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Synthesis and characterization of soluble, photoluminescent polyamides, polyesters and polyethers containing 9,10-di(4-biphenylyl)anthracene segments in the main chain

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Abstract

New rigid polyamides and polyesters as well as semiflexible polyethers containing substituted 9,10-di(4-biphenylyl)athracene segments in the main chain were synthesized through pyrylium salts. They were characterized by viscosimetry, FT-IR, NMR, X-ray, differential scanning calorimetry, thermomechanical analysis, UV–vis and luminescence spectroscopy. All polymers were practically amorphous and showed an enhanced solubility. Polyamides, that displayed a very high hydrophilicity, dissolved in polar aprotic solvents, strong acids and pyridine. Polyesters and polyethers were soluble in all tested solvents and even in chloroform and THF. Polyamides had higher T_gs (165–220°C) than polyesters (100–106°C) and polyethers (98–105°C). The polymers with biphenylyl pendent groups showed lower T_gs and higher thermal stability than their counterparts with phenyl pendent groups. All polymers displayed violet to blue photoluminescence in solution and in solid state with maxima at 366–422 and 435–463 nm, respectively. The polymers carrying biphenylyl pendent groups exhibited in solution more broad emission spectra and higher quantum yields than the corresponding polymers with phenyl pendent groups. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamides; Polyesters; Polyethers

1. Introduction

Conjugated polymers can be recognized by alternation of double and single bonds along the chain. Their semiconducting properties arise from delocalization of π bonding and π^* antibonding molecular orbitals along the chain. Conjugated polymers are utilized, due to their luminescent properties, in several electronic applications, including light emitting diodes [1–4]. The photo- and electroluminescent polymeric materials, compared with the inorganic luminescent materials, offer a number of advantages, such as low operating voltages, easy colour tuning, fast response time, high quality of display and an improved processability.

The most widely used luminescent polymer is poly(*p*-phenylenevinylene) (PPV) which emits green light [5]. There is a great interest in obtaining high efficient blue light emitting devices. Several organic conjugated systems with higher bandgaps suitable for blue light emission have been studied. They consisted mainly of small conjugated molecules [6,7], poly(*p*-phenylene) (PP) polymers [8], and PPV oligomers attached to polymer chains [9]. More particularly, blue light emitting polymers based on phenylenevinylene (PV) systems, with PV either as a side chain or part of the polymer backbone have been reported [10,11–13].

In this article, we describe the synthesis and characterization of a new series of blue photoluminescent polymers that contained 9,10-di(4-biphenylyl)anthracene units in the main chain. Specifically, the synthesized polymers were rigid-rod polyamides and polyesters as well as semiflexible polyethers. Their synthesis was accomplished through pyrylium salts by a convenient and inexpensive method applied in our laboratory recently [14–23]. Phenyl or 4-biphenylyl pendent groups were attached along the polymer backbone to enhance the solubility. In addition, long aliphatic spacers were introduced into the backbone of polyethers to reduce their stiffness and further improve their solubility. Since the polymers contained oligophenyl moieties both in the main chain and in the lateral substituents, they possessed interesting optical properties. Especially, the existence of the anthracene segment in each repeat unit of the polymers was expected to reduce the electronic bandgap [24,25] and increase the luminescence efficiency. A literature survey revealed that several anthracene bearing polymers have been recently synthesized [26–31], and the majority of them behaved as strongly luminescent materials. More

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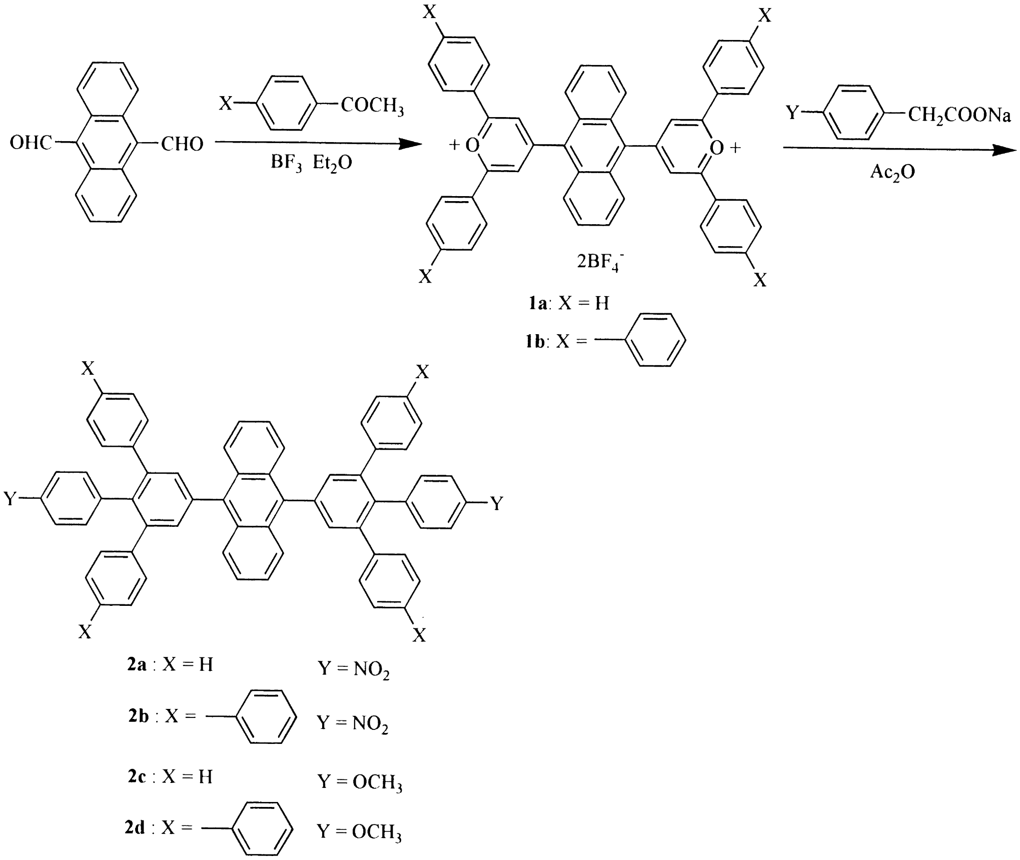


Scheme 1.

recently, the synthesis of rigid–flexible polyethers carrying bis(biphenyl)anthracene units in the main chain have been reported [32].

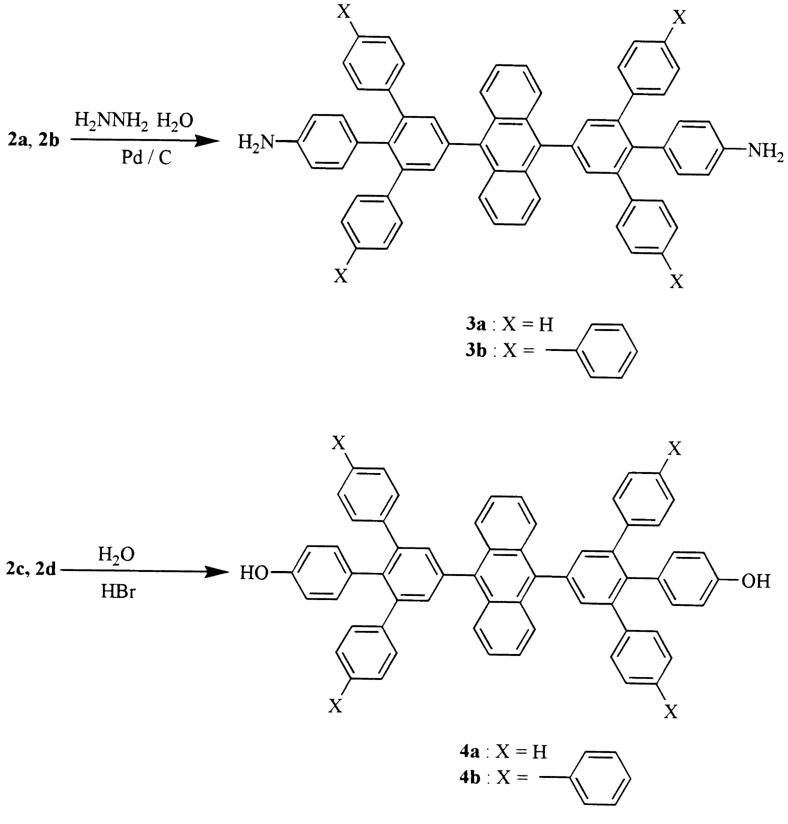
2. Experimental

2.1. Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin–Elmer 16PC FT-IR spectrometer with KBr pellets. The ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were obtained using a Brucker spectrometer with DMSO-d_6 or $CDCl_3$ as solvent. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Varian Cary 1E spectrometer. The emission spectra were obtained with a Perkin–Elmer LS50B luminescence spectrometer. DSC and TGA were performed on a DuPont 990 thermal analyser system. Ground polymer samples of about 10 mg each were examined by TGA and the weight loss comparisons were made between comparable specimens. The DSC thermograms were obtained at a heating rate of 10°C/min in N_2 atmosphere at a flow rate of 60 cm^3/min. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 10°C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted at least in duplicate to assure the accuracy of the results. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powder of polymer for 3 min under 5–7 kpsi at ambient temperature. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 ml in THF or DMF at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyser. The wide-angle X-ray diffraction patterns were obtained for powder specimens on a X-ray PW-1840 Philips diffractometer.

To determine the equilibrium water absorption, polymer samples were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator where 65% r.h. (relative humidity) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20°C, and were periodically weighted.

To measure the fluorescence quantum yields, a degassed solution (DMF for polyamides and THF for other polymers)



Scheme 2.

was prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The exciting wavelength was 310 nm and a solution in 1 N H_2SO_4 of quinine sulphate, which has a quantum yield of 0.546, was used as standard.

2.2. Reagents and solvents

9,10-Anthracenedicarboxaldehyde was prepared by the reaction of 9,10-bis(chloromethyl)anthracene with sodium salt of 2-nitropropane in dimethyl sulfoxide [33]. 9,10-Bis(chloromethyl)anthracene was synthesized by reacting anthracene with paraformaldehyde, in the presence of glacial acetic acid, H_3PO_4, and concentrated HCl, according to a reported method [34]. Acetophenone was purified by distillation under reduced pressure. 4′-Phenylacetophenone was recrystallized from ethanol. Terephthaloyl chloride was recrystallized from *n*-hexane. Dimethylacetamide (DMAc) and 1,2-dichloroethane were dried by distillation over CaH_2. 4-Nitrophenylacetic acid sodium salt and 4-methoxyphenylacetic acid sodium salt were prepared by reacting equimolar amounts of 4-nitrophenylacetic acid or 4-methoxyphenylacetic acid with aqueous sodium hydroxide. 1,10-Dibromodecane, boron trifluoride etherate, acetic anhydride, hydrazine hydrate, anthracene, and hydrobromic acid 47–49% were used as supplied.

2.3. Preparation of diamines and bisphenols (Schemes 1 and 2)

2.3.1. 4,4′-(9,10-Anthrylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**1a**)

A flask was charged with a mixture of 9,10-anthracenedicarboxaldehyde (1.00 g, 4.27 mmol), acetophenone (2.05 g, 17.08 mmol) and 1,2-dichloroethane (20 ml). Boron trifluoride etherate (2.70 ml, 21.35 mmol) was added portionwise to the stirred mixture at room temperature, and it was refluxed for 5 h. The solution was concentrated under reduced pressure, and ether was added to the concentrate. The dark brown precipitate was filtered, washed with ether and dried to afford **1a**. It was recrystallized from a mixture of THF/ether (1:1 (v/v)) (1.39 g, yield 40%, m.p. 98–100°C).

IR (KBr) cm^{-1}: 1626, 1596, 1466 (aromatic and pyrylium structure); 1056 (BF_4^-). ^{1}H-NMR (DMSO-d_6) δ: 8.75 (m, 4H, aromatic *meta* to O^+); 8.20–7.15 (m, 28H, other aromatic).

2.3.2. 4,4′-(9,10-Anthrylene)bis[2,6-di(4-biphenylyl) pyryliumtetrafluoroborate] (**1b**)

Compound **1b** was similarly prepared from 9,10-anthracenedicarboxaldehyde (1.60 g, 6.83 mmol), 4′-phenylacetophenone (5.30 g, 27.32 mmol) and boron trifluoride etherate (4.3 ml, 34.15 mmol). It was recrystallized from a mixture of THF/ether (1:1 (v/v)) (4.24 g, yield 55%, m.p. 121–123°C).

IR (KBr) cm^{-1}: 1620, 1600, 1484 (aromatic and pyrylium structure); 1056 (BF_4^-). ^{1}H-NMR (DMSO-d_6) δ: 8.54 (s, 4H, aromatic *meta* to O^+); 8.03–7.41 (m, 44H, other aromatic).

2.3.3. 9,10-Bis[(3,5-diphenyl-4-p-nitrophenyl)benzene] anthracene (2a)

A mixture of **1a** (1.22 g, 1.50 mmol), 4-nitrophenylacetic acid sodium salt (1.52 g, 7.50 mmol), and acetic anhydride (3 ml) was stirred and refluxed for 5 h. It was cooled at about −10°C overnight, and the brown solid precipitate was filtered, washed firstly with methanol, then with water and dried to afford **2a**. It was recrystallized from a mixture of CH_2Cl_2/ether (1:2 (v/v)) (1.27 g, yield 97%, m.p. 158–160°C).

IR (KBr) cm^{-1}: 1596 (aromatic); 1518, 1344 (NO_2). ^{1}H-NMR (DMSO-d_6) δ: 8.20–8.15 (m, 4H, aromatic *ortho* to NO_2); 7.93–7.87 (m, 4H, aromatic *meta* to NO_2); 7.70–7.10 (m, 32H, other aromatic).

2.3.4. 9,10-Bis{[3,5-di(4-biphenylyl)-4-p-nitrophenyl] benzene}anthracene (2b)

Compound **2b** was similarly prepared from **1b** (4.16 g, 3.72 mmol), 4-nitrophenylacetic acid sodium salt (3.78 g, 18.6 mmol) and acetic anhydride (8 ml). It was recrystallized from a mixture of THF/ether (1:2 (v/v)) (4.06 g, yield 92%, m.p. 121–123°C).

IR (KBr) cm^{-1}: 1598 (aromatic); 1518, 1344 (NO_2). ^{1}H-NMR (DMSO-d_6) δ: 8.27–8.25 (m, 4H, aromatic *ortho* to NO_2); 8.03–8.01 (m, 4H, aromatic *meta* to NO_2); 7.81–7.35 (m, 48H, other aromatic).

2.3.5. 9,10-Bis[(3,5-diphenyl-4-p-methoxyphenyl) benzene]anthracene (2c)

Compound **2c** was similarly prepared from **1a** (1.92 g, 2.36 mmol), 4-methoxyphenylacetic acid sodium salt (2.22 g, 11.8 mmol), and acetic anhydride (5 ml). It was recrystallized from a mixture of CH_2Cl_2/ether (1:2 (v/v)) (1.88 g, yield 94%, m.p. 108–110°C).

IR (KBr) cm^{-1}: 2930 (C–H stretching of OCH_3); 1604, 1508 (aromatic); 1244, 1030 (ether). ^{1}H-NMR (DMSO-d_6) δ: 7.55–7.10 (m, 36H, aromatic except those *ortho* to OCH_3); 6.86 (m, 4H, aromatic *ortho* to OCH_3); 3.75 (s, 6H, OCH_3).

2.3.6. 9,10-Bis{[3,5-di(4-biphenylyl)-4-p-methoxyphenyl] benzene}anthracene (2d)

Compound **2d** was similarly prepared from **1b** (0.50 g, 0.45 mmol), 4-methoxyphenylacetic acid sodium salt (0.42 g, 2.25 mmol), and acetic anhydride (3 ml). It was recrystallized from a mixture of DMF/ethanol (1:1 (v/v)) (0.40 g, yield 78%, m.p. 158–160°C).

IR (KBr) cm^{-1}: 2930 (C–H stretching of OCH_3); 1598 (aromatic); 1246, 1030 (ether). ^{1}H-NMR (DMSO-d_6) δ: 7.84–7.17 (m, 52H, aromatic except those *ortho* to OCH_3); 6.87 (m, 4H, aromatic *ortho* to OCH_3); 3.72 (s, 6H, OCH_3).

2.3.7. 9,10-Bis[(3,5-diphenyl-4-p-aminophenyl)benzene] anthracene (3a)

A flask was charged with a mixture of **2a** (1.46 g, 1.66 mmol), 1,4-dioxane (20 ml) and a catalytic amount of palladium 10% on activated carbon. Hydrazine hydrate (5 ml) was added dropwise to the stirred mixture at 101°C and refluxing was continued for 48 h. The mixture was subsequently filtered, and the filtrate was concentrated under reduced pressure. Water was added to the residue and **3a** was obtained as a pale brown precipitate. It was recrystallized from a mixture of 1,4-dioxane/water (1:2 (v/v)) (1.12 g, yield 82%, m.p. 207–209°C).

IR (KBr) cm^{-1}: 3350 (N–H stretching); 1618 (N–H deformation); 1514 (aromatic); 1278 (C–N stretching). ^{1}H-NMR (DMSO-d_6) δ: 7.84–7.23 (m, 32H, aromatic except those *ortho* and *meta* to NH_2); 6.80 (m, 4H, aromatic *meta* to NH_2); 6.50 (m, 4H, aromatic *ortho* to NH_2); 4.96 (br, 4H, NH_2). ^{13}C-NMR (DMSO-d_6) δ: 150.79, 146.98, 142.11, 140.68, 138.56, 132.67, 130.47, 129.72, 128.54, 127.76, 126.35, 125.63, 124.54, 122.12, 114.61. Anal. Calcd. for $C_{26}H_{44}N_2$: C, 91.14; H, 5.43; N, 3.43. Found: C, 90.76; H, 5.49; N, 3.98.

2.3.8. 9,10-Bis{[3,5-di(4-biphenylyl)-4-p-aminophenyl] benzene}anthracene (3b)

Compound **3b** was similarly prepared as a pale brown solid in 74% yield by catalytic hydrogenation of **2b**. It was recrystallized from a mixture of 1,4-dioxane/water (1:1 (v/v)).

IR (KBr) cm^{-1}: 3360 (N–H stretching); 1620 (N–H deformation); 1514 (aromatic); 1280 (C–N stretching). ^{1}H-NMR (DMSO-d_6) δ: 7.99–7.46 (m, 48H, aromatic except those *ortho* and *meta* to NH_2); 6.77 (m, 4H, aromatic *meta* to NH_2); 6.51 (m, 4H, aromatic *ortho* to NH_2); 4.97 (br, 4H, NH_2). Anal. Calcd. for $C_{86}H_{60}N_2$: C, 92.11; H, 5.39; N, 2.50. Found: C, 91.63; H, 5.33; N, 2.61.

2.3.9. 9,10-Bis[3,5-diphenyl-4-p-hydroxyphenyl) benzene]anthracene (4a)

A mixture of **2c** (2.39 g, 2.82 mmol), glacial acetic acid (40 ml) and hydrobromic acid 47–49% (8 ml) was refluxed for 2 days. At this time, hydrobromic acid (8 ml) was added to the mixture and it was refluxed for two other days. The reaction mixture was poured into water and the brown precipitate was filtered, washed thoroughly with water and dried to afford **4a**. It was recrystallized from a mixture of THF/ether (1:2 (v/v)) (1.73 g, yield 75%, m.p. > 300°C).

IR (KBr) cm^{-1}: 3052 (O–H stretching); 1598 (aromatic); 1370 (O–H deformation); 1260, 1174 (C–OH stretching). ^{1}H-NMR (DMSO-d_6) δ: 8.87 (br, 2H, OH); 8.12–7.15 (m, 36H, aromatic except those *ortho* to OH); 6.80 (m, 4H, aromatic *ortho* to OH). ^{1}H-NMR (DMSO-d_6) δ: 154.20,

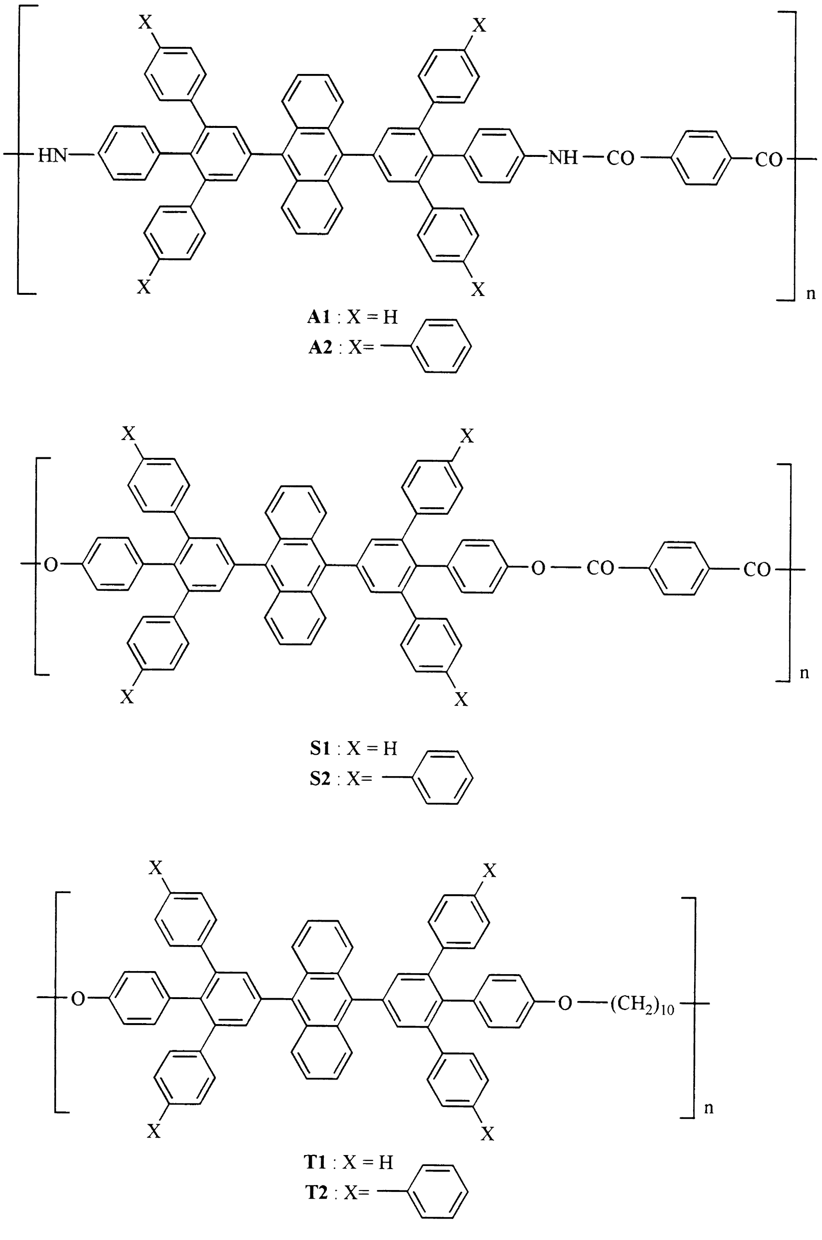


Chart 1.

131.00, 130.69, 129.36, 128.42, 127.36, 126.54, 125.13, 124.46, 122.36, 121.48, 120.74, 116.20. Anal. Calcd. for $C_{62}H_{42}O_2$: C, 90.92; H, 5.17. Found: C, 90.05; H, 5.23.

*2.3.10. 9,10-Bis{[3,5-di(4-biphenylyl)-4-p-hydroxyphenyl] benzene}anthracene (**4b**)*

Compound **4b** was similarly prepared in 82% yield as a brown solid by hydrolysis of **2d**. It was recrystallized from a mixture of chloroform/ether (1:2 (v/v)) (m.p. 233–235°C).

IR (KBr) cm^{-1}: 3050 (O–H stretching); 1600 (aromatic); 1390 (O–H deformation); 1258, 1194 (C–OH stretching). ^{1}H-NMR (DMSO-d$_6$) δ: 9.07 (br, 2H, OH); 8.16–7.40 (m, 52H, aromatic except those *ortho* to OH); 6.90 (m, 4H, aromatic *ortho* to OH). Anal. Calcd. for $C_{86}H_{58}O_2$: C, 91.95; H, 5.20. Found: C, 91.12; H, 5.26.

2.4. Preparation of polymers (Chart 1)

*2.4.1. Polyamides **A1** and **A2***

The synthesis of **A1** is given as a typical example for the preparation of polyamides: a flask was charged with a solution of **3a** (0.4000 g, 0.05 mmol) in DMAc (10 ml) containing 5 wt% LiCl. To the mixture was added 0.5 ml of propylene oxide. Terephthaloyl chloride (0.0994 g, 0.05 mmol), dissolved in DMAc (8 ml), was added dropwise to the stirred solution at −10°C under N_2. The stirring of the mixture was continued at this temperature for 5 h and then at room temperature overnight in a steam of N_2. It was poured into water and the pale brown precipitate was filtered, washed firstly with water, then with acetone, and dried to afford **A1** (0.45 g, yield 97%).

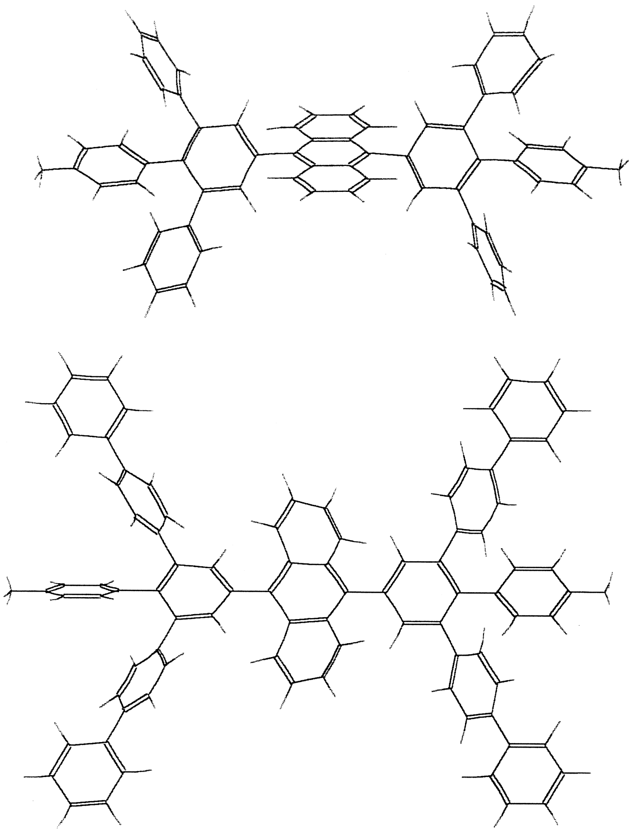


Fig. 1. Optimized geometries for bisphenols **4a** (top) and **4b** (bottom) (CS Chem3D pro Molecular Modelling System, Version 3.2, 1995; Cambridge-Soft Corporation, 1995).

Anal. Calcd. for $(C_{70}H_{46}N_2O_2)_n$: C, 88.77; H, 4.89; N, 2.96. Found: C, 88.04; H, 4.93; N, 2.85.

2.4.2. Polyesters *S1* and *S2*

The synthesis of **S1** is given as a typical example for the preparation of polyesters: a flask was charged with a solution of **4a** (0.2676 g, 0.03 mmol) in DMAc (15 ml). Then, 0.5 ml of propylene oxide was added to the mixture. Terephthaloyl chloride (0.0663 g, 0.03 mmol), dissolved in DMAc (6 ml), was added dropwise to the mixture at room temperature under N_2. The mixture was subsequently stirred and heated at 100°C overnight in a stream of N_2. It was poured into water and the brown precipitate was filtered, washed with water and dried to afford **S1** (0.29 g, yield 94%).

Anal. Calcd. for $(C_{70}H_{44}O_4)_n$: C, 88.58; H, 4.67. Found: C, 88.13; H, 4.72.

2.4.3. Polyethers *T1* and *T2*

The synthesis of **T1** is given as a typical example for the preparation of polyethers: a mixture of **4a** (0.6000 g, 0.07 mmol), 1,10-dibromodecane (0.2198 g, 0.07 mmol), K_2CO_3 (0.2100 g, 1.54 mmol) and DMAc (20 ml) was stirred and refluxed overnight under N_2. It was poured into water and the pale brown precipitate was filtered, washed with water and dried to afford **T1** (0.67 g, yield 96%).

Anal. Calcd. for $(C_{72}H_{60}O_2)_n$: C, 90.34; H, 6.32. Found: C, 89.56; H, 6.37.

3. Results and discussion

3.1. Synthesis and characterization of monomers

Two diamines and two bisphenols, which are derivatives of the substituted 9,10-di(4-biphenylyl)anthracene, were synthesized by a convenient method, as shown in Schemes 1 and 2. More particularly, 9,10-anthracenedicarboxaldehyde reacted with acetophenone or 4′-phenylacetophenone in the presence of boron trifluoride etherate to afford pyrylium salts **1** [35]. The latter reacted subsequently with 4-nitro- or 4-methoxyphenylacetic acid anhydrides, generated in situ from the corresponding phenylacetic acid sodium salts and excess of acetic anhydride, to yield aromatic compounds **2** [36]. Finally, the nitro or the methoxy groups of the latter were hydrogenated or hydrolyzed to afford diamines **3** and bisphenols **4**.

Characterization of monomers was accomplished by elemental analyses as well as FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Certain structural characteristics of bisphenols **4a** and **4b** were determined by means of the CS Chem3D Pro v.3.2 modelling system. Fig. 1 presents the optimized geometries of these bisphenols, which were obtained after energy minimization. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles). It seems that both monomers deviated significantly from the coplanar conformation. Particularly, all phenyl rings formed with the adjacent phenyls dihedral angles ranging from 40 to 60°. In addition, the twist angle between the anthracene unit and the adjacent phenyls was 70 and 30° for **4a** and **4b**, respectively. Diamines **3a** and **3b** showed similar features. These structural characteristics of the parent monomers can influence some properties of the resulting polymers. For example, it is well known, that in poly(phenylene)s a twist angle greater than 40° can diminish or even suppress the conjugation and therefore limit the fluorescence.

3.2. Synthesis and structural characterization of polymers

A new class of rigid-rod polyamides and polyesters as well as of semiflexible polyethers were synthesized, the structures of which are shown in Chart 1. Specifically, polyamides **A** and polyesters **S** were prepared from the reactions of terephthaloyl chloride with diamines **3** or bisphenols **4** by the solution polycondensation method at low and high temperatures, respectively. Propylene oxide was used as an acid acceptor for these reactions. Finally, polyethers **T** were prepared from the reactions of bisphenols **4** with 1,10-dibromodecane in the presence of K_2CO_3. Polar aprotic solvents, such as DMAc, were utilized as reaction medium

Table 1
Yields, inherent viscosities, glass transition temperatures, fluorescence wavelength maxima in solution and in thin film and fluorescence quantum yields in solution (λ_f, max represents the fluorescence maxima, E_f, max the corresponding energies and Φ_f the fluorescence quantum yields)

Polymer	**A1**	**A2**	**S1**	**S2**	**T1**	**T2**
Yield (%)	97	88	94	95	96	94
n_{inh} (dl/g)	0.50[a]	0.56[a]	0.48[b]	0.53[b]	0.56[b]	0.61[b]
T_g from DSC (°C)	–	–	115	108	110	105
T_g from TMA (°C)	220	165	106	100	105	98
$\lambda_{f,\max}$ in solution[c] (nm)	422	366, *412*	400, *418*	378, *412*	404, *419*	381, *411*
$E_{f,\max}$ in solution[c] (eV)	2.94	3.39, *3.01*	3.10, *2.97*	3.28, *3.01*	3.07, *2.96*	3.26, *3.02*
$\lambda_{f,\max}$ in thin film (nm)	435	463	445	446	448	450
$E_{f,\max}$ in thin film (eV)	2.85	2.68	2.79	2.78	2.77	2.76
Φ_f in solution	0.09	0.17	0.08	0.19	0.08	0.16

[a] Inherent viscosity in DMF (0.5 g/dl) at 30°C
[b] Inherent viscosity in THF (0.5 g/dl) at 30°C.
[c] *Underlined* numerical values denote absolute maxima.

for all polymerization reactions. The polymers remained in solution and they were isolated after precipitation in water. They were obtained in high yields (88–97%) and their inherent viscosities ranged from 0.48 to 0.61 dl/g (Table 1).

The structures of the polymers were confirmed by elemental analyses, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The elemental analyses of polymers were consistent with chemical structures. Fig. 2 presents typical FT-IR spectra of polymers **A2**, **S2** and **T2**. Polyamide **A2** showed characteristic absorption bands at 3362 (N–H stretching); 1659 (C=O); 1598, 1486 (aromatic); 1514 (aromatic and NH deformation) and 1316 cm^{-1} (C–N stretching). Polyester **S2** displayed absorptions at 1712 (C=O stretching); 1600 (aromatic) and 1264, 1108 (C–O–C stretching). Finally, polyether **T2** exhibited absorptions at 2922, 2850 (C–H stretching of aliphatic); 1598, 1482 (aromatic) and 1242, 1170 cm^{-1} (ether). All polymers showed a strong absorption around 750 cm^{-1}, which was assigned to the four adjacent hydrogens of the anthrylene moiety [37].

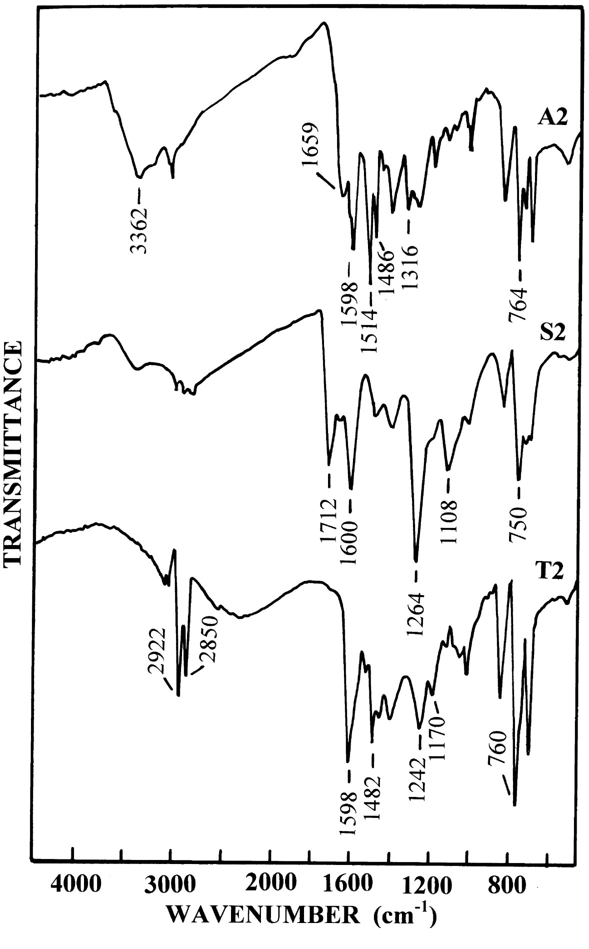


Fig. 2. FT-IR spectra of polymers **A2** (top), **S2** (middle) and **T2** (bottom).

The ^{1}H-NMR spectra of polymers displayed rather broad signals owing to the polymeric materials. The peaks of polyamide **A2** in DMSO-d_6 solution are given as an example: 10.40 (br. 2H, NHCO); 8.12 (m, 4H, aromatic of terephthalic acid segment); 7.90–6.50 (m, 40H, other aromatic). The ^{13}C-NMR spectrum of **A2** showed a characteristic peak at 164 ppm associated with the NHCO segment. The ^{1}H-NMR spectrum of polyether **T1** in $CDCl_3$ solution displayed peaks at 8.02 (m, 4H, aromatic of anthracene at positions 1, 4, 5, 8); 7.63–7.43 (m, 32H, other aromatic except those *ortho* to O); 6.94 (m, 4H, aromatic *ortho* to O); 4.10 (m, 4H, OCH_2); 2.08–1.32 (m, 16H, $OCH_2(CH_2)_8$). Fig. 3 presents the ^{13}C-NMR spectrum of **T1** and assignment of peaks.

3.3. Crystallinity, hydrophilicity and solubility of polymers

The wide-angle X-ray scattering curves of polymers revealed that they were practically amorphous owing to the presence of the bulky pendent groups. Polyester **S2** as well polyethers **T1** and **T2** had higher crystallization tendency than other polymers. The long aliphatic moieties in the backbone of polyethers **T1** and **T2** reduced the chain rigidity and allowed more efficient packing, thus contributing to their higher crystallization tendency. Polymers **S2** and **T2** displayed an intense peak at 20°, which is interpreted as being due to a local stacking of 4.5 Å. Polyether **T1** had a

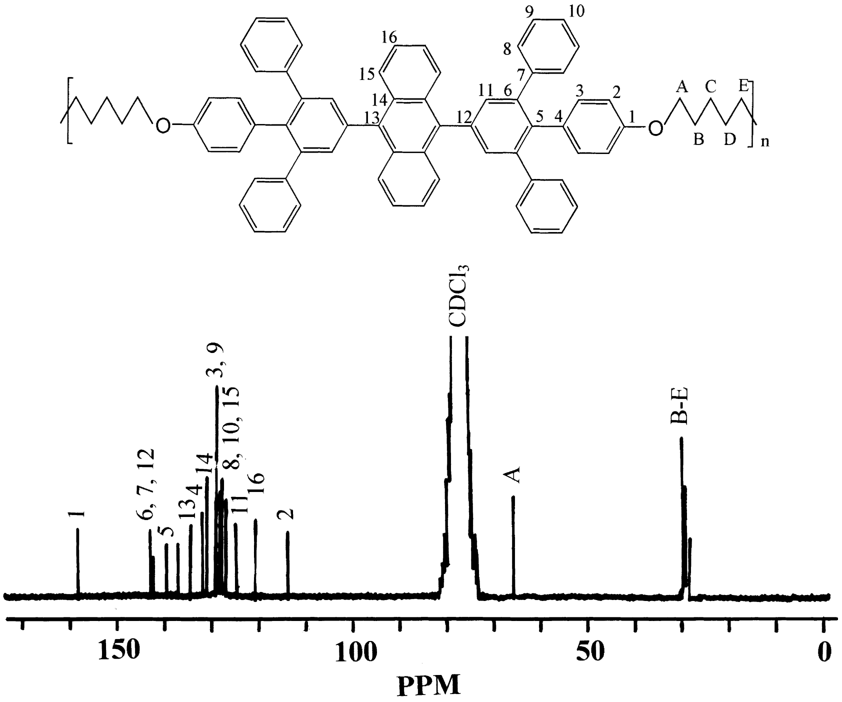


Fig. 3. ^{13}C-NMR spectrum of polyether **T1** in CDCl$_3$ solution.

local stacking of 7.3 Å, since it exhibited a strong reflection hump at 12°.

It is well established that for polyamides the moisture uptake is generally proportional to the number of amide groups present in the repeat unit [38]. The isothermal water absorption of polyamides **A1** and **A2** was determined to estimate their hydrophilicity. Following exposure for 50 h, the water uptake was 5.33 and 3.58%, respectively, and the corresponding numbers of absorbed water per amide equivalent weight (NMAW) were 1.40 and 1.24. These values are very high compared to those of the corresponding polyamides, which contained phenylene instead of anthrylene segment and displayed NMAW values of 0.57 and 0.43 [18]. The amorphous nature of the present polyamides along with the loose chain packing that increased the water accessibility should be responsible for this behaviour. It is noteworthy that **A2** showed lower hydrophilicity than **A1**, which conforms with our previously obtained data [18].

The solubilities of polymers were tested in various solvents and the results are summarized in Table 2. Polyamides dissolved in polar aprotic solvents (DMF, NMP), certain acids (CCl_3COOH, H_2SO_4) and pyridine. It is seen that **A2**, with biphenylyl pendent groups, showed higher solubility than **A1**, which conforms with the literature data [18]. Polyesters and polyethers displayed an excellent solubility being soluble at room temperature or upon heating almost in all tested solvents. They dissolved readily at ambient temperature even in 1,1,2,2-tetrachloroethane, chloroform and THF. Generally, the enhanced solubility of the present polymers reflects their amorphous character.

3.4. Thermal and thermomechanical properties of polymers

The thermal behaviour of polymers was investigated by DSC, TMA and TGA. Fig. 4 presents typical DSC and TMA thermograms of polymers, **A1**, **S2** and **T2**, while the T_g values of all polymers are summarized in Table 1. All polymers did not show a melting endotherm by DSC and this confirmed their amorphous character. The DSC traces of polyamides **A1** and **A2** displayed at the first heating run a broad endotherm at around 125°C. Since this endotherm disappeared completely at the second heating, it should be attributed to the evaporation of residual water. The DSC curves of polyamides, obtained at the second scanning, did not show a distinct step drop associated with T_g. In contrast, the DSC traces of polyesters and polyethers exhibited T_g transitions, which were in agreement with those determined by TMA. The T_gs of all polymers were determined by TMA using a penetration probe. As expected, polyamides had remarkably higher T_gs (165–220°C) than the corresponding polyesters (100–106°C) due to the hydrogen bonding interactions. Polyethers possessed the lowest T_gs (98–105°C) owing to their semiflexible nature. In any case, the polymers with 4-biphenylyl pendent groups showed lower T_gs than their counterparts with phenyl pendent groups. This feature was assigned to the higher free volume of the former.

The thermal stability of polymers was ascertained by TGA. The temperatures (TD) at which weight losses of 1, 5 and 50% were observed in both N_2 and air as well as the anaerobic char yield (Y_c) at 800°C for all polymers are

Table 2
Solubilities of polymers (solubility: ++, soluble at room temperature; +, soluble in hot solvent; + −, partially soluble; −, insoluble)

Polymer	Solvents^{a}								
	DMF	NMP	CCl_3COOH	H_2SO_4	TCE	$CHCl_3$	THF	Py	1,4-Dioxane
A1	+^{b}	+	+	+	−	−	−	+	−
A2	++	++	++	++	+ −	−	−	++	+ −
S1	++	++	++	+	+	++	++	++	+ −
S2	++	++	++	+	++	++	++	++	++
T1	++	++	++	+	++	++	++	++	++
T2	++	++	++	+	++	++	++	++	++

[a] DMF, *N*,*N*-dimethylformamide; NMP, *N*-methylpyrrolidone; TCE, 1,1,2,2-tetrachloroethane; THF, tetrahydrofurane; Py, Pyridine.

[b] Solvent containing 5% (w/w) LICl.

summarized in Table 3. The polymers were stable up to 294–390°C and afforded Y_c of 36–68% at 800°C. Since the polymers containing biphenylyl pendent groups displayed higher values of TD and Y_c than their counterparts with phenyl pendent groups, they were more heat resistant. Finally, polyethers exhibited lower Y_c (36–51%) than polyamides and polyesters (58–68%) owing to the presence of the thermally unstable aliphatic moieties.

3.5. Optical properties of polymers

The polymers contained substituted 9,10-di(4-biphenylyl)anthracene segments along the main chain and therefore presented optical properties of primary importance for our study. The UV–vis spectra of polymers in solution (DMF for polyamides and THF for polyesters and polyethers) were recorded and only those of **A1**, **S1** and **T1** are depicted in Fig. 5 because of their similarity. All of them exhibited the first absorption band around 260 nm assigned to the aromatic groups and the second absorption at 320–420 nm, which is characteristic of the 9,10-diphenylanthracene structure [39,40]. In addition, the UV–vis spectra of polymers in thin film were recorded and that of **S1** is given in Fig. 5 as a typical example. The films were prepared by spin coating on quartz plates from the solutions of polymers. Upon comparing the absorption spectrum of **S1** in solid state with that of **S1** in solution, it is seen that the former showed a broadening and its low energy tail raised up, due to the formation of aggregates [41].

The polymers displayed violet to blue photoluminescence in solution and in with maxima at 366–422 nm and 435–463 nm, respectively (Figs. 6 and 7). The emission wavelengths at peak maxima and the corresponding energies are listed in Table 1. The emission spectra of all the polymers were independent of the excitation wavelength but depended highly on the structure of polymers. Polyamide **A1** showed in solution an emission maximum at 422 nm, while **A2** displayed two well-separated maxima at 336 and 412 nm. Obviously, the introduction of the 4-biphenylyl pendent group instead of phenyl broadened the emission spectrum to lower wavelengths. The two maxima of **A2** corresponded to two different conjugation lengths, one of which was almost similar with to that of **A1**. The same behaviour was observed upon comparing **S1** with **S2** and **T1** with **T2**. These differences indicated that, when the fluorophore segment in the side groups was elongated, there is a higher probability for intra- as well as intermolecular interactions among the fluorophores, which in turn causes broadening of the emission spectrum.

Polyamide **A1** could be compared with the corresponding polyamide containing in the main chain 1,4-phenylene instead of the 9,10-anthrylene unit that has been previously prepared in our laboratory. The latter exhibited in DMF solution an emission maximum at 404 nm. This supported

Table 3
Thermal stabilities of polymers

Polymer	In N_2				In air		
	DT_1^{a} (°C)	DT_5^{a} (°C)	DT_{50}^{a} (°C)	Y_c^{b} (%)	DT_1^{a} (°C)	DT_5^{a} (°C)	DT_{50}^{a} (°C)
A1	390	471		68	377	411	477
A2	397	478		71	397	441	487
S1	313	404		58	310	400	493
S2	333	377		59	313	403	578
T1	311	359	649	36	291	344	476
T2	321	363		51	294	367	556

[a] DT_1, DT_5, DT_{50}: temperatures at which weight loss of 1, 5 and 50%, respectively, was obtained.

[b] Char yield at 800°C.

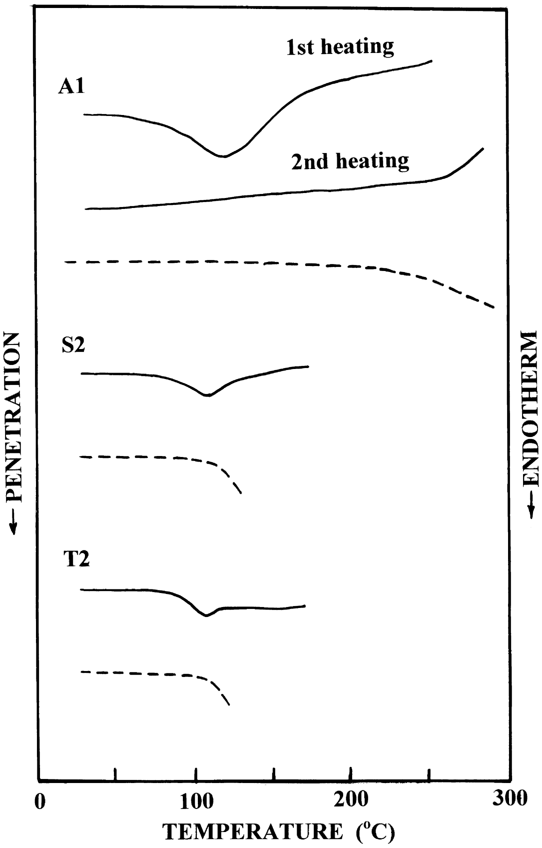


Fig. 4. DSC thermograms (first heating; solid line) as well as TMA thermograms (second heating; dashed line) of polymers **A1**, **S2** and **T2**. Conditions: N_2 flow, 60 cm^3/min; heating rate, 10°C/min.

that the attachment of the anthrylene unit to the polymer backbone reduced the electronic bandgap [24,25] and caused a red shift by 18 nm. It has been established that the attachment of the 9,10-anthrylene moiety into the polymer backbone minimizes the energy difference between the aromatic and quinoid resonance in comparison with the 1,4-phenylene segment.

Fig. 7 depicts typical emission spectra of polyamides **A1** and **A2** as well as of polyethers **T1** and **T2** in solid state. They were reproduced several times using thin films to assure the accuracy of the results. Upon going from solution to the solid state, the spectra became broader and their maxima showed considerable red shifts, which indicates an increased conjugation. This feature was attributed to the existence of appreciable stacking interactions in the solid film and the formation of aggregates [42,43]. Evidence for this behaviour was also obtained from the absorption spectra, as has been mentioned above.

The emission spectra of polymers in solution as well as in solid state were much broader especially in the longer wavelength region than that of 9,10-diphenylanthracene itself. This supports that various intra- and interchain interactions between fluorophores can easily occur in the present polymers.

The photoluminescence quantum yields (Φ) of polymers in solution were measured [44] relative to quinine sulphate ($\Phi = 0.546$) and the results are summarized in Table 1. The Φ values were of the order **A1** < **A2**, **S1** < **S2** and **T1** < **T2**. The longer side groups of 4-biphenylyl relative to phenyl in polymers **A2**, **S2** and **T2** resulted in greater π-delocalization of the entire conjugated system and, hence, an increase in the luminescence efficiency. However, the present polymers did not show high Φ values, taking into account the quantum yield (0.91 in nonpolar solvents) of 9,10-diphenylanthracene. Probably the bulky side groups along the rigid segments of polymers that resulted in nonplanar conformations are responsible for this behaviour.

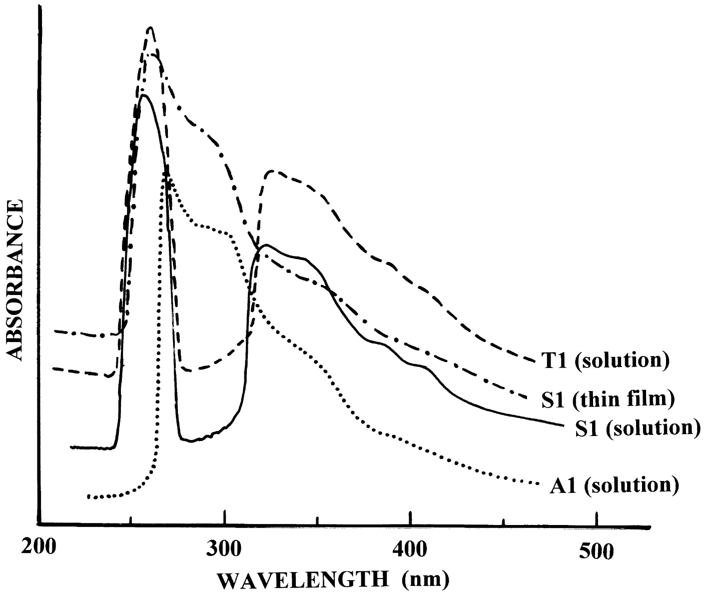


Fig. 5. UV–vis spectra of polymer **A1** in DMF solution as well as of polymers **S1** and **T1** in THF solution. UV–vis spectrum of polymer **S1** in thin film.

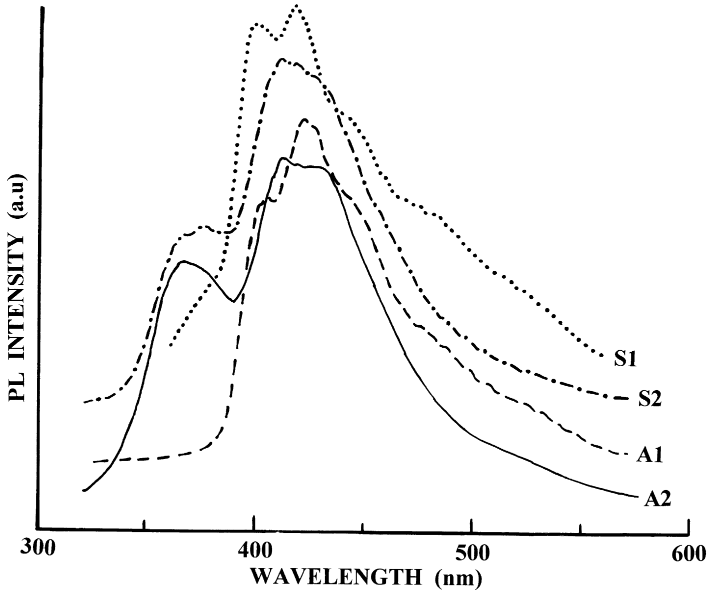


Fig. 6. Emission spectra for polymers **A1** and **A2** in DMF solution as well as of polymers **S1** and **S2** in THF solution (excitation at 310 nm).

4. Conclusions

Starting from pyrylium salts two new aromatic diamines **3a** and **3b** as well as two bisphenols **4a** and **4b** were synthesized and used for the preparation of polyamides, polyesters and polyethers. It was shown by means of a modelling system that bisphenols **4a** and **4b** deviated considerably from the coplanar confirmation. All polymers were generally amorphous. However, **S2**, **T1** and **T2** had higher crystallization tendency. Polyamides **A1** and **A2** showed very high hydrophilicity that was estimated by determination of their isothermal water absorption. Polyamides dissolved in polar aprotic solvents, strong acids and pyridine. Polyesters and polyethers dissolved in all tested solvents and even in chloroform and THF. The T_g values were 165–220°C for polyamides, 100–106°C for polyesters and 98–105°C for polyethers. All polymers were stable up to 294–390°C and afforded anaerobic char yields of 36–68% at 800°C. The polymers with biphenylyl pendent groups showed lower T_gs and higher thermal stability than their counterparts with phenyl pendent groups. All polymers displayed violet and/or blue photoluminescence in solution and in solid state with maxima at 366–422 nm and 435–463 nm, respectively. The introduction of the biphenylyl pendent

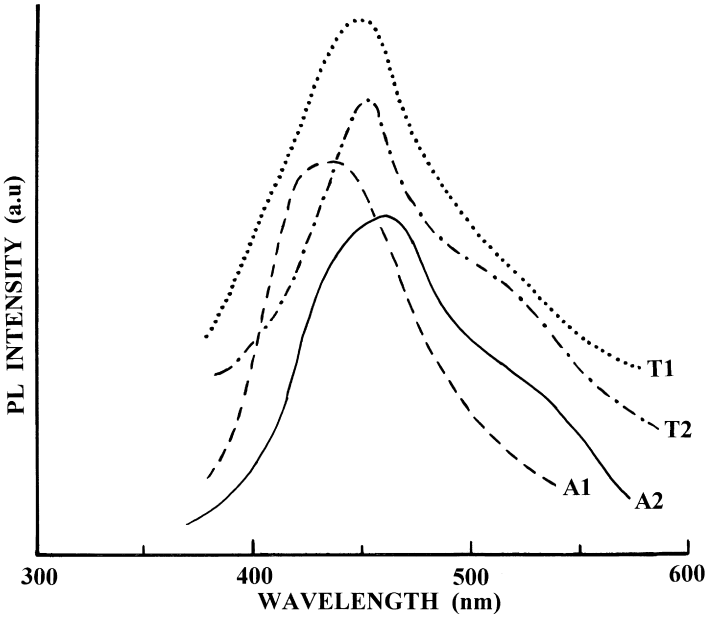


Fig. 7. Emission spectra of polymers **A1** and **A2** in thin film (excitation at 310 nm).

group instead of phenyl broadened the emission spectrum in solution to lower wavelengths and increased the quantum yield.

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