

Synthesis and Characterization of Fluorescent Poly(aryl ether thiadiazole)s and Poly(aryl ether oxadiazole)s

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Introduction

Since the first report on poly(*p*-phenylenevinylene) ¹⁾, the electroluminescent properties of many conjugated polymers such as poly(*p*-phenylenevinylene) (PPV), polythiophene (PT), poly(*p*-phenylene) (PPP), and polyfluorene (PF) have been investigated because of their potential for use in display technology. However, in the application of polymer light-emitting diodes (PLEDs), there are yet three fundamental issues to be considered: (1) full color capability, (2) emission efficiency, (3) stability (lifetime). In recent years polymers containing 1,3,4-thiadiazole and 1,3,4-oxadiazole heterocycle in the main chain had been reported ²⁻³⁾. For example, polymers with oxadiazole unit used in PLEDs were investigated by Peter Stroehriegel and his coworkers ⁴⁾. In this paper, we will describe the synthesis of novel luminescent poly(aryl ether)s and their thermal and fluorescent properties.

Experimental part

Synthesis of monomers

Bis(4-fluorobenzoyl)hydrazine (3)

4-Fluorobenzoylhydrazine (1.54 g, 10 mmol) (2) and 4-fluorobenzoyl chloride (1.59 g, 10 mmol) were dissolved in pyridine (30 ml). The solution was refluxed with stirring for 30 min under nitrogen. And the solution was poured into water and the precipitates were filtered. The resulting product was washed with water and dried in a vacuum oven (yield: 88%). ¹H NMR (DMSO): δ (ppm) = 7.4 (4H), 8.0 (4H), 10.6 (2H).

1,1'-(2,5-Didodecyloxyterephthaloyl)bis[2-(4-fluorobenzoyl)hydrazine] (8)

(2,5-Didodecyloxyterephthaloyl)dihydrazine (1.13 g, 2 mmol) (7) and pyridine (0.32 g, 4 mmol) were dissolved in chloroform (30 ml). 4-Fluorobenzoyl chloride (0.65 g, 4 mmol) in chloroform (20 ml) was added into the solution dropwise. The solution was heated to 30 °C with stirring for 1 hr under

nitrogen. After cooling and filtration the resulting product was washed with water and dried in a vacuum oven (yield: 89%). ¹H NMR (DMSO): δ (ppm) = 0.8 (6H), 1.2 - 1.4 (36H), 4.2 (4H), 7.3 (4H), 7.6 (2H), 8.0 (4H), 10.0 (2H), 10.6 (2H).

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (4O)

Bis(4-fluorobenzoyl)hydrazine (1.38 g, 5 mmol) (**3**) was dissolved in phosphorus oxychloride (50 ml). The solution was refluxed for 5 hr. And the solution was poured into iced water (500 ml). The precipitates were filtered, washed with water, and dried in a vacuum oven (yield: 91%). ¹H NMR (DMSO): δ (ppm) = 7.5 (4H), 8.2 (4H).

2,2'-[2,5-Didodecyloxy(1,3-phenylene)]bis[5-(4-fluorophenyl)-1,3,4-oxadiazole] (9O)

1,1'-(2,5-Didodecyloxyterephthaloyl)bis[5-(4-fluorobenzoyl)hydrazine] (1.07 g, 1.33 mmol) was dissolved in phosphorus oxychloride (50 ml). The solution was refluxed for 12 hr and poured into iced water (500 ml). After filtration of the precipitates the resulting product was washed with water and dried in a vacuum oven (yield: 93%). ¹H NMR (DMSO): δ (ppm) = 0.9 (6H), 1.2 - 1.5 (36H), 1.9 (4H), 4.3 (4H), 7.5 (4H), 7.8 (2H), 8.2 (4H).

2,5-Bis(4-fluorophenyl)-1,3,4-thiadiazole (4S)

Bis(4-fluorobenzoyl)hydrazine (1.10 g, 4 mmol) (**3**) and Lawesson's reagent (1.78 g, 4.4 mmol) were dissolved in pyridine (50 ml). After refluxing for 1 hr the solution was poured into cold aqueous 1.25 N NaOH solution. After filtration the resulting product was washed with water, recrystallized from ethanol, and dried in a vacuum oven (yield: 53%). ¹H NMR (DMSO): δ (ppm) = 7.5 (4H), 8.1 (4H).

2,2'-[2,5-Didodecyloxy(1,3-phenylene)]bis[5-(4-fluorophenyl)-1,3,4-thiadiazole] (9S)

1,1'-(2,5-Didodecyloxyterephthaloyl)bis[2-(4-fluorobenzoyl)hydrazine] (1.21 g, 1.5 mmol) (**8**) and Lawesson's reagent (1.33 g, 3.3 mmol) were dissolved in pyridine (50 ml). The solution was heated to 130 °C with stirring for 12 hr. And the solution was poured cold aqueous 1.25 N NaOH solution. After filtration the resulting product was washed with water, recrystallized from ethylacetate, and dried in a vacuum oven (yield: 55%). ¹H NMR (DMSO): δ (ppm) = 0.8 (6H), 1.2 - 1.5 (36H), 1.9 (4H), 4.3 (4H), 7.4 (4H), 8.1 (4H), 8.2 (2H).

Polymerization

A 100 ml three-necked flask fitted with a Dean-Stark trap, a reflux condenser, and an nitrogen inlet was charged with bisphenol (2 mmol), activated aromatic difluoride (2 mmol), and potassium carbonate (4.4 mmol). In the nitrogen atmosphere diphenyl sulfone (30 g) and toluene (30 ml) were added. The suspension was heated to 160 °C for 1 hr and the water was gradually removed by azeotropic distillation

with toluene through the Dean-Stark trap. And the temperature rised to 200 °C and was maintained at this temperature for 18hr. The mixture was poured into hot methanol and neutralized with acetic acid. After filtration of the precipitates the resulting product was washed with water and hot methanol and dried in a vacuum oven.

Results and discussion

Preparation and characterization of poly(aryl ether)s

Poly(aryl ether)s were prepared by nucleophilic aromatic substitution reaction between activated aromatic difluorides and bisphenols in a dipolar aprotic solvent in the presence of a suitable base. All monomers and polymers were identified by FTIR and ¹H-NMR spectroscopy. Yield and molecular weight of poly(aryl ether)s are summarized in Table 1.

Table 1. Yield and molecular weight of poly(aryl ether)s

Poly(aryl ether)	Yield In %	Mn ^{a)}	Mw ^{a)}	Mw/Mn ^{a)}
PO1FP	64	23,900	44,300	1.85
PT1FP	88	14,900	26,300	1.75
PD12O2FP	80	14,000	23,500	1.67
PD12T2FP	76	5,000	8,200	1.47

^{a)} Determined by GPC with polystyrene standards, THF as eluent

Thermal properties

All poly(aryl ether)s are characterized by high thermal stability (Table 2). Their high thermal properties were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The onset of decomposition and the 10% weight loss temperature are generally higher for three aromatic poly(aryl ether)s, PO1FP and PT1FP, compared to five aromatic poly(aryl ether)s, PD12O2FP and PD12T2FP. The DSC investigation of poly(aryl ether)s shows glass transition for three aromatic poly(aryl ether)s, but five aromatic poly(aryl ether)s don't show. These results must be related to low degree of polymerization and rigidity in the backbone.

Optical properties

In the UV spectra of poly(aryl ether oxadiazole)s PO1FP, PD12O2FP measured in chloroform absorption maxima are observed at 301nm and 370(310)nm, respectively. And poly(aryl ether

thiadiazole)s PT1FP, PD12T2FP show their absorption maxima at 322nm and 394(333)nm, respectively. Five aromatic poly(aryl ether)s are more bathochromic than three aromatic poly(aryl ether)s as a consequence of an increase in π -conjugation.

Table 2. Thermal and optical properties of poly(aryl ether)s

Poly(aryl ether)	$T_{dec}/^{\circ}\text{C}^{\text{a}}$	$T_{10\%}/^{\circ}\text{C}^{\text{a}}$	$T_g/^{\circ}\text{C}^{\text{b}}$	ABS ^{c)}	PL ^{d)}
				λ_{max}/nm	λ_{max}/nm
PO1FP	467	493	208	301	408
PT1FP	472	501	200	322	422
PD12O2FP	395	410	-	370(310)	450
PD12T2FP	373	389	-	394(333)	478

^{a)} Determined by TGA in N_2 , 10 $^{\circ}\text{C}/\text{min}$

^{b)} Determined by DSC in N_2 , second heating, 10 $^{\circ}\text{C}/\text{min}$

^{c)} Absorption(ABS), measured in CHCl_3 solution

^{d)} Photoluminescence(PL), measured in spin-coated film, Exciton wavelength corresponds to the absorption maximum.

The photoluminescence spectra show the same trend (Table 2). The photoluminescence spectra of poly(aryl ether oxadiazole)s show strong emission at 408nm and 450nm, whereas those of poly(aryl ether thiadiazole)s show strong emission at 422nm and 478nm, respectively. The photoluminescence spectra of poly(aryl ether thiadiazole)s are generally stronger than poly(aryl ether oxadiazole)s.

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References

- 1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature*, **1990**, 347(11), 539.
- 2) Saegusa, Y.; Tswasaki, T.; Nakamura, S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, 32, 249.
- 3) Peng, Z.; Bao, Z.; Galvin, M. E. *Adv. Mater.* **1998**, 10(9), 680.
- 4) Brütting, R.; Pösch, P.; Strohriegl, P.; Buchwald, E.; Brütting, W.; Schwoerer, M. *Macromol. Chem. Phys.* **1995**, 198, 2743.