/v)) solutions (**7d**) were normalized to absorption peak maxima at 335.5–344.0 nm associated with the $\pi-\pi^*$ electron transition of the PEPT unit, whose peak maxima were shifted to longer wavelengths in the following order: **7a** < **7b** < **7c** < **7d**. Their molar absorption coefficients ($\log \epsilon$) were 4.49–4.91 and energy band gaps (E_g) calculated from extrapolated absorption edges of the UV-visible spectra were 3.06–3.16 eV. The PL spectra of polymers **7a–7d** in solution, excited at the absorption maxima of 335.5–344.0 nm, displayed blue-emitting peak maxima at 406.0–415.5 nm based on the PEPT unit, the Stokes shifts being 70.5–75.5 nm. The peak maxima have a tendency of shift into longer wavelengths in the order of **7a** < **7b** < **7c** \approx **7d**, as well as those for the absorption spectra. Quantum efficiencies of polymers **7a–7c**, however, were lower than those for the polyesters composed of the BPET [16, 17], the DPTD [11, 12] and poly(*p*-phenylenevinylene)s [24, 25] containing OXD. In the polymer **7d**, the value was recognized with difficulty.

The solid-state UV-visible spectra of polymers **7a–7d** displayed maximum absorbances at 328.5–340.5 nm. In the PL spectra in the solid state, when the polymers **7a–7d** were excited at 328.5–340.5 nm, peak maxima were observed at 419.0–447.0 nm with blue emissions, which were Stokes shifted by 78.5–111.5 nm and were shifted to lower energies than the data from the solutions, perhaps due to intermolecular aggregation effects [26].

Figures 3 and 4 show the solid-state UV-visible and PL spectra of polymers **7a–7d**, respectively. Table 5 tabulates the UV-visible and fluorescent spectral data for the polymers in solution and in the solid state.

These data suggest that polymers **7a–7d** have solution and solid-state UV-visible absorption spectra, on the basis of π - π^* electron transition of the PEPT moiety, at the shorter wavelengths than the polyesters built up of the BPET moieties [16, 17] and at the longer wavelengths than the polymers with the DPTD [11, 12], as expected from the molecular structure of PEPT. However, the fluorescent properties of polyesters **7a–7d**, emitting blue light, are poorer than those for the above-described polymers containing the BPET and the DPTD units [9–12, 16, 17]. Two reasons why weak fluorescent behaviours are observed in these polymers are presumed. The one is owing to intermolecular quenching between the PEPT units on the basis of the asymmetric rigid-rod structures and cis–trans isomerism of the PEPT rings, which might bring changes of HOMO and LUMO levels on excited states. Another one is that excited photons are quenched by terminal phenolic OH groups in the polymer chains, because the M_n values of the polymers are not so high. In the present case, it is probably due to the intermolecular quenching between the PEPT units, because the quantum efficiency of the 4,4'-dimethoxy derivative of

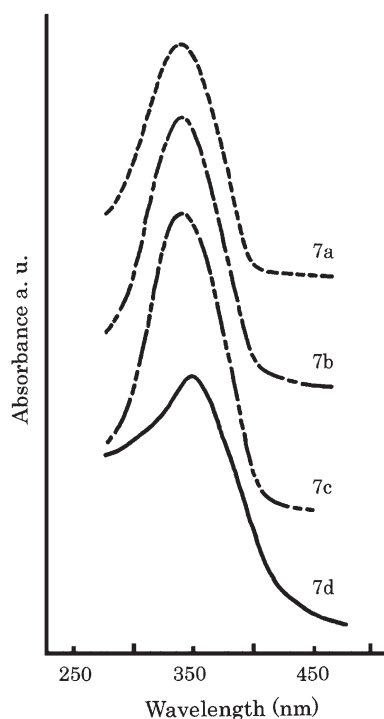


Figure 3. Solid-state UV-visible spectra of polyesters **7a–7d**.

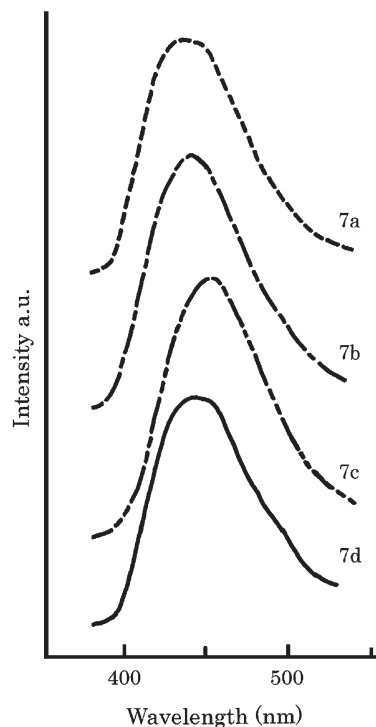


Figure 4. Solid-state PL spectra of polyesters **7a–7d**.

PEPT (**5d**) in chloroform is as low as those for the polymers **7a–7c**.

2.4. Polarized fluorescence in LC states

Polarized fluorescent spectra of the polymers (**7b–7d**) with frozen LC phases retained by quenching (rapid cooling) from the LC states below room temperature are measured and the dichroic ratios (R_I) are presented in table 4, which shows that these polymers emit polarized fluorescent blue light at room temperature, although their intensities of fluorescence polarized parallel to the shearing direction (I_{\parallel}) in the LC states are almost the same as those polarized perpendicular to the shearing direction (I_{\perp}) and the R_I values are very low (1.15–1.51) at 435–447 nm. The value of polymer **7d** is higher than those in polymers **7b** and **7c**. This might be due to the fact that polymer **7d** tends to crystallize on the measurements of R_I values and on being kept at room temperature.

3. Conclusions

1. The LC formation of semirigid polyesters composed of PEPT moieties and an octamethylene chain depend on the polymer repeating unit structures: the polymer containing the 4,4'-PEPT with the most linear molecular structure formed an enantiotropic nematic LC phase and the polymers

Table 5. Solution and solid-state UV-visible and PL spectral data for polyesters **7a–7d**.

Polymer	Solution ^a				Solid state			
	$\lambda_{\max, \text{abs}}/\text{nm}$	$\log \epsilon$	$\lambda_{\max, \text{PL}}/\text{nm}$	E_g^b/eV	Φ^c	$\lambda_{\max, \text{abs}}/\text{nm}$	E_g/eV	$\lambda_{\max, \text{PL}}/\text{nm}$
7a	335.5	4.55	406.0	3.10	0.04	340.5	3.08	419.0
7b	336.0	4.81	408.0	3.16	0.04	340.5	3.09	435.0
7c	340.0	4.91	415.5	3.12	0.04	340.5	3.05	447.0
7d ^d	344.0	4.49	415.0	3.06		328.5	3.02	440.0

^aIn chloroform. ^bBand gap energy calculated from UV-visible spectra. ^cQuantum efficiency determined by using coumarin 311 as a standard. ^dIn chloroform (90% (v/v))+DCAA (10% (v/v)) solution.

composed of the 3,4'-, 4,3'- and 3,3'-PEPT moieties with less linear structures showed frozen monotropic smectic phase or no LC phase.

- The polyesters absorbed UV-visible light and fluoresced blue light based on the PEPT moiety in solution and in the solid state, but low or no quantum efficiencies of fluorescence were detected, probably due to intermolecular quenching between the PEPT moieties. Among the polymers, the polyesters having more linear PEPT structure tended to show the absorption and the fluorescent peak maxima at longer wavelengths. They emitted polarized fluorescent light at room temperature, but the intensities were low.

4. Experimental

4.1. Materials

3-Methoxycinnamic acid (**1a**), 4-methoxycinnamic acid (**1b**), *m*-anisic hydrazide (**2a**), triphenyl phosphite, Lawesson's reagent, sebacoyl chloride (**6**), hydrobromic acid and tetra-*n*-butylammonium bromide (TBAB) were used as received. *p*-Anisic hydrazide (**2b**) was synthesized by the reaction of *p*-anisic acid ethyl ester with hydrazine monohydrate (yield 71%, m.p. 138.7–139.4°C). NMP and *N,N*-dimethylformamide (DMF) were used after purification by vacuum distillation.

4.2. Monomer synthesis

4.2.1. 2-[2-(3-Methoxyphenyl)ethenyl]-5-(3-methoxyphenyl)-1,3,4-thiadiazole (4a). A mixture of *m*-anisic hydrazide (**2a**) (0.06 mol, 9.97 g) and triphenylphosphite (0.12 mol, 37.23 g) was added into NMP (400 ml) including LiCl (0.26 mol, 11.02 g). To this solution, 3-methoxycinnamic acid (**1a**) (0.06 mol, 10.69 g) was added and the reaction solution was heated at 120°C for 5 h in a nitrogen atmosphere. After the reaction, the solution was cooled to room temperature and poured into water to precipitate the intermediate hydrazide derivative (**3a**). The precipitated solid (**3a**) was washed thoroughly with water, filtered off,

recrystallized from methanol twice and dried at 60°C under vacuum for 24 h. Subsequently, the intermediate hydrazide (**3a**) (0.025 mol, 8.16 g) was refluxed in 1,4-dioxane (40 ml) in the presence of Lawesson's reagent (0.035 mol, 14.16 g) for 3 h. After the reaction, the solution was poured into an excess of 1M NaOH solution containing ice and held at room temperature. The precipitate was filtered off, washed thoroughly with water and methanol. The obtained product (**4a**) was recrystallized from ethanol three times and dried at 60°C for one day in vacuo. Yield: 48%, m.p. 124.5–126.5°C. (C₁₈H₁₆N₂O₂S) (324.4) Calcd. C 66.63, H 4.98, N 8.64%; found C 66.41, H 4.96, N 8.38%. FTIR (KBr): 2961, 2837 (CH stretching), 1594, (C=C), 1407 (thiadiazole), 1270, 1040 cm⁻¹ (C-O-C). ¹H NMR (CDCl₃): δ 7.08–7.60 (10H, m), 3.87 (3H, s), 3.77 ppm (3H, s).

The other dimethoxy derivatives (**4b–4d**) of PEPT were synthesized according to the same methods as those for compound **4a**.

4.2.2. 2-[2-(3-Methoxyphenyl)ethenyl]-5-(4-methoxyphenyl)-1,3,4-thiadiazole (4b). Yield: 63%, m.p.: 137.5–138.5°C. (C₁₈H₁₆N₂O₂S) (324.4) Calcd. C 66.63, H 4.98, N 8.64%; found C 66.39, H 4.82, N 9.06%. FTIR (KBr): 2967, 2831 (CH stretching), 1599 (C=C), 1411 (thiadiazole), 1257, 1027 cm⁻¹ (C-O-C). ¹H NMR (CDCl₃): δ 6.89–7.94 (10H, s), 3.86 (3H, s), 3.84 ppm (3H, s).

4.2.3. 2-[2-(4-Methoxyphenyl)ethenyl]-5-(3-methoxyphenyl)-1,3,4-thiadiazole (4c). Yield: 72%, m.p. 130–131°C. (C₁₈H₁₆N₂O₂S) (324.4) Calcd. C 66.63, H 4.98, N 8.64%; found C 66.66, H 4.98, N 8.50%. FTIR (KBr): 2973, 2838 (CH stretching), 1602 (C=C), 1250, 1015 cm⁻¹ (C-O-C). ¹H NMR (CDCl₃): δ 6.90–7.59 (10H, m), 3.88 (3H, s), 3.83 ppm (3H, s).

4.2.4. 2-[2-(4-Methoxyphenyl)ethenyl]-5-(4-methoxyphenyl)-1,3,4-thiadiazole (4d). Yield: 63%, m.p. 290.0–290.5°C. (C₁₈H₁₆N₂O₂S) (324.4) Calcd. C 66.63, H 4.98, N 8.64%; found C 66.70, H 5.07, N 8.61%. FTIR (KBr): 2962, 2837 (CH stretching), 1302 (C=C),

1404 (thiadiazole), 1241, 1027 cm^{-1} (C-O-C). ^1H NMR (CDCl_3): δ 6.90–7.94 (10H, m), 3.86 (3H, s), 3.84 ppm (3H, s).

4.2.5. 2-[2-(3-hydroxyphenyl)ethenyl]-5-(3-hydroxyphenyl)-1,3,4-thiadiazole (5a). The dimethoxy compound (**4a**) (0.018 mol, 5.84 g) was heated in refluxing hydrobromic acid (270 ml) for 3 h. The solution was poured into an excess of water, and the precipitated solid was collected by filtration and dissolved in 1M NaOH solution. Then the aqueous solution was acidified with acetic acid to precipitate the dihydroxy compound (**5a**). The precipitated solid (**5a**) was filtered off, washed with water, recrystallized from DMF twice and dried at 60°C for one day in vacuo. Yield: 77%, m.p. 275–277°C. ($\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$) (296.4) Calcd. C 64.84, H 4.09, N 9.45%; found C 64.92, H 4.22, N 9.25%. FTIR (KBr): 3443 (OH stretching), 1594 (C=C), 1215, 1082 cm^{-1} (C-O-C). ^1H NMR ($\text{DMSO}-d_6$): δ 9.80 (2H, s), 6.82–7.60 ppm (10H, m).

The other dihydroxy derivatives (**5b–5d**) of PEPT were prepared by a similar procedure to that for dihydroxy compound **5a**.

4.2.6. 2-[2-(3-hydroxyphenyl)ethenyl]-5-(4-hydroxyphenyl)-1,3,4-thiadiazole (5b). Yield: 65%, m.p. 306–309.5°C. ($\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$) (296.4) Calcd. C 64.84, H 4.09, N 9.45%; found C 63.02, H 4.79, N 8.71%. FTIR (KBr): 3440, (OH stretching), 1610 (C=C), 1417 (thiadiazole), 1224, 1083 cm^{-1} (C-O-C). ^1H NMR ($\text{DMSO}-d_6$): δ 10.32 (1H, s), 9.70 (1H, s), 6.82–7.95 ppm (10H, m).

4.2.7. 2-[2-(4-hydroxyphenyl)ethenyl]-5-(3-hydroxyphenyl)-1,3,4-thiadiazole (5c). Yield: 68%, m.p. 316.5–318°C. ($\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$) (296.4) Calcd. C 64.84, H 4.09, N 9.45%; found C 64.31, H 4.25, N 9.12%. FTIR (KBr): 3347 (OH stretching), 1604 (C=C), 1201, 1077 cm^{-1} (C-O-C). ^1H NMR ($\text{DMSO}-d_6$): δ 9.97 (1H, s), 9.95 (1H, s), 6.683–7.62 ppm (10H, m).

4.2.8. 2-[2-(4-hydroxyphenyl)ethenyl]-5-(4-hydroxyphenyl)-1,3,4-thiadiazole (5d). Yield: 62%, m.p. 204.5–206.7°C. ($\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$) (296.4) Calcd. C 64.84, H 4.09, N 9.45%; found C 63.97, H 4.67, N 8.64%. FTIR (KBr): 3006 (OH stretching), 1604 (C=C), 1415 (thiadiazole), 1240, 1074 cm^{-1} (C-O-C). ^1H NMR ($\text{DMSO}-d_6$): δ 9.97 (2H, s), 6.82–7.93 ppm (10H, m).

4.3. Synthesis of polymers (7a–7d)

A typical procedure for the polyester **7a** is described. The monomer (**5a**) (0.5 mmol, 0.148 g) was dissolved in aqueous NaOH solution (3 ml), where NaOH (1 mmol)

is dissolved in water (3 ml). To this solution, TBAB (2 wt % of polymer yield) was added as a phase-transfer catalyst. Subsequently, sebacoyl chloride (**6**) (0.5 mmol, 0.120 g) was dissolved in chloroform (5 ml). Then the chloroform solution was quickly added to the aqueous NaOH solution and vigorously stirred for 30 min. After the reaction, acetone was added to this mixture and the resulting solution was poured into an excess of water to precipitate the expected polymer (**7a**). The precipitated solid was filtered off, washed thoroughly with water, cooled and refluxed with methanol three times and dried at 60°C for 24 h at a reduced pressure. Yield: 96%.

4.4. Measurements

FTIR, ^1H NMR, UV-visible and fluorescent spectroscopies, molecular weight, inherent viscosity and DSC measurements, polarizing microscope observations and powder X-ray analyses were carried out according to the methods described in previous papers [9–18]. Order parameters (S) were evaluated from the polarized absorption spectra of polymer samples measured with a polarizer. Aligned samples for solid-state polarized absorption and emission spectroscopies were prepared by quenching the sheared polymers from the LC states.

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