Polymer 40 (1999) 1943–1953

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Fluorescing wholly aromatic polyesters containing diphenylanthracene fluorophores

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Received 7 January 1998; revised 18 May 1998; accepted 28 May 1998

Abstract

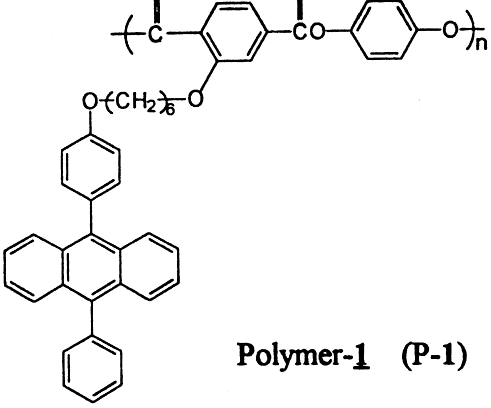
New, wholly aromatic polyesters carrying 9,10-diphenylanthracene fluorophores along the main chain or both in the pendent and main chain were prepared and their properties were studied by differential scanning calorimetry, wide-angle X-ray diffractometry and fluorometry in solution as well as in thin solid films. The diphenylanthracene pendent groups are attached to the terephthaloyl unit of the aromatic polyester main chains through the oxyhexamethyleneoxy spacer. Two of the polymers were found to be thermotropic and all of the polymers exhibited relatively strong photoluminescence in solution as well as in thin films. Their fluorescence behavior is discussed in relation to their structures. When the diphenylanthracene fluorophores exist either both in the main chain and the side chain or only in the side chain, the polyesters reveal photoluminescence over a broad range of wavelength from 400 to about 700 nm with the maximum emitting intensity at about 450 nm. The polymer that contains the same fluorophore only in the main chain, however, shows a rather sharp luminescence from about 420 to 550 nm, although its maximum emitting intensity is observed at the same wavelength (ca. 450 nm) as for other polyesters.

Keywords: Aromatic polyester; 9,10-Diphenylanthracene; Concentration quenching

1. Introduction

Polymers revealing photo- and electroluminescence properties are attracting a great deal of interest due to academic as well as technical importance. Especially after the Cambridge group's report [1] on the electroluminescence characteristics of poly(*p*-phenylenevinylene) (PPV), luminescing properties of various PPV derivatives have been reported [2–6]. In addition, fluorescence of organic compounds and polymers in solution and bulk has been an important topic for many years in photochemistry and photophysics [7–9]. Mainly, vinyl polymers carrying fluorophores, however, have been the subjects of many investigations.

While we were studying liquid crystalline properties of a series of aromatic polyesters [10,11] and electrical and optical properties of some PPV derivatives [6,12,13], we became interested in the photoluminescence of liquid crystalline aromatic polyesters. This report describes the synthesis, liquid crystallinity and initial findings on photoluminescence of the following four aromatic polyesters:



Polymer-1 (P-1)

Poly[oxy-1,4-phenyleneoxy-2-{6-[4-(9-phenylanthracen-10-yl)phenoxy]hexamethyleneoxy}terephthaloyl]

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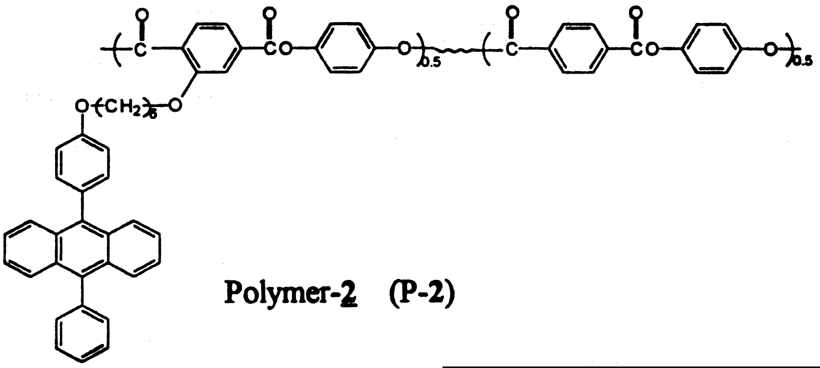
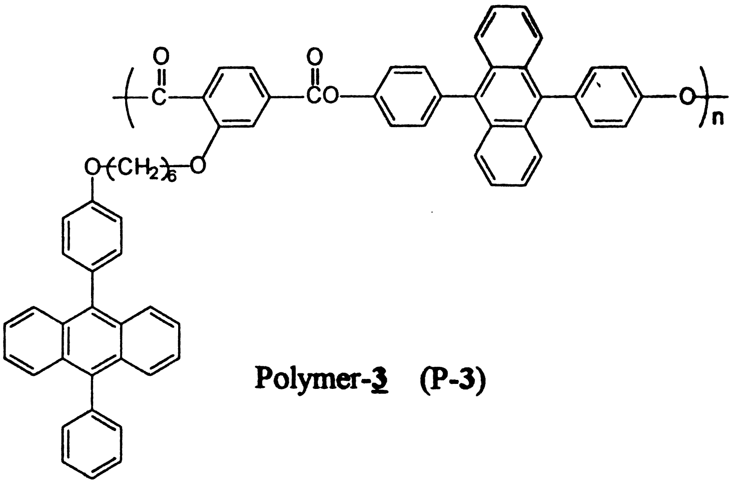
PII: S0032-3861(98)00420-0



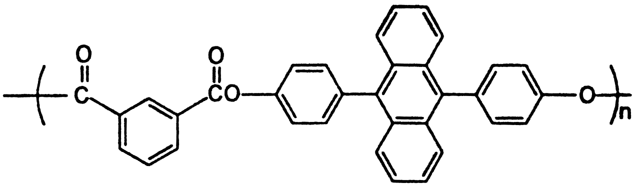
Polymer-2 (P-2)

Poly[[oxy-1,4-phenyleneoxy-2-{6-(4-(9-phenylanthracen-10-yl)phenoxy)hexamethyleneoxy}terephthaloyl]-co-(oxy-1,4-phenyleneoxyterephthaloyl)]



Polymer-3 (P-3)

Poly[oxy-1,4-phenylene-9,10-anthracenediyl-1,4-phenyleneoxy-2-{6-(4-(9-phenylanthracen-10-yl)phenoxy)-hexamethyleneoxy}terephthaloyl]



Polymer-4 (P-4)

Poly[oxy-1,4-phenylene-9,10-anthracenediyl-1,4-phenyleneoxyisophthaloyl]

Polymer **1** is an aromatic polyester that carries the 9,10-diphenylanthracene moiety connected to the terephthaloyl unit through the oxyhexamethyleneoxy spacer, while polymer **2** is a 1:1 random copolyester with the unsubstituted terephthalic acid monomer. In contrast, polymer **3** carries the 9,10-diphenylanthracene unit as the pendent group as well as the integral part of the main chain. Polymer **4** contains the 9,10-diphenylanthracene fluorophore only in the main chain. Instead of the terephthaloyl unit included in other polymers, the isophthaloyl unit is included in polymer **4** in order to improve its solubility in organic solvents.

2. Experimental

2.1. Synthesis of dicarboxylic acid monomer **5**: 2-[6-{4-(9-(phenylanthracen-10-yl)phenoxy}hexamethyleneoxy]-terephthalic acid

*2.1.1. 9-(4-Methoxyphenyl)-10-phenylanthracene (*1*)*

9-Bromo-10-phenylanthracene (15 g; 4.5 × 10^{-2} mol) was dissolved in 300 ml of toluene containing 2.08 g of the tetrakis(triphenylphosphine)palladium(0) catalyst. To this solution was added 8.9 g (5.85 × 10^{-2} mol) of *p*-methoxyphenylboric acid dissolved in 30 ml of ethanol and 65 ml of 2 M sodium carbonate solution. The mixture was refluxed for 24 h with vigorous stirring. The toluene layer was separated and toluene was removed by distillation, leaving behind a solid residue. The soluble portion in the solid residue was extracted using a mixture of methylene chloride and acetone (v/v = 1/5). After the solvents were removed, the residual product was dried in vacuum at room temperature. Product **1** thus obtained (yield 13 g; 80%; m.p. 239–240°C) was utilized in the next step without further purification. Anal.: Calcd. (%) for $C_{27}H_{20}O$: C, 89.97; H, 5.59; Found: C, 89.89; H, 5.57. IR spectrum (KBr, cm^{-1}): 3041 (aromatic C–H stretching), 2950 and 2835 (aliphatic

C–H stretching), 1605 and 1506 (aromatic C=C stretching), 1241 (unsymmetric C–O–C stretching) and 1025 (symmetric C–O–C stretching). ^{1}H-NMR spectrum (acetone-d$_6$, δ (ppm)): 4.0 (s, 3H, OCH$_3$), 7.1–7.8 (m, 17H, Ar).

*2.1.2. 9-(4-Hydroxyphenyl)-10-phenylanthracene (**2**)*

Hydrobromic acid (48%, 41 ml) was added slowly with stirring to the solution of compound **1** (13 g; 3.6×10^{-2} mol) dissolved in 700 ml of a mixture of acetone and trifluoroacetic acid (v/v = 6/1). The reaction mixture was refluxed for 50 h under a nitrogen atmosphere during which period the whole mixture became homogeneous. After the mixture was cooled down to room temperature, the precipitate formed was collected on a filter and washed thoroughly with distilled water. The product was recrystallized from *n*-hexane. The yield was 11.2 g (88%; m.p. 249–251°C). Anal.: Calcd. (%) for $C_{26}H_{18}O$: C, 90.14; H, 5.23; Found: C, 90.08; H, 5.22. IR spectrum (KBr, cm^{-1}): 3375 (O–H stretching), 3054 (aromatic C–H stretching), 1610 and 1507 (aromatic C=C stretching), 1234 (C–O–C stretching). ^{1}H-NMR spectrum (acetone-d$_6$, δ (ppm)): 7.1–7.8 (m, 17H, Ar).

*2.1.3. 9-{4-(6-Bromohexamethyleneoxy)phenyl}-10-phenylanthracene (**3**)*

Compound **2** (11 g; 3.18×10^{-2} mol), 1,6-dibromohexane (35 ml; 0.31 mol), potassium carbonate (8 g; 5.7×10^{-2} mol) and tetrabutylammonium bromide (0.1 g) were dissolved in 600 ml of acetone. The mixture was refluxed for 48 h under a nitrogen atmosphere. The insoluble was removed by filtration. Acetone in the filtrate was removed by distillation using a rotary evaporator. The residue was thoroughly washed with ethanol and dried. The product (14.2 g; 87%, m.p. 164–165°C) thus obtained was pure enough to be used in the next step. Anal.: Calcd. (%) for $C_{32}H_{29}OBr$: C, 75.44; H, 5.73; Found: C, 75.50; H, 5.73. IR spectrum (KBr, cm^{-1}): 3050 (aromatic C–H stretching), 2934 (aliphatic C–H stretching), 1605 and 1502 (aromatic C=C stretching), 1237 (unsymmetric C–O–C stretching) and 1032 (symmetric C–O–C stretching), 692 (aliphatic C–Br stretching). ^{1}H-NMR spectrum (acetone-d$_6$, δ (ppm)): 1.6 (m, 4H, O–CH$_2$CH$_2$($\underline{CH_2}$)$_2$–), 1.9 (m, 4H, O–CH$_2$–($\underline{CH_2}$)$_2$–), 3.5 (t, 2H, $\underline{CH_2}$–Br), 4.15 (m, 4H, O–$\underline{CH_2}$), 7.1–7.8 (m, 17H, Ar).

*2.1.4. Dimethyl 2-[6-{4-(9-phenylanthracen-10-yl)phenoxy}hexamethyleneoxy]terephthalate (**4**)*

Compound **3** (10 g; 1.96×10^{-2} mol), dimethyl 2-hydroxyterephthalate (4.2 g; 2.0×10^{-2} mol), potassium carbonate (6.5 g) and tetrabutylammonium bromide (0.1 g) were dissolved in 500 ml of acetone. The mixture was refluxed for 54 h under a nitrogen atmosphere. The insoluble was removed by filtration. Acetone in the filtrate was removed by distillation using a rotary evaporator. The residue was thoroughly washed with ethanol. The product was recrystallized from a mixture of *n*-hexane and ethyl acetate (v/v = 9/1). The yield was 9.5 g (76%; m.p. 142°C). Anal.: Calcd. (%) for $C_{42}H_{38}O_6$: C, 78.97; H, 5.99; Found: C, 78.95; H, 5.76. IR spectrum (KBr, cm^{-1}): 3051 (aromatic C–H stretching), 2928 (aliphatic C–H stretching), 1727 and 1700 (C=O stretching), 1605 and 1502 (aromatic C=C stretching), 1290 and 1235 (C–O–C stretching). ^{1}H-NMR spectrum (chloroform-d$_1$, δ (ppm)): 1.6 (m, 8H, O–CH$_2$($\underline{CH_2}$)$_4$–), 3.9 (s, 6H, OCH$_3$), 4.15 (m, 4H, O–CH$_2$), 7.1–7.8 (m, 17H, Ar).

*2.1.5. 2-[6-{4-(9-(Phenylanthracen-10-yl)phenoxy}hexamethyleneoxy]terephthalic acid (**5**)*

Compound **4** (3.0 g; 4.7 mmol) and 1.05 g of potassium hydroxide were dissolved in a mixture of 250 ml of ethanol and 50 ml of tetrahydrofuran. The mixture was refluxed for 14 h, and it became homogeneous as the reaction proceeded. The mixture was poured with vigorous stirring into large excess 1 M hydrochloric acid. The precipitate was thoroughly washed with distilled water. The crude product was recrystallized from ethyl acetate. The yield was 2.4 g (85%; m.p. 271–273°C). Anal.: Calcd. (%) for $C_{40}H_{34}O_6$: C, 78.48; H, 5.60; Found: C, 78.04; H, 5.56. IR spectrum (KBr, cm^{-1}): 3600–2100 (COOH stretching), 1694 (C=O stretching) 1602 and 1505 (aromatic C=C stretching), 1298 and 1242 (C–O–C stretching). ^{1}H-NMR spectrum (chloroform-d$_1$, δ (ppm)): 1.6–2.0 (m, 8H, O–CH$_2$($\underline{CH_2}$)$_4$–), 4.15 (m, 4H, O–CH$_2$), 6.9–7.8 (m, 20H, Ar), 13.0 (s, 2H,–COOH).

*2.1.6. Synthesis of 9,10-bis(4-acetoxyphenyl)anthracene (**8**)*

9,10-Dibromoanthracene (10 g; 2.98×10^{-2} mol) dissolved in 200 ml of toluene, 2.3 g (2 mmol) of tetrakis (triphenylphosphine)palladium(0), *p*-methoxyphenylboric acid (11.8 g; 7.75×10^{-2} mol) dissolved in 30 ml of ethanol and 75 ml of 2 M sodium carbonate aqueous solution were mixed together. The mixture was stirred at 110°C for 48 h. The toluene layer was then separated. After toluene was removed by distillation using a rotary evaporator, the residue was thoroughly washed with warm methanol. The product thus obtained (yield 9.4 g; 81%, m.p. 300°C) was pure enough to be utilized in the next step. Anal.: Calcd. (%) for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68; Found: C, 86.40; H, 5.46. IR spectrum (KBr, cm^{-1}): 3037 (aromatic C–H stretching), 2932 and 2827 (aliphatic C–H stretching), 1602 and 1512 (aromatic C=C stretching), 1235 (unsymmetric C–O–C stretching) and 1025 (symmetric C–O–C stretching). ^{1}H-NMR spectrum (benzene-d$_6$, δ (ppm)): 3.0 (s, 6H,–OCH$_3$), 6.5–7.6 (m, 16H, Ar).

*2.1.7. 9,10-Bis(4-hydroxyphenyl)anthracene (**7**)*

Hydrobromic acid (48%, 75 ml) was slowly added with vigorous stirring to a warm (50°C) solution of compound **6** (9.0 g; 2.3×10^{-2} mol) dissolved in 800 ml of acetic acid. The mixture was refluxed for 36 h under a nitrogen atmosphere and then poured into excess distilled water. The precipitate was recrystallized from a mixture of acetic acid and water (v/v = 6/1). The product yield was 7.6 g

(91%, m.p. 338–340°C). Anal.: Calcd. (%) for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01; Found: C, 86.70; H, 5.11. IR spectrum (KBr, cm^{-1}): 3413 (O–H stretching), 3034 (aromatic C–H stretching), 1603 and 1500 (aromatic C=C stretching), 1224 (C–O–C stretching). ^{1}H-NMR spectrum (trifluoroacetic acid-d_1, δ (ppm)): 6.5–7.6 (m, 16H, Ar).

2.1.8. *9,10-Bis(4-acetoxyphenyl)anthracene (***8***)*

Compound **7** (7.0 g; 1.93×10^{-2} mol) was dissolved in 100 ml of acetic anhydride. The solution was refluxed for 24 h under a nitrogen atmosphere. The reaction mixture was then poured into excess distilled water. The precipitate was collected on a filter and washed thoroughly with warm ethanol. The product (yield; 5.2 g, (60%), m.p. 304–306°C) thus obtained was pure enough to be utilized in the synthesis of polymer **3**. Anal.: Calcd. (%) for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97; Found: C, 80.67; H, 5.01. IR spectrum (KBr, cm^{-1}): 3052 (aromatic C–H stretching), 1750 (C=O stretching), 1603 and 1500 (aromatic C=C stretching), 1224 and 1189 (C–O–C stretching). ^{1}H-NMR spectrum (benzene-d_6, δ (ppm)): 1.5 (s, 6H,–CH_3), 6.8–7.6 (m, 16H, Ar).

2.2. *Synthesis of polymers*

Polymers were synthesized in the similar manner. Therefore, only the synthetic procedure of polymer **1** is described in detail as a representative example. 4,4′-Diacetoxybenzene (0.79 g; 4.08 mmol) and monomer **5** (2.45 g; 4.08 mmol) were placed in a polymerization tube and heated to 200°C. Under a steady stream of nitrogen, the mixture was kept at 230°C for 40 min, at 260°C for 50 min, at 270°C for 110 min, at 280°C for 60 min and finally at 290°C for 100 min. The nitrogen stream was then stopped and the pressure inside the polymerization tube was lowered to 360 Torr at 290°C. The polymerization mixture was kept under the reduced pressure for 10 min. Finally, the pressure was further lowered to 1 Torr at 290°C and the mixture was kept for 50 min at the same condition. The polymer obtained was powdered and was subjected to Soxhlet extraction for 2 days using a mixture of ethanol and tetrahydrofuran (v/v 1/5). The weight of recovered polymer was 2.37 g (86.5%). Its structure was confirmed by elemental and spectroscopic analyses.

Polymer **1**; Anal.: Calcd. (%) for $CH_{46}H_{36}O_6$: C, 80.66; H, 5.30; Found: C, 79.26; H, 5.50. IR spectrum (KBr, cm^{-1}): 3049 (aromatic C–H stretching) 1739–1690 (C=O stretching), 1603 and 1500 (aromatic C=C stretching), 1294 and 1173 (C–O–C stretching).

Polymer **2**; Anal.: Calcd. (%) for $C_{30}H_{22}O_5$: C, 77.90; H, 4.79; Found: C, 77.02; H, 4.31. IR spectrum (KBr, cm^{-1}): 3052 (aromatic C–H stretching), 1750 (C=O stretching), 1603 and 1500 (aromatic C=C stretching), 1224 and 1189 (C–O–C stretching).

Polymer **3**; Anal.: Calcd. (%) for $C_{66}H_{48}O_6$: C, 84.59; H, 5.16; Found: C, 85.62; H, 5.23. IR spectrum (KBr, cm^{-1}): 3044 (aromatic C–H stretching), 1750–1690 (C=O stretching), 1613 and 1514 (aromatic C=C stretching), 1220 and 1190 (C–O–C stretching).

Polymer **4**; Anal.: Calcd. (%) for $C_{34}H_{20}O_4$: C, 82.91; H, 4.09; Found: C, 82.42; H, 4.16. IR spectrum (KBr, cm^{-1}); 3050 (aromatic C–H stretching), 1750–1688 (C=O stretching), 1602 and 1504 (aromatic C=C stretching), 1225 and 1190 (C–O–C stretching).

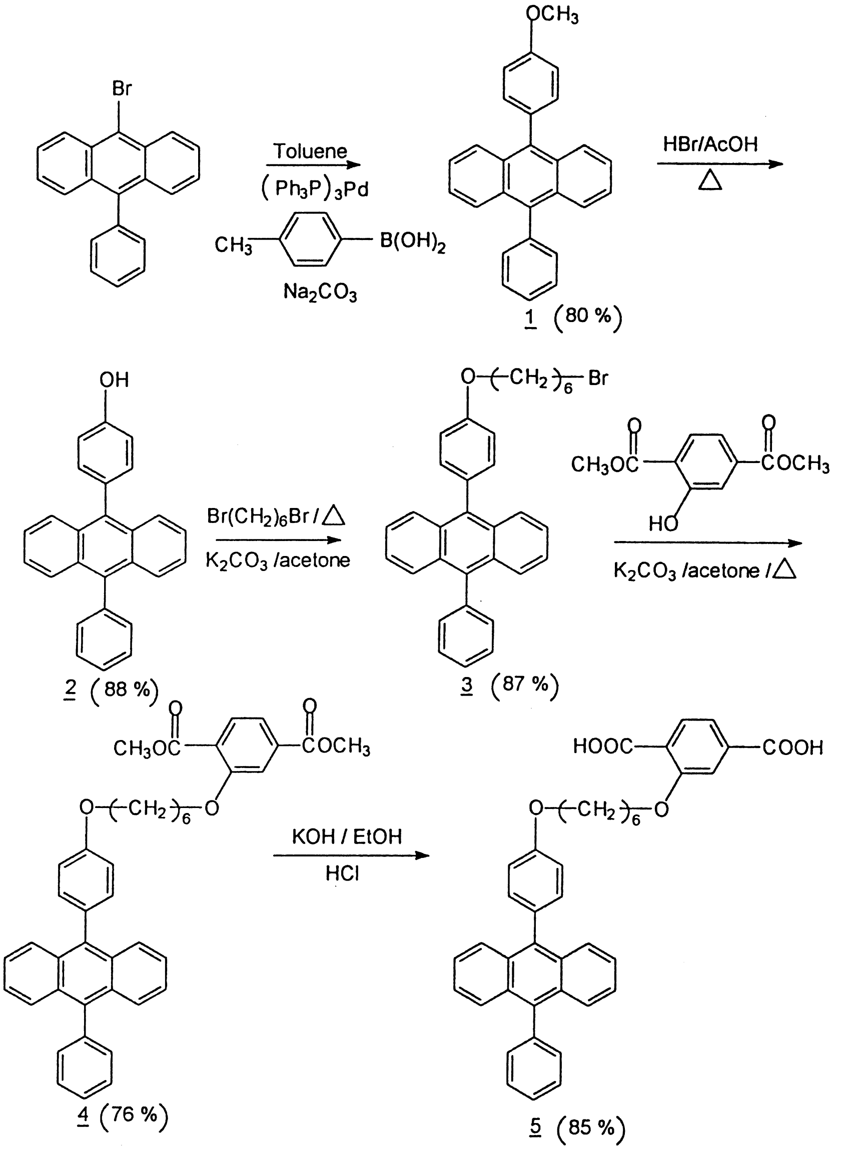
2.2.1. *Characterization*

Infrared (IR) and ^{1}H-NMR spectroscopic data were obtained on a Bomen Michelson FTIR instrument and on a Varian Gemini 300, respectively. Thermal properties were studied under a nitrogen atmosphere on a differential scanning calorimeter (Perkin-Elmer DSC 7) and also on a thermogravimetric analyzer (Stanton Redoroft TGA 1000). Heating and cooling rates in thermal analysis were maintained at 10°C min^{-1}. UV–Vis spectra were obtained on a Hewlett-Packard HP8452A diode array spectrophotometer. Photoluminescence spectra were obtained at room temperature on an AMINCO-Bowman Series 2 Spectrometer with a Xe lamp as a source and GaAs photomultifier detector. The excitation wavelength was kept at 365 nm. The bandpass of the monochromator was kept at 4 nm. The scan rate was 10 nm s^{-1}. When films were used for fluorescence study, they were prepared by spin-coating of polymer solutions in 1,1,2,2-tetrachloroethane on a $1.5 \times 1.5\ cm^2$ quartz plate. The solutions were filtered through a 0.45 μm syringe filter (Nalgene cat. no. 195-2545) prior to spin-coating. Thickness of the films was measured by an α-step Stylus Profilometer (Tenchor Instrument). Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa using nickel-filtered Cu Kα radiation. The optical texture of liquid crystalline polymers were observed on a hot-stage (Mettler FP-82HT) attached to a polarizing microscope (Olympus BH-2).

3. Results and discussion

3.1. *Synthesis of the monomer*

The synthetic route to the dicarboxylic acid monomer (**5**) carrying the diphenylanthracene fluorophore is shown in Scheme 1. 9-(4-Methoxyphenyl)-10-phenylanthracene (**1**) was prepared from 9-bromo-10-phenylanthracene and *p*-methoxyphenyl boric acid via the Suzuki reaction [14]. Compound **1** was converted to the corresponding phenolic compound **2** by acidic cleavage of the ether linkage, which then was reacted in acetone with excess 1,6-dibromohexane in the presence of potassium carbonate to produce 9-{4-(6-bromohexamethyleneoxy)phenyl}-10-phenylanthracene (**3**). Compound **3** was subjected to a nucleophilic substitution by refluxing it in acetone with dimethyl 2-hydroxyterephthalate in the presence of potassium



Scheme 1. Synthetic route to the substituted terephthalic acid monomer **5**.

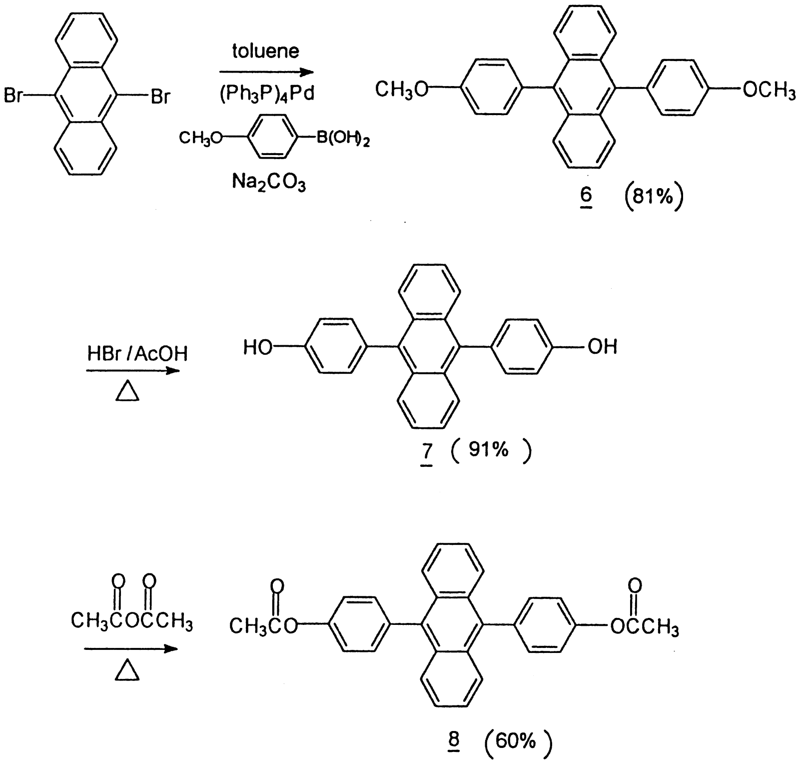
carbonate and tetrabutylammonium bromide. Compound **4**, thus obtained, was hydrolyzed to the corresponding dicarboxylic acid monomer (**5**), 2-[6-{4-(9-(phenylanthracen-10-yl)phenoxy}hexamethyleneoxy] terephthalic acid.

Another monomer (**8**), 9,10-bis(4-acetoxyphenyl)anthracene, was prepared via the synthetic route shown in Scheme 2. 9,10-Dibromoanthracene was converted to 9,10-bis(4-methoxyphenyl)anthracene (**6**) by reacting the former with *p*-methoxyphenyl boric acid. The ether bonds of compound **6** were cleaved to produce the corresponding dihydroxy compound (**7**) by using hydrogen bromide dissolved in anhydrous acetic acid [15]. Compound **7** was transformed into the corresponding diacetate (**8**) by reaction with acetic anhydride. The structures of all of the intermediates and the final monomers were confirmed by IR and NMR spectroscopy and also by elemental analysis.

3.2. Synthesis and properties of polymers

Polymers were prepared by bulk, melt polymerization at elevated temperatures initially under a nitrogen atmosphere followed by gradual reduction in pressure inside the polymerization tube to 1 Torr. The polymerization temperature was raised from 230 to 359°C. Obtained polymers were ground and then subjected to Soxhlet extraction for two days using tetrahydrofuran (THF) or a THF:ethanol (5:1 by volume) mixture in order to remove soluble, low molar mass impurities and oligomers. Recovered yields after solvent extraction ranged from 84 to 87%. Their structures were confirmed by their IR spectra and elemental analysis.

The solution viscosity values of the polymers measured at 30°C for 0.2 g dl^{-1} solutions in 1,1,2,2-tetrachloroethane are about 0.7–1.0 (see Table 1) suggesting that molecular



Scheme 2. Synthetic route to 9,10-bis(4-acetoxyphenyl)anthracene.

weights of the polymers are reasonably high. The glass transition temperatures (T_g) determined by differential scanning calorimetry (DSC) (Fig. 1) were 127, 135, 176 and 142°C, respectively for polymers **1**, **2**, **3** and **4**. Polymer **2** contains the unsubstituted repeating unit, which causes an increase in the T_g value due to a decrease in the free volume when compared with polymer **1**. Polymer **3** exhibits the highest T_g value among the four polymers. This observation can be ascribed to the increase in the rigidity of the main chain due to 9,10-diphenylanthracene moieties existing along the main chain in place of the hydroquinone moieties in polymers **1** and **2**. The 9,10-diphenylanthracene moiety in the main chain of polymer **3** is comprised of three consecutive *p*-phenylene units in a linear fashion, which will definitely make the segmental motions more difficult.

According to DSC (Fig. 1) and wide-angle X-ray diffraction studies (Fig. 2), these polymers appear to be amorphous or very low in crystallinity. The large size of the pendents attached on the terephthaloyl units and also their non-regioregular isomeric positioning are thought to be major reasons for the destruction of the crystallization tendency of polymers **1** and **3**. Polymers **1** and **2** are found to be thermotropically liquid crystalline, but polymers **3** and **4** are not. The optical textures of polymers **1** and **2** observed through a polarizing microscope reveal that they are nematic. The increased molecular breath of polymer **3** due to the presence of the anthracene structure along the main chain in addition to the bulky pendent group seems to deprive the polymer of its ability to form a mesophase. In addition, the bent isophthaloyl unit in polymer **4** also makes the polymer non-liquid crystalline. The nematic-to-isotropic phase transition (T_i), i.e. clearing temperature, of polymer **1** is relatively low (270°C), whereas the isotropization temperature of polymer **2** is significantly higher. In fact, clearing

Table 1
General properties of polymers

Polymer	η_{inh} [a] (dl g^{-1})	T_g (°C)	T_m (°C)	T_d^i [b] (°C)	T_i [c] (°C)	LC [d]
1	1.06	127	–	308	270	nematic
2	0.99	135	371 (371) [e]	380	>380	nematic
3	0.94	176	–	327	–	no LC
4	0.67	142	381 (383) [e]	402	–	no LC

[a] Inherent viscosity values were measured at 30°C for 0.2 g dl^{-1} solution in 1,1,2,2-tetrachloroethane.

[b] Initial decomposition temperature determined by thermogravimetry.

[c] Judged by the observed optical textures on an optical polarizing microscope.

[d] Liquid crystallinity.

[e] T_m observed for the annealed (4 h at 250°C) samples.

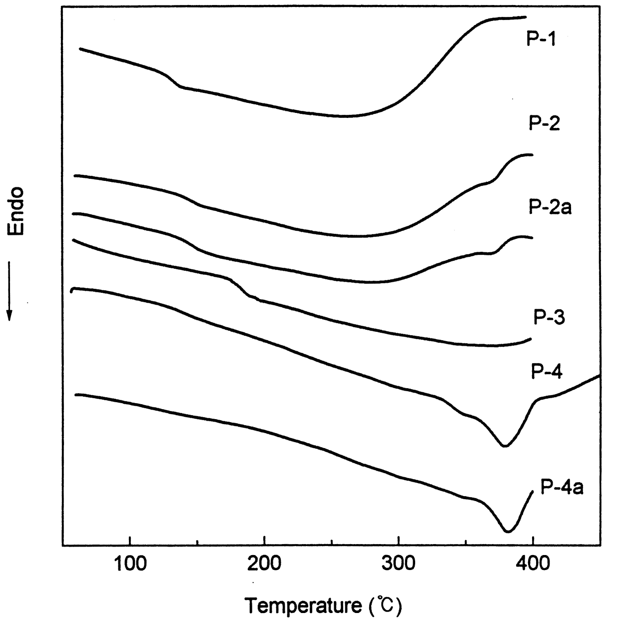


Fig. 1. DSC thermograms of polymers (heating rate, 10°C min^{-1}). (a) Annealed for 4 h at 250°C.

transition of polymer **2** cannot be detected either by DSC or by optical microscopy, because it starts to undergo thermal decomposition at about 380°C before reaching T_i. The presence of 50 mol.% of the unsubstituted *p*-phenyleneterephthalate units along the main chain certainly increases the thermal stability of the mesophase due to reduction in the overall molecular breadth.

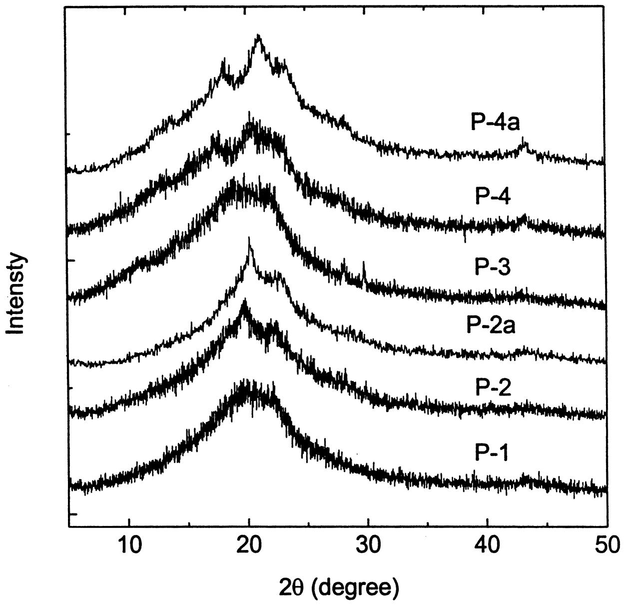


Fig. 2. Wide-angle X-ray diffractograms of polymers. (a) Annealed for 4 h at 250°C.

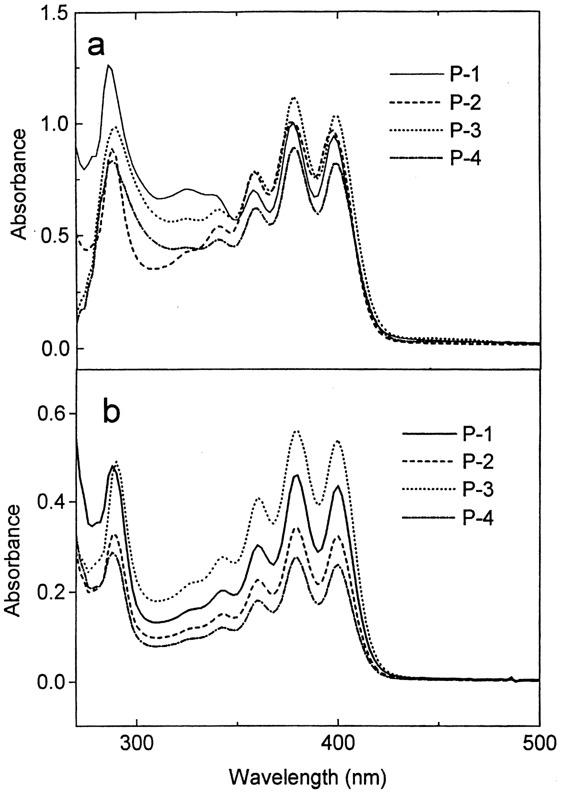


Fig. 3. UV–Vis spectra of (a) thin films (thickness, 1 μm) and (b) the solution (3×10^{-5} mol l^{-1} in the fluorophore unit) of polymers **1**, **2**, **3** and **4**.

Fig. 3(a) and 3(b) compare the UV–Vis spectra of the four polyesters obtained for bulk films and in 1,1,2,2-tetrachloroethane solutions. The spectra obtained for solutions and solid films are practically the same; no shift in absorption position is observed. All of them exhibit the first absorptions at 260–320 nm due to aromatic groups and the second absorption at 320–420 nm characteristic to the 9,10-diphenylanthracene structure [16,17]. The peak maxima positions for the 9,10-diphenylanthracene unit appear at 341, 360, 378 and 401 nm both for films and solutions regardless of the polymer structures. Practically, there is no changes in absorption positions by the 9,10-diphenylanthracene units for the four polymers. Although the absorption positions by the anthracene moiety are almost invariant regardless of the detailed structure of the polymers, we observe a strong dependence of absorbance on their structures. As expected, polymer **3** reveals the strongest absorption due to the presence of the two anthracene moieties in the repeating unit. But the situation is much complicated for the rest of the polymers; the solutions of the same concentration in the anthracene moiety give rise to much differing absorbance. This strongly suggests that the anthracene moieties in the polymers are in a very different electronic environment leading to differences in their absorptibities.

Photoluminescence (PL) behavior of the polymers was studied for bulk films of about 1 μm thick (Fig. 4) and also in 1,1,2,2-tetrachloroethane solution (Fig. 5(a)–5(d)) at the excitation wavelength of 365 nm. The polymer **4** film emits blue light and others emit blue light with a very weak greenish tone. The peak maxima of the PL spectrum

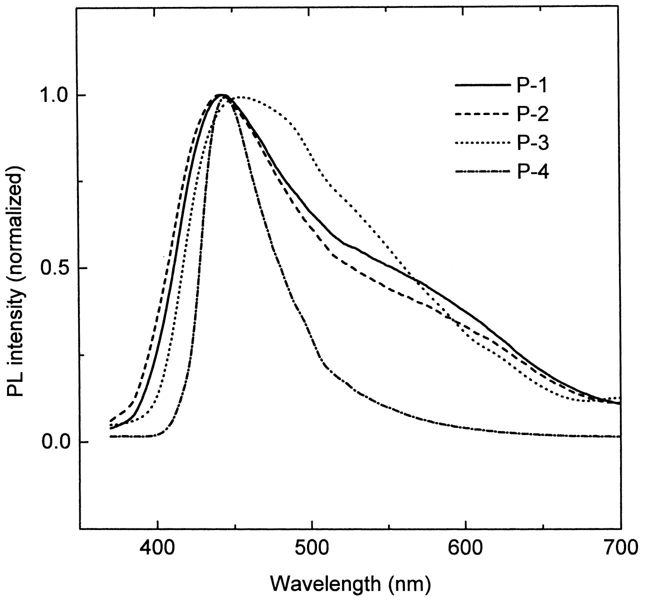


Fig. 4. PL spectra of thin films (thickness, 1 μm) of polymers **1**, **2**, **3** and **4**.

appear at about 440–450 nm. According to Fig. 4, the PL spectra for the films of polymer **1** and polymer **2** are about the same, whereas the spectrum for the polymer **3** film is a little red-shifted and broader. In contrast, the spectrum for the polymer **4** film is the sharpest among the four. These differences indicate that, when there are fluorophores both in the main chain and the side chain, there is a higher probability for intra- as well as intermolecular interactions among the fluorophores, which, in turn, causes broadening of the PL spectrum accompanied with a red-shift [18,19]. On the contrary, when the fluorophore is included only in the main chain, such interactions are reduced resulting in the sharper spectrum. Although the fluorophore under discussion has the two phenyl substituents at the 9 and 10 positions of the central anthracene moiety that are known to effectively prevent intermolecular interactions leading to excimer formation [20], loose interactions among the fluorophores are, of course, still possible [21]. Such loose interactions among the fluorophores are much more facile in polymers **1**–**3**, because the diphenylanthracene groups are hanging in the side branch and, thus, their motions are less hindered. Therefore, shoulder-like tails in the 500–650 nm region of the PL spectra of these three polymers are readily recognizable in Fig. 4, which is very weak in the PL spectrum of polymer **4**. Another fact to be noted is that fluorescence spectra of the present polymer films are much broader, especially in the longer wavelength region than that of diphenylanthracene itself and those for the solutions of the polymers. This can be explained by a combination of charge-transfer type interaction between electron-donating and electron-accepting structural units, as recently described by Watanabe et al. [19] for fluorescence characteristics of aromatic polyesters, the formation of weakly bound excimer state between fluorophores as claimed by Hargreaves and Webber [20], and interactions between fluorophores, and also among fluorophores and other aromatic structures, in the polymers. Anyway, it is believed that short- as well as long-range interactions between and among fluorophores with the formation of loose excimers as well as multimers in addition to various intra- and interchain interactions can easily occur in the present polymers.

The concentration of the fluorophore-containing repeating units examined in solutions ranges from 3.0×10^{-7} to 3.0×10^{-3} mol l^{-1}. The fluorescence spectra of the solutions are presented in Fig. 5(a)–5(d). The fluorescence maxima appear at about 425 and 440 nm [16]. The values are slightly red-shifted when compared with those of monomer **5**, whose chemical structure is shown in Scheme 1. These figures show that, in general, fluorescence intensity sharply decreases when the concentration of the repeating unit becomes higher, indicating that concentration quenching [22] occurs even at a very low concentration. It is very possible that intramolecular interactions between fluorophores and also between the fluorophores and the main chain segments cause this phenomenon even for very dilute solutions. For example, Fig. 5(a) clearly demonstrates that the total fluorescence area of the spectrum for the solutions of 3.0×10^{-3} mol l^{-1} is significantly less than that for the solution of 3.0×10^{-4} mol l^{-1}. In other words, the solution of 10 times concentration reveals much weaker PL. The same phenomenon is observed for other polymers as shown in Fig. 5(b)–5(d). However, the solutions of polymers **1** and **2** reveal stronger fluorescence (Fig. 5(a) and 5(b)) at the concentration of 3×10^{-3} mol l^{-1} when compared with polymer **3** (Fig. 5(c)). This must be due to the fact that polymer **3** contains the diphenylanthracene moieties along the main chain as well as in the side pendents, which will facilitate more ready intra- and intermolecular contact interactions between the fluorophores, leading to a diminished fluorescence efficiency or concentration quenching. Fig. 5(c) also tells us that the concentration quenching for polymer **3** occurs even at the concentration of 3×10^{-4} mol l^{-1} in the repeating unit. This again is due to the fact that the repeating unit of polymer **3** contains two different diphenylanthracene groups, one in the main chain and the other in the side chain. Another point to be noted is that polymer **4** reveals the strongest PL properties (Fig. 5(d)) in the concentration range of 10^{-3} to 10^{-4} mol l^{-1} of the repeating unit.

Fig. 6(a) compares quantitatively the concentration dependence of fluorescence intensities of the four polymers. The integrated fluorescence intensity was obtained by measuring the areas of the emission spectral peaks. We arrive at the same conclusion as previously with regard to the structure–PL behavior relationship for the present polymers.

Fig. 6(b) represents the fluorescence intensity per anthracene unit and it shows a steady decrease in PL throughout the concentration range up to 10^{-5} mol l^{-1} in the fluorophore unit, which indicates that concentration quenching begins at a very low concentration due to intramolecular contacts between and among the fluorophores. Since the

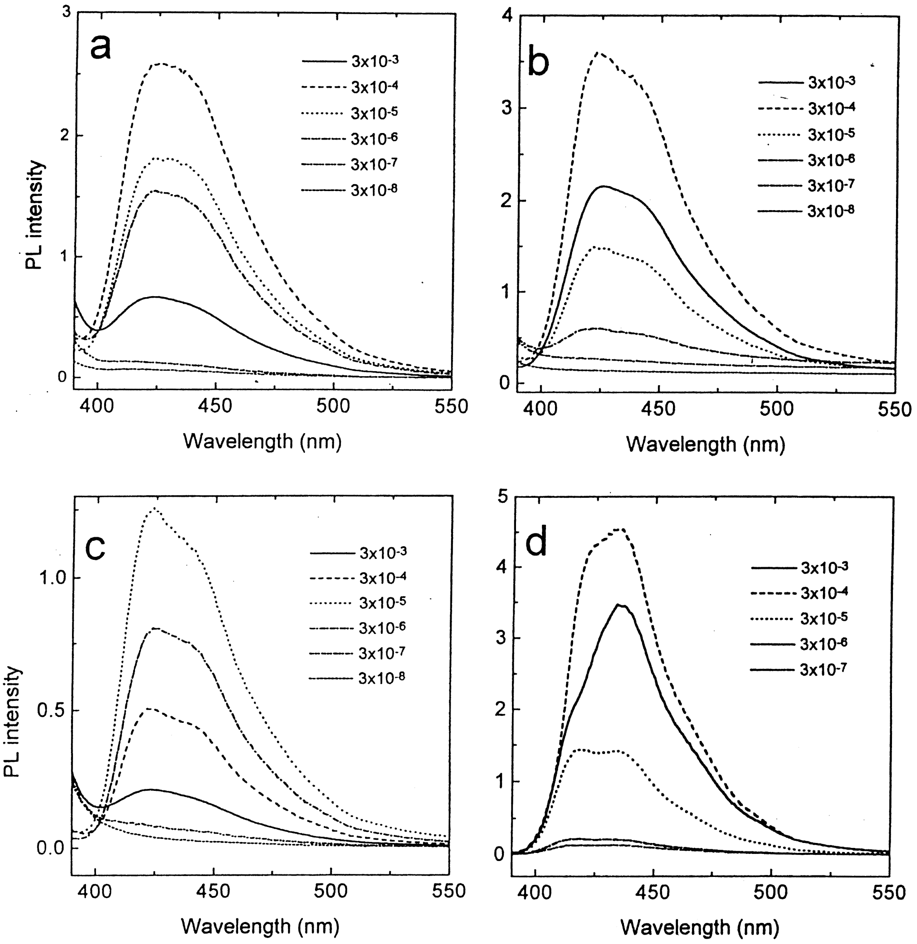


Fig. 5. PL spectra of the solutions of polymers **1** (a), **2** (b), **3** (c) and **4** (d) in 1,1,2,2-tetrachloroethane at room temperature.

fluorophores are bonded to polymer chains, they are more readily involved in intrachain interactions when compared to the low molar mass molecules that are expected to be far separated from each other in very dilute solutions free from any interactions between and among them.

As one increases the concentration further, chances for interchain interactions in addition to the already existing intrachain interactions become higher. This will cause additional reduction in the fluorescence intensity as one can see from Fig. 6(b) around the fluorophore concentration of 10^{-5} to 10^{-4} mol l^{-1}. Approximate fluorescence quantum efficiencies of the polymers were measured for the solutions of 3.0×10^{-4} mol l^{-1} in the fluorophore-containing repeating units. 9,10-Diphenylanthracene was utilized as a reference and 1,1,2,2-tetrachloroethane as a solvent. 9,10-Diphenylanthracene is known to reveal the quantum yield of 1.0 in dilute solutions [16,20]. The values thus obtained are 0.76, 0.97, 0.11 and 0.90 for polymer **1**, **2**, **3**, and **4**, respectively. The quantum efficiency of polymer **3** for the solution of 3.0×10^{-5} mol l^{-1}, however, is much higher at 0.70. Such an abrupt decrease in the quantum yield strongly suggests the occurrence of interchain contacts at about this concentration ($\sim 10^{-5}$ mol l^{-1}) of the fluorophore unit leading to extra concentration quenching. For other polymers, the similar reduction in the quantum efficiency starts to occur at a higher fluorophore concentration of about 10^{-4} mol l^{-1}, as one can see from Fig. 6(b). Such a difference is again ascribed to the unique structure of polymer **3** being different from the others: it contains the fluorophore structure in the main chain as well as in the side branch. It is well established that interchain contact of a spherically coiled macromolecule occurs at a concentration of about $1.4 \times 10^{-25}\ M/\langle R_G^2\rangle^{3/2}$ g cm^{-3} [23], where $\langle R_G\rangle$ stands for radius of gyration. The critical concentration depends on the molar mass (M) and structure (hence, $(\langle R_G^2\rangle)^{1/2}$) of the polymers. For example, for a polymer of molar mass of 1 million and $(\langle R_G^2\rangle)^{1/2}$ of 100 nm, the critical concentration is about 10^{-4} g cm^{-3}. Therefore, if the polymer consists of the repeating unit of the molar mass of about 1000 as for the present polymers, this concentration is translated to be about 10^{-4} mol l^{-1}. Although we do not know the molar mass and R_G values of the present polymers, our observations appear to coincide well with known solution theories [23]. Although electroluminescence (EL) of the polymers is not discussed in this article, it should be noted that electroluminescence characters of polymer **1** were reported previously by us [24]. The polymer emitted the blue light when an EL device was constructed by sandwiching the

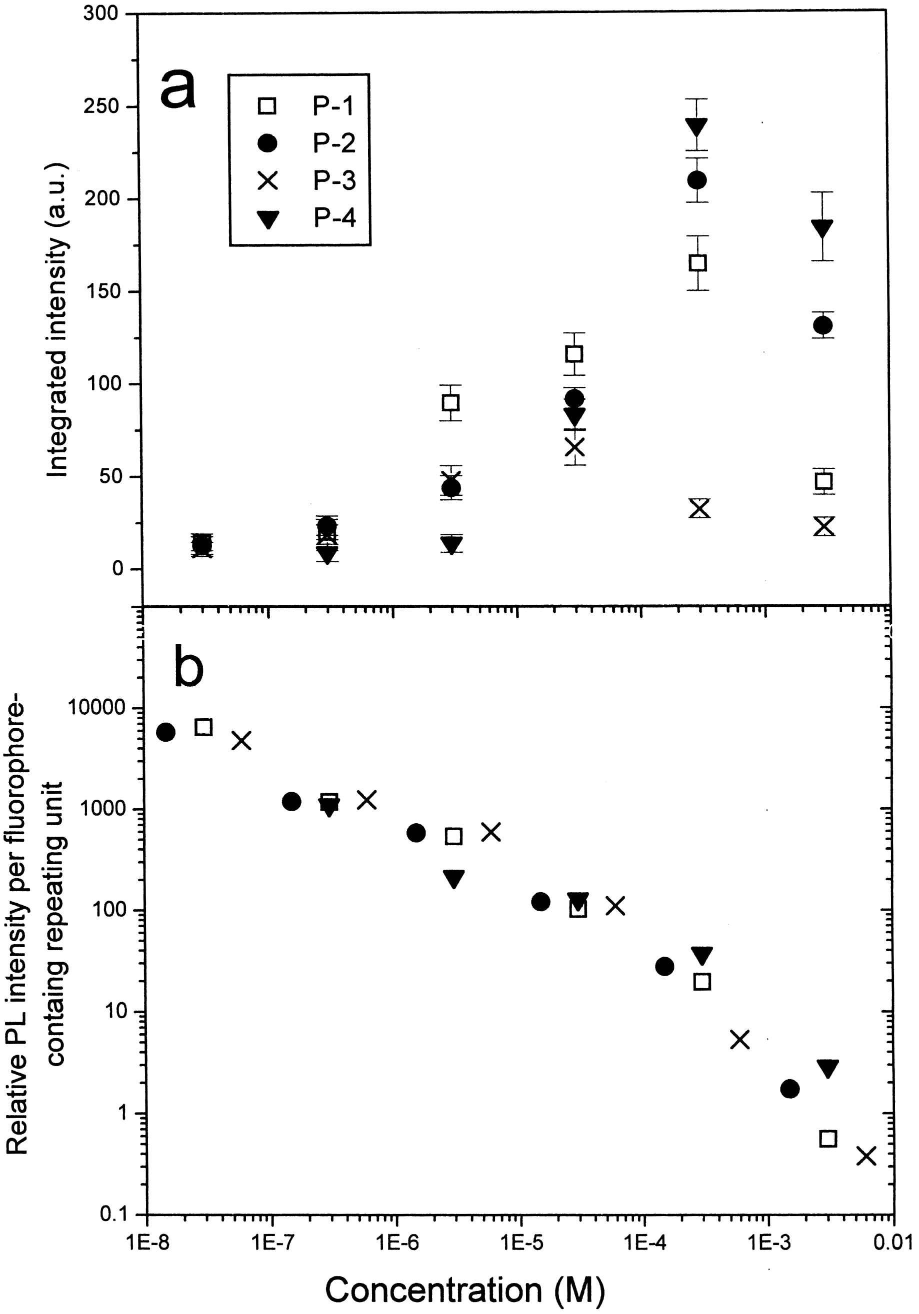


Fig. 6. Comparison of (a) integrated fluoroscence intensity and (b) fluoroscence intensity per the diphenylanthracene unit of polymers **1**, **2**, **3** and **4**.

polymer between the ITO glass and a deposited metal electrode.

4. Conclusion

We have synthesized new blue light-emitting aromatic polyesters carrying the diphenylanthracene fluorophores either only in the main chain, or only in the side chain, or in both. Polymers **1** and **2** were found to be thermotropic. Polymers **3** and **4** failed to be thermotropic due to their broadened molecular breath by inclusion of the diphenylanthracene moiety along the main chain or due to the nonlinear molecular shape. Although the present polymers emit blue light in solution, their solid films luminesce blue light with a very weak green tone, with the only exception of polymer **4** emitting genuine blue light. The relative emission intensity of the green region is stronger for polymer **3** than the other three. For this polymer, the presence of the diphenylanthracene structures in the main chain as well as in the pendent appears to cause various intra- and intermolecular interactions leading to changes in the electronic band structure of excited as well as ground states, which results in relative intensification of light emission in a longer wavelength region. The results reported in this article clearly demonstrate that photoluminescence behavior of the polymers depend very strongly on their structures. Moreover, intramolecular interactions between and among the fluorophores appear to be the main reason for the concentration quenching of photoluminescence observed even at the very low concentration of the fluorophores. This is ascribed to the structural characteristics of the polymers where the fluorophores are connected on the same chain, which results in ready interactions of various types among them.

Acknowledgements

This research was supported by the Korea Research Foundation through the basic science supporting program in the fiscal year of 1997 (Project no. BSRI 97-3406) for the Basic Science Research Institute of Korea University. S-J Chung would like to express his thanks to the Dae-Woo Foundation for a special scholarship award to enable him to carry out this research.

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