Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Thermotropic liquid crystalline polymers containing five-membered heterocyclic groups VIII. Synthesis, and liquid crystalline and photoluminescent properties of semi-rigid polyesters based on a distyrylbenzene analogue of 1,3,4-thiadiazole

Moriyuki Sato; Rena Ohta; Makoto Handa; Kuninobu Kasuga

To cite this Article Sato, Moriyuki , Ohta, Rena , Handa, Makoto and Kasuga, Kuninobu(2002) 'Thermotropic liquid crystalline polymers containing five-membered heterocyclic groups VIII. Synthesis, and liquid crystalline and photoluminescent properties of semi-rigid polyesters based on a distyrylbenzene analogue of 1,3,4-thiadiazole', Liquid Crystals, 29: 11, 1441 — 1446

To link to this Article: DOI: 10.1080/0267829021000033363

URL: http://dx.doi.org/10.1080/0267829021000033363

LIQUID CRYSTALS, 2002, VOL. 29, NO. 11, 1441–1446

Taylor & Francis
Taylor & Francis Group

Thermotropic liquid crystalline polymers containing five-membered heterocyclic groups
VIII. Synthesis, and liquid crystalline and photoluminescent properties of semi-rigid polyesters based on a distyrylbenzene analogue of 1,3,4-thiadiazole†

MORIYUKI SATO*, RENA OHTA, MAKOTO HANDA and
KUNINOBU KASUGA

Department of Material Science, Faculty of Science and Engineering,
Shimane University, 1060 Nishikawatsu, Matsue-shi, Shimane 690-8504, Japan

(*Received 29 April, 2002; accepted 24 June, 2002*)

New semi-rigid polyesters composed of the distyrylbenzene analogue of 1,3,4-thiadiazole, 2,5-bis(2-phenylethenyl)-1,3,4-thiadiazole and aliphatic (dodeca-, deca- and octamethylene) chains were prepared by high temperature solution polycondensation; their liquid crystalline (LC) and photoluminescent properties were investigated. Differential scanning calorimetry, polarizing microscopy and powder X-ray diffraction show that the polyesters having both dodeca- and decamethylene chains form a thermotropic smectic C phase and a lyotropic LC phase in trifluoroacetic acid, but the polyester containing octamethylene chains only exhibits a thermotropic smectic C phase. Solution and solid state absorption and fluorescent spectra indicate that all the polyesters in this work display absorption maxima based on the 2,5-bis(2-phenylethenyl)-1,3,4-thiadiazole moiety, emitting blue light in HFIP solutions and bluish-green light in solids; the Stokes shifts are 80.1–80.7 nm in solution and 74.2–87.2 nm in the solid state.

1. Introduction

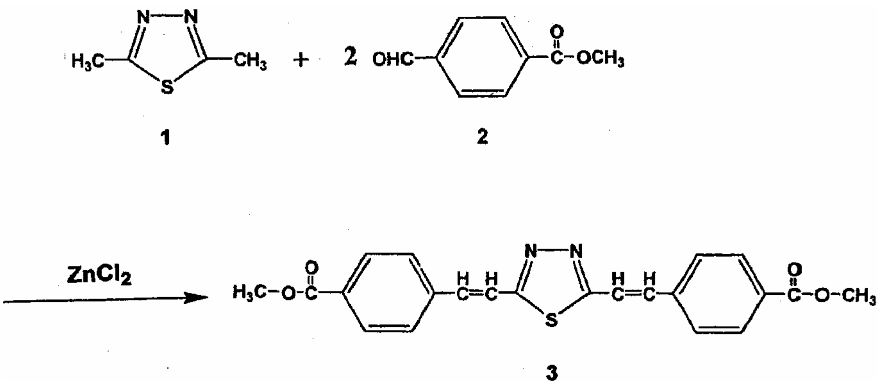
There is a considerable body of research concerning conjugated polymers [1–3] composed of heterocyclic units such as carbazoles, thiophenes and 1,3,4-oxadiazoles, and aromatic rings. These polymers have application potential as light-emitting and charge-transporting materials in organic electroluminescent (EL) diodes [1–10], following the discovery that poly(*p*-phenylenevinylene) (PPV) could be used as the emitting layer in EL devices [11]. In recent years, polymers comprising well defined and partially conjugated structures such as the distyrylbenzene unit, acting as the light-emitting material, and aliphatic spacer blocks in the main chain, have attracted much attention as organic materials for EL devices because they emit blue or bluish-green light at short and defined wavelengths [12–14]. Our previous articles reported the preparation and fluorescent properties of conjugated polymers containing dialkoxybenzenes and the 1,3,4-thiadiazole ring [15]; this is analogous to 1,3,4-oxadiazole, being a five-membered heterocycle, of low molecular mass compounds [16] and of aromatic-aliphatic polyesters [17, 18] built from well defined quaterphenyl and terphenyl analogues of 1,3,4-thiadiazole. They were found to show photoluminescent (PL) and EL properties and to be light-emitting and electron-transporting materials for EL devices. Among these, the polyesters containing terphenyl and quaterphenyl analogues of 1,3,4-thiadiazole were found not only to emit blue and bluish-green PL light as solids [17, 18], but also to form stable liquid crystalline (LC) thermotropic smectic mesophases, even though the 1,3,4-thiadiazole unit has a bent molecular structure [19, 20].

The purpose of this work was to prepare new semi-rigid light emitting and LC polyesters **5a–c** by the high temperature solution polycondensation of a dimethyl ester derivative of a distyrylbenzene analogue having the 1,3,4-thiadiazole ring in the centre (2,5-bis[2-(4-methoxycarbonylphenyl)ethenyl]-1,3,4-thiadiazole), **3** with three aliphatic diols **4a–c** (**4a**: $m=12$, **4b**: $m=10$, **4c**: $m=8$) (schemes 1 and 2) and to investigate their LC and PL properties. It was expected that the polyesters **5a–c** would show both thermotropic and lyotropic LC phases in addition to PL properties with blue or bluish-green

---

*Author for correspondence;
e-mail: msato@riko.shimane-u.ac.jp
†For part VII see reference [18]

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290210000333363



Scheme 1.

emission based on the distyrylbenzene analogue of 1,3,4-thiadiazole, 2,5-bis(2-phenylethenyl)-1,3,4-thiadiazole, in solution and as solids, owing to their linear, rigid-rod, well defined and partially conjugated units in the main chain, although they show no intermolecular interactions such as hydrogen bonding as seen for amide linkages [21, 22].

2. Synthesis of monomer 3

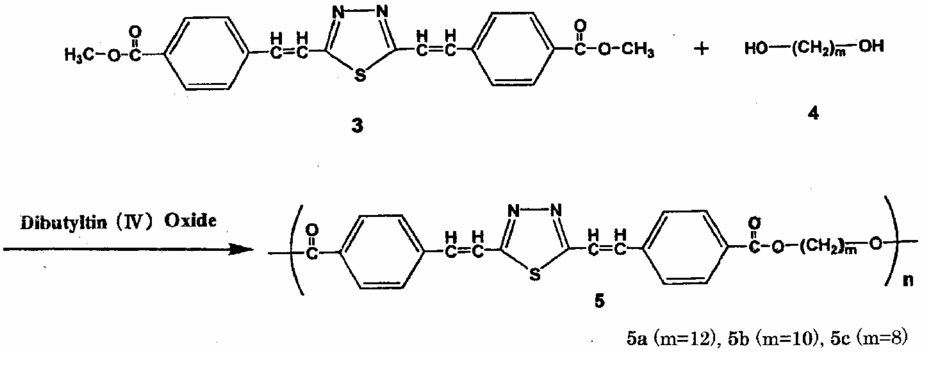
2,5-Dimethyl-1,3,4-thiadiazole 1, methyl 4-formylbenzoate 2, zinc chloride and di-n-butyltin oxide were commercially available and used as received. 1,12-Dodecanediol 4a, 1,10-decanediol 4b and 1,8-octanediol 4c were recrystallized from methanol before use. Trifluoroacetic acid (TFAA), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), N,N-dimethylformamide (DMF) and 1-chloronaphthalene were purified by vacuum distillation.

2,5-Dimethyl-1,3,4-thiadiazole 1 (0.02 mol, 2.283 g) and methyl 4-formylbenzoate 2 (0.04 mol, 6.566 g) were reacted at 180°C for 4 h in the presence of zinc chloride (0.005 mol, 0.706 g) under a nitrogen atmosphere. The by product, water, was removed under reduced pressure every 30 min. After the reaction, the solid obtained was dissolved in TFAA (6 ml) and the solution poured into methanol to precipitate the product. The yellow solid was filtered off, recrystallized three times from DMF and dried at 60°C for 24 h under vacuum; yield 43%, m.p. 252.5–254°C. FTIR (KBr): $\nu = 2958$ (CH stretching), 1722 (ester C=O), 1604 (C=C), 1403 (thiadiazole ring), 1207 cm^{-1} (C−O−C). ^{13}C NMR (67.8 MHz, TFAA/CDCl$_3$ = 1/3(v/v)): $\delta = 169.0$ (ester C−O), 168.7 (carbons at 2,5-positions of 1,3,4-thiadiazole), 144.8, 131.8, 130.7, 128.6 (benzene), 138.2 (−*C*H=CHC$_6$H$_4$−), 115.6 (−CH=*C*HC$_6$H$_4$−), 53.3 ppm (CH$_3$). UV (in HFIP): $\lambda_{max} = 345.0$ nm ($\log \varepsilon = 4.55$). $C_{22}H_{18}N_2O_4S$ (406.5): calc. C 65.00, H 4.47, N 6.89; found C 65.10, H 4.58, N 6.63%.

3. Polymerization

A typical polycondensation method for polymer 5c is described. The monomer 3 (0.75 mmol, 0.285 g) and 1,8-octanediol 4c (0.75 mmol, 0.110 g) were reacted at 190–195°C for 5 h in 1-chloronaphthalene in the presence of di-n-butyltin oxide (5 mg) under nitrogen. After the polymerization, the reaction mixture was dissolved in HFIP and the solution poured into methanol to reprecipitate polymer 5c. The precipitate was collected by filtration, washed thoroughly with water and refluxing methanol three times. The polymer 5c obtained was dried at 60°C for 24 h under vacuum; yield 88%, $\eta_{inh} = 0.61$ dl g^{-1}. $(C_{28}H_{28}N_2O_4S)_n$ $(488.7)_n$: calc. C 68.82, H 5.79, N 5.73; found C 68.18, H 5.77, N 5.26%.

Polymers 5a and 5b were prepared by the same method described.



Scheme 2.

5a: yield 79%, $\eta_{\mathrm{inh}} = 0.34$ dl g^{-1}. $(C_{32}H_{36}N_2O_4S)_n$ $(544.8)_n$: calc. C 70.55, H 6.67, N 5.14; found C 69.97, H 6.53, N 4.99%.

5b: yield 98%, $\eta_{\mathrm{inh}} = 0.59$ dl g^{-1}. $(C_{30}H_{32}N_2O_4S)_n$ $(516.7)_n$: calc. C 69.73, H 6.25, N 5.42; found C 69.31, H 6.08, N 5.29%.

4. Characterization

Differential scanning calorimetry (DSC), hot-stage polarizing microscopy, powder diffraction X-ray analyses, FTIR and ^{13}C NMR spectroscopy, UV-Vis and PL spectrum measurements were carried out according to our published methods [15–18]. Inherent viscosity measurements were conducted at a concentration of 0.2 g dl^{-1} in HFIP at 30°C using an Ostwald viscometer.

5. Results and discussion

The solid-state condensation of compound **1** with benzaldehydes in the presence of zinc chloride or bases has been reported to afford distyrylbenzene analogues of 1,3,4-thiadiazole, 2,5-bis(2-phenylethenyl)-1,3,4-thiadiazoles [23]. Monomer **3**, having the 1,3,4-thiadiazole ring in the centre, was prepared in a yield of 43% from compound **1** and methyl 4-formylbenzoate **2**, in the presence of zinc chloride by this reaction. The expected structure of monomer **3** was confirmed using FTIR, ^{13}C NMR and UV spectroscopy, and elemental analysis.

The novel semi-rigid polyesters **5a–c** containing the distyrylbenzene analogue, comprising central 1,3,4-thiadiazole ring, 2,5-bis(2-phenylethenyl)-1,3,4-thiadiazole, and aliphatic chain blocks, were prepared by the high temperature solution polycondensation of monomer **3** with three aliphatic diols **4a–c** (1,12-dodecanediol **4a**, 1,10-decanediol **4b** and 1,8-octanediol **4c**) in 1-chloronaphthalene in the presence of di-*n*-butyltin oxide as catalyst. The yellow polymers, **5a–c**, which precipitated during the polycondensation were obtained in yields of 79–98%, and showed poor solubilities in organic solvents except, for example, TFAA, dichloroacetic acid (DCAA), and HFIP. The inherent viscosities of polymers **5a–c** measured at a concentration of 0.2 g dl^{-1} in HFIP at 30°C were 0.34–0.61 dl g^{-1}.

The polymers **5a–c** were characterized using FTIR and ^{13}C NMR spectroscopy and elemental analysis. The FTIR spectra of polymers **5a–c** showed characteristic absorption bands associated with CH stretching at 2852–2924 cm^{-1}, ester C=O at 1712 cm^{-1}, C=C at 1604 cm^{-1}, 1,3,4-thiadiazole at 1403 cm^{-1} and C–O–C at 1277 cm^{-1}. In the ^{13}C NMR spectra of polymer **5c** in TFAA/CDCl$_3$ = 1/3(v/v), signals associated with the ester C=O at 169.3 ppm, the 2- and 5-positions of 1,3,4-thiadiazole at 168.9 ppm, the benzene ring at 146.1, 132.4, 130.9 and 128.9 ppm, $-\mathit{C}H{=}CHC_6H_4-$ at 138.0 ppm, $-CH{=}\mathit{C}HC_6H_4-$ at 115.0 ppm, $-\mathit{C}H_2OC(O)-$ at 67.5 ppm and $-CH_2-$ at 29.2, 28.5 and 25.9 ppm were observed. The polymers **5a** and **5b** showed ^{13}C NMR spectra similar to that of **5c**. The elemental analysis data of polymers **5a–c** were in agreement with calculated values. These data confirm the successful syntheses of polymers **5a–c**.

The thermotropic and lyotropic LC properties of polymers **5a–c** were investigated by DSC, textural observations using a polarizing microscope equipped with a hot plate and powder X-ray diffraction. These measurements indicate that polymers **5a** and **5b** form both thermotropic smectic C phases and lyotropic LC phases in TFAA (at 15 wt%). Figure 1 shows the DSC curves of polymers **5a–c** for the second heating scans. In the second heating DSC curve of polymer **5a**, four endothermic peaks are present and assigned as solid–solid transitions (T_k) at 212 and 227°C, a solid–LC transition (T_m) at 235°C and the LC–isotropic (T_i) transition at 245°C. In addition, a glass transition was observed at 75°C (T_g). Only two endotherms were observed, at 196 and 244°C, on the first heating run. Polymers **5b** and **5c** both showed two endotherms in the first and second heating scans, associated with melting T_m (**5b**: 252°C, **5c**: 257°C) and clearing T_i (**5b**: 263°C, **5c**: 280°C) together a T_g (**5b**: 78°C, **5c**: 81°C). In the cooling runs, the corresponding two exotherms associated with the isotropic–LC (T_i) and LC–solid (T_c) transitions were observed. Phase transition data for the polymers **5a–c** are listed in table 1. The transition temperatures (T_g, T_m and T_i) and the LC temperature ranges tend to increase with decreasing lengths of aliphatic chains (m = 12, 10 and 8) in the polymer backbones.

Polarizing microscopy observations of the textures show that polymers **5a–c** form an enantiotropic LC phase (fine texture) between T_m and T_i, although the LC temperature ranges are narrow (ΔT = 10–23°C). The LC phase was characterized by powder X-ray diffraction. The powder patterns of polymers **5a–c** quenched from the LC phase are shown in figure 2. Sharp reflections in the middle angle region (2θ = 3.30° for **5a**, 3.60° for **5b**) and broad reflections at wide angles (2θ = 15–26°) together with reflections due to the crystal phase are observed in

Table 1. Transition temperatures (°C) of polyesters **5a–c**. Observed on the second heating scans; T_g = glass transition temperature, T_k = solid–solid transition temperature, T_m = solid–smectic C transition temperature, T_i = isotropization temperature, $\Delta T = T_i - T_m$ = LC temperature range.

Polymer	T_g	T_k	T_m	T_i	ΔT	LC phase
5a	75	212, 227	235	245	10	Smectic C
5b	78	—	252	263	11	Smectic C
5c	81	—	257	280	23	Smectic C

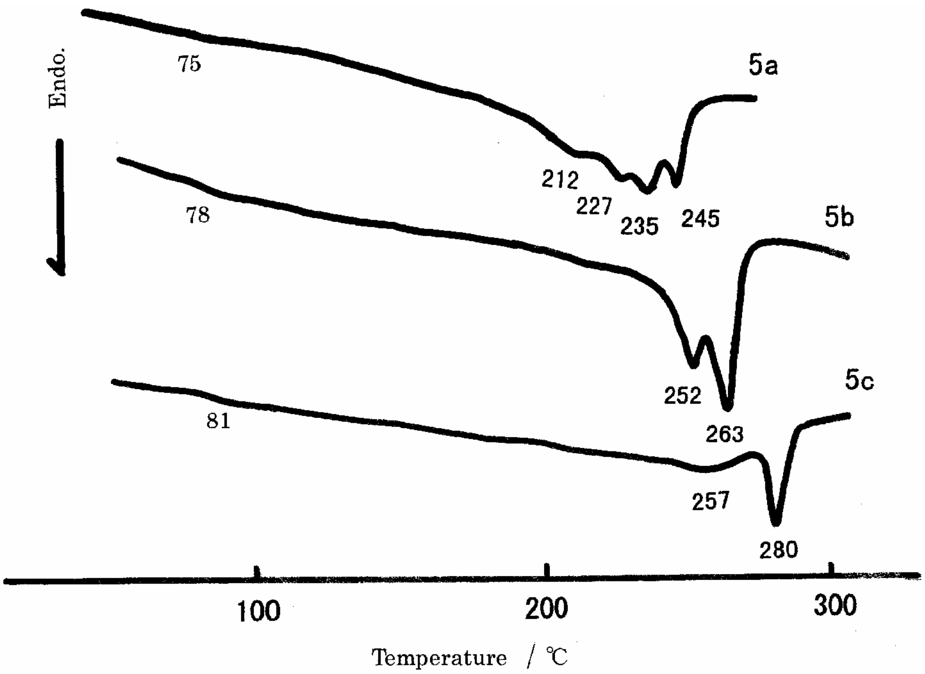


Figure 1. DSC curves of polyesters **5a–c** for the second heating runs.

the patterns of polymers **5a** and **5b**. The pattern of polymer **5c** contains a sharp reflection at $2\theta = 3.22^\circ$ and a broad reflection around $2\theta = 22^\circ$. These patterns suggest that the LC phase of polymers **5a–c** is a smectic C or A phase. As listed in table 2, the *d*-spacings calculated from the X-ray data are 26.8 Å (**5a**), 24.65Å (**5b**) and 27.4 Å (**5c**), and are shorter than the molecular lengths of the repeating units of the polymers, 36.1 Å (**5a**), 33.5 Å (**5b**) and 31.1 Å (**5c**). Therefore, the LC phase **5a–c** is assigned as a smectic C phase, although the crystal phase coexists with the LC phase in polymers **5a** and **5b**.

The lyotropic LC properties of polymers **5a–c** were evaluated at concentrations of 15, 20 and 25 wt % in TFAA, DCAA and HFIP. Polymers **5a** and **5b** formed a lyotropic LC phase at 15 wt % in TFAA despite the absence of intermolecular interactions such as hydrogen

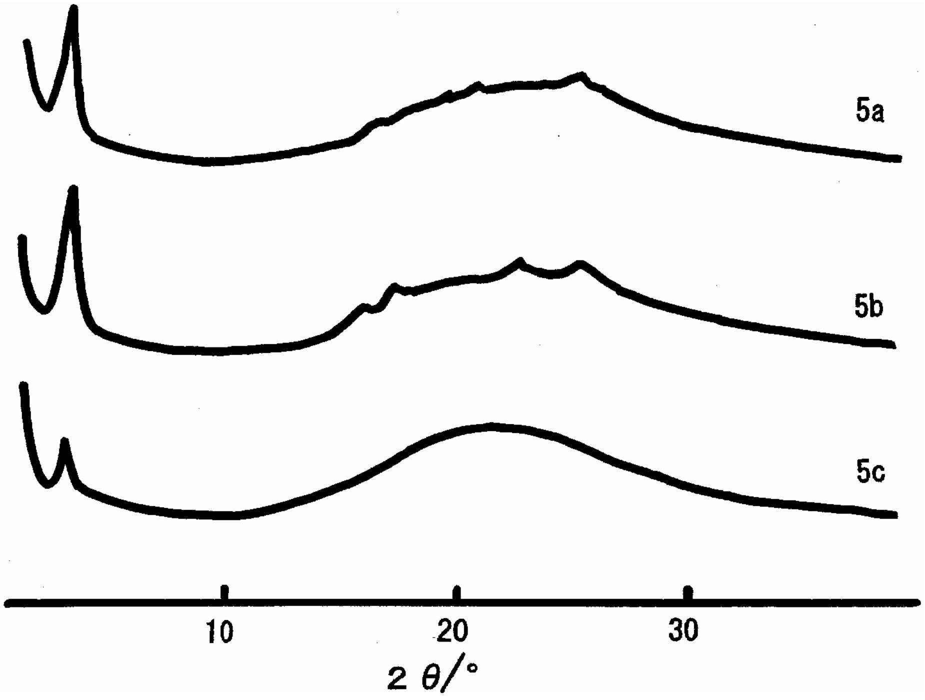


Figure 2. X-ray diffraction patterns of polyesters **5a–c**.

Table 2. X-ray data and calculated molecular lengths for polyesters **5a–c**.

Polymer	Middle angle $(2\theta)/°$	d-spacing/Å	Molecular length/Å[a]
5a	3.30	26.8	36.1
5b	3.60	24.6	33.5
5c	3.22	27.4	31.1

[a] Length of polymer repeating unit.

bonding involving amide linkages [21, 22], but LC phases were not found for concentrations of 20 and 25 wt% or in DCAA and HFIP. Polymer **5c** showed no lyotropic properties under the experimental conditions. The polarizing photomicrograph for the lyotropic LC phase of polymer **5a** at 15 wt% in TFAA is shown in figure 3.

The UV-Vis and PL properties of polymers **5a–c** in HFIP solution and in the solid state were investigated. The UV-Vis spectra of polymers **5a–c** in HFIP solutions showed absorption maxima at 351.5–353 nm associated with the π–π* electron transition of the distyrylbenzene analogue of 1,3,4-thiadiazole, 2,5-bis(2-phenyl-ethenyl)-1,3,4-thiadiazole. In the PL spectra of HFIP solutions of polymers **5a–c**, blue-emitting maxima were observed at 432.2–433.3 nm when excited around 352 nm, which are red-shifted by 80.1–80.7 nm. The solid state UV-Vis spectra of polymers **5a–c** exhibited broad maximum absorbances around 412.5–418.5 nm. The solid state PL spectra of polymers **5a–c** (excited at 412.5–418.5 nm), see figure 4, display bluish-green emissions at 492.7–499.7 nm, which show the Stokes shift of 74.2–87.2 nm, and their band edges extend beyond 600 nm. The PL spectra of the solids were red-shifted to lower energies compared with the solution spectrum data, owing to intermolecular aggregation effects [24]. The absorption and emission spectral data for polymers **5a–c** in HFIP solutions and in the solid phase are summarized in table 3. From these data, it is found that polyesters **5a–c** display solid state absorptions and fluorescences at longer wavelengths than those of the polyesters reported previously, which contain the terphenyl and quaterphenyl analogues of the 1,3,4-thiadiazole ring [16, 18]. Thus, polymers **5a–c** are candidates for use in organic EL devices.

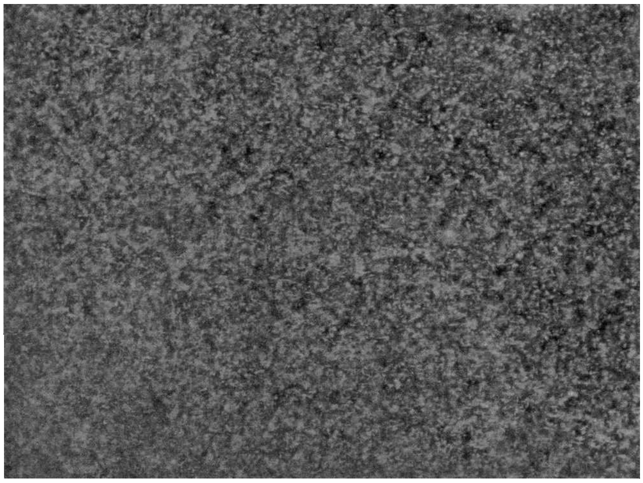


Figure 3. Polarizing photomicrograph of polyester **5a** at 15 wt% in TFAA (magnification: ×200).

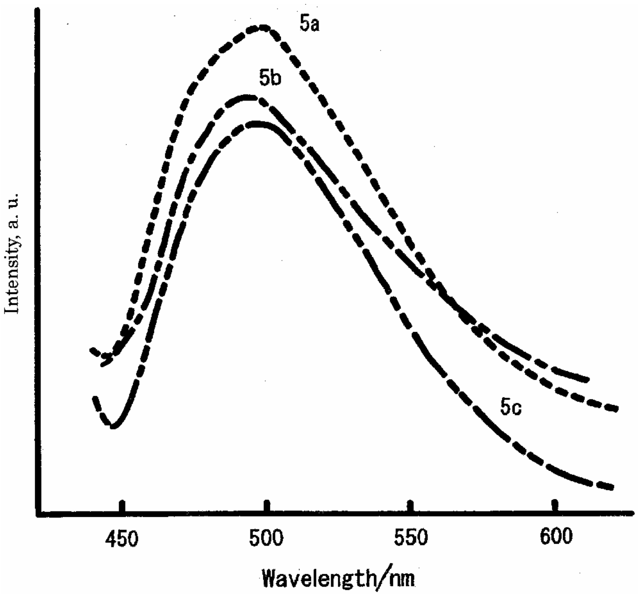


Figure 4. Solid state PL spectra of polyesters **5a–c**.

6. Summary

In conclusion, the polyesters **5a–c** containing the distyrylbenzene analogue of 1,3,4-thiadiazole, 2,5-bis-(2-phenylethenyl)-1,3,4-thiadiazole, and aliphatic (dodeca-, deca- and octamethylene) chains in the main chain, prepared by high temperature solution polycondensation, showed not only a thermotropic smectic C phase, but also PL properties with blue emission in HFIP solutions and bluish-green emission in the solid states as expected. The polyesters with dodeca- and decamethylene chains also formed lyotropic LC phases at 15 wt% in TFAA.

Table 3. UV-Vis and PL spectroscopic data of polyesters **5a–c**.

	Solution in HFIP		Solid state	
Polymer	$\lambda_{max,abs}$/nm	$\lambda_{max,PL}$/nm	$\lambda_{max,abs}$/nm	$\lambda_{max,PL}$/nm
5a	352.5	432.6	412.5	499.7
5b	353.0	433.3	418.5	492.7
5c	351.5	432.2	417.0	497.5

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

References

[1] Greenham, N. G., and Friend, R. H., 1995, *Solid State Physics*, Vol. 49, edited by H. Enhrenreich and F. Spaepen (San Diego: Academic Press), p. 1.

[2] Hudson, A. J., and Weaver, M. S., 2000, *Functional Organic and Polymeric Materials*, edited by T. H. Richardson (Chichester: John Wiley), p. 365.

[3] Chandrasekhar, P. (editor), 1999, *Conductive Polymers, Fundamental and Applications—A Practical Approach* (Boston: Kluwer Academic).

[4] Wang, S., Hua, W., Zhang, F., and Wang, Y., 1999, *Synth. Met.*, **99,** 249.

[5] Xue, M., Huang, D., and Liu, Y., 2000, *Synth. Met.*, **110,** 203.

[6] Meng, H., Chen, Z.-K., Yu, W.-L., Pei, J., Liu, X.-L., Lai, Y.-H., and Huang, W., 1999, *Synth. Met.*, **100,** 297.

[7] Yu, W.-L., Meng, H., Pei, J., Huang, W., Li, Y., and Heeger, A. J., 1998, *Macromolecules*, **31,** 4838.

[8] Pei, Q., and Yang, Y., 1995, *Chem. Mater.*, **7,** 1568.

[9] Janietz, S., and Anlauf, S., 2002, *Macromol. Chem. Phys.*, **203,** 427.

[10] Charas, A., Barbagallo, N., Morgado, J., and Alcacer, L., 2001, *Synth. Met.*, **122,** 23.

[11] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L., and Holes, A. B., 1990, *Nature*, **347,** 539.

[12] Chen, Y., and Lai, S.-P., 2001, *J. polym. Sci. A, polym. Chem.*, **39,** 2571.

[13] Blumstengel, S., Sokolik, I., Dorsinville, R., Voloschenko, D., He, M., Lavrentovich, O., and Chien, L.-C., 1999, *Synth. Met.*, **99,** 85.

[14] Chen, Y., and Huang, C.-F., 2002, *Synth. Met.*, **125,** 379.

[15] Sato, M., Yamauchi, K., Handa, M., and Kasuga, K., 2000, *Macromol. rapid Commun.*, **21,** 1234.

[16] Sato, M., Ishii, R., Nakashima, S., Yonetake, K., and Kido, J., 2001, *Liq. Cryst.*, **28,** 1211.

[17] Sato, M., and Uemoto, Y., 2000, *Macromol. rapid Commun.*, **21,** 1220.

[18] Sato, M., Notsu, M., Nakashima, S., and Uemoto, Y., 2001, *Macromol. rapid Commun.*, **22,** 681.

[19] Nygaard, L., Hansen, R. L., Nielsen, J. T., Rastrup-Andersen, J., Sorensen, G. O., and Steiner, P. A., 1972, *J. mol. Struct.*, **12,** 59.

[20] Nygaard, L., Hansen, R. L., and Sorensen, G. O., 1971, *J. mol. Struct.*, **9,** 163.

[21] Yang, H. H., 1993, *Kevlar Aramid Fiber* (Chichester: J. Wiley).

[22] Neuber, C., Giesa, R., and Schmidt, H.-W., 2002, *Macromol. Chem. Phys.*, **203,** 598.

[23] Ohta, M., and Kimoto, H., 1956, *J. pharm. Soc. Jpn.*, **76,** 10; 1956, *Chem. Ab.*, **50,** 12992c.

[24] Conwell, E., 1997, *Trends polym. Sci.*, **7,** 218.