Facile Synthesis and Characterization of Poly(dialkoxy-*p*-phenylene 1,3,4-oxadiazole-*alt*-phenylene 1,3,4-oxadiazole)s

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Abstract: Poly(dialkoxyphenylene 1,3,4-oxadiazole)s were conveniently synthesized to compare their material properties of solvent solubility, thermal stability and molecular alignment with respect to alkyl chain length and *meta/para*-phenylene structure. All prepared polymers exhibited good solubility in co-solvents containing various volume levels of chloroform to trifluoroacetic acid. *Meta*-polymers showed slightly better solubility than *para*-polymers. All polymers produced were thermally stable up to 320 °C. Photoluminescence of polymer films was observed with blue light emission at around 450 nm. X-ray diffraction patterns of all polymers indicated that they were composed of stacked molecular sheets with the same layer-to-layer distance of 3.4 Å. However, side chain-to-side chain and main chain-to-main distances within the layers increased with increasing alkyl chain lengths. The *meta*-polymer chains were separated more than the *para*-polymer chains.

Keywords: conjugated polymer, polyoxadiazole, solubility, XRD.

Introduction

Organic semiconductors have been the subject of intense research over the last three decades, because of their high electrical conductivities through a chemical doping.[1] The conjugated polymers have been utilized as active materials in various electronic applications such as light emitting diodes (LEDs),[2,3] photovoltaic cells,[4,5] and field effect transistors (FETs).[6] However, improvements in the physical properties, e.g. electronic conductivities, of these polymer systems are required.

Conjugated polymers are characterized by electron delocalization along their backbones, which consists of aromatic rings or alternating double bonds. This molecular property often causes polymer insolubility and infusibility and limits application. Poly(aryl oxadiazole) has been considered due to their long-term stability and processabilities, despite with potential metal-like electric conductivities of doped polyacetylenes. The development of soluble conjugated polymers is an important goal for synthetic chemists. Poly(aryl oxadiazole)s, which have excellent thermal stabilities are incompatible with other polymer system and insoluble in common organic solvents due to their rigidities at the molecu-

lar level.[7-9] Numerous studies have been performed to improve the processabilities of poly(aryl oxadiazole), e.g. by producing polymer blends[10] and processable precursor polymers[11] and by increasing their solubilities by flexibilizing the main chain[12] or a side chain.[13-17] For example, the solubility of polyoxadiazole was improved by the copolymerizing it with *m*- and *p*-phenylenes.[18]

In the present study, we designed novel poly(dialkoxy phenylene 1,3,4-oxadiazole)s (DPODs), in which two alkoxy groups increased the polymer solubility, and while so doing developed a facile synthetic pathway. The introduction of two alkoxy groups on the phenyl ring is a synthetically favorable approach because this leads to achieving a convenient monomer synthesis. Moreover, the development of this pathway allowed us to increase alkoxy chain length and to study the effect of using *m*-phenylene and *p*-phenylene in the main polymer chain, as changes were likely to substantially alter chain arrangements. Two different types of oxadiazole polymers were developed using previously described a prepolymer synthesis scheme based on dichloride and dihydrazide monomers.[18] Thus, oxadiazole polymers were prepared using isophthaloyl chloride or terephthaloyl chloride, which produced 1,3,4-oxadiazole attached to the *m*-phenylene or *p*-phenylene units. The structural effects of substituent chain length and the *meta-/para*-polymers were

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examined by XRD analysis. The polymers were also characterized by FT-IR and ¹H-NMR spectroscopy and by thermal gravimetric analysis.

Experimental

Materials and Characterization. All reagents were purchased from Sigma-Aldrich Chemical Co. and the reagent-grade solvents were dried when necessary and purified by a vacuum distillation. ¹H-NMR spectra were recorded on a Varian Mecury 300 spectrometer. Polyoxadiazoles were analyzed using a co-solvent of CDCl₃/CF₃COOD. ¹³C-NMR spectra were recorded on a Varian Mecury 200 spectrometer. FT-IR spectra were obtained using a Varian 800 FT-IR. TGA was performed on a TGA/SDTAᵉ using a heating rate 10 °C/min under a nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) powder patterns were recorded at room temperature on a Shimadzu XRD-7000 with a Ni-filtered Cu Kα radiation.

Synthesis of Monomers.

Diethyl 2,5-diethoxy terephthalate (1a): Compound **1a** was prepared according to the literature[15] and was modified as follows. Diethyl 2,5-dihydroxy terephthalate (1.00 g, 3.82 mmol) was alkylated with a large excess of iodoethane (2.38 g, 15.26 mmol) in the presence of potassium carbonate (1.58 g, 11.45 mmol) and tetrabutylammonium bromide (0.49 g, 1.53 mmol) under acetone reflux (15 mL). After 24 h, water was added and the organic phase was extracted with ethyl acetate. The organic layer was washed twice with water and dried over magnesium sulfate. The solvent was evaporated and the residual oily phase was purified by a column chromatography (0.66 g, yield 56%). IR (solid, cm⁻¹): 2978 (aliphatic C-H), 2932, 1736, 1690 (C=O), 1504, 1466, 1420, 1381, 1304, 1211 (C-O-C), 1103, 1026, 941, 895, 856, 779, 610. ¹H-NMR (CDCl₃, ppm): δ = 7.36 (s, 2H, aromatic), 4.38 (q, J = 7.2 Hz, 4H), 4.09 (q, J = 6.9 Hz, 4H), 1.46-1.37 (m, 12H).

Diethyl 2,5-dibutoxy terephthalate (1b): (0.84 g, yield 60%). IR (solid, cm⁻¹): 2955 (aliphatic C-H), 2932, 2870, 1728, 1705 (C=O), 1497, 1466, 1420, 1381, 1296, 1204 (C-O-C), 1103, 1065, 1018, 972, 887, 864, 787, 733, 625. ¹H-NMR (CDCl₃, ppm): δ = 7.35 (s, 2H, aromatic), 4.38 (q, J = 7.2 Hz, 4H), 4.02 (t, J = 6.6 Hz, 4H), 1.82-1.75 (m, 4H), 1.58-1.46 (m, 4H), 1.40 (t, J = 7.2 Hz, 6H), 0.98 (t, J = 7.2 Hz, 6H).

Diethyl 2,5-dioctyloxy terephthalate (1c): (1.18 g, yield 65%). IR (solid, cm⁻¹): 2924 (aliphatic C-H), 2855, 1736, 1690 (C=O), 1497, 1466, 1420, 1381, 1304, 1211 (C-O-C), 1134, 1111, 1057, 1018, 972, 918, 880, 864, 826, 787, 748, 725, 610. ¹H-NMR (CDCl₃, ppm): δ = 7.34 (s, 2H, aromatic), 4.38 (q, J = 7.2 Hz, 4H), 4.01 (t, J = 6.6 Hz, 4H), 1.85-1.76 (m, 4H), 1.52-1.26 (m, 26H), 0.89 (t, J = 6.9 Hz, 6H).

2,5-Diethoxy terephthaloyl dihydrazide (2a): Compound **2a** was synthesized according to reported procedures.[13,19] A

mixture of **2a** (0.66 g, 2.12 mmol) and hydrazine hydrate (30 mL) in ethanol (30 mL) was refluxed for 3 h. The product was precipitated during cooling. The white precipitate was filtered, washed with water and dried at 90 °C in a vacuum. The product was recrystallized from THF/methanol (0.58 g, yield 96%). IR (solid, cm⁻¹): 3395 (N-H), 3318, 3240, 2986 (aliphatic C-H), 2932, 2886, 1643, 1574 (C=O), 1512, 1497, 1466, 1389, 1335, 1296, 1204 (C-O-C), 1111, 1034, 980, 926, 895, 841, 779, 648. ¹H-NMR (CDCl₃, ppm): δ = 9.22 (s, br, 2H), 7.86 (s, 2H), 4.32-4.05 (m, 8H), 1.52 (t, J = 6.9 Hz, 6H). ¹³C-NMR (DMSO-d_6, ppm): δ = 163.4, 149.1, 124.7, 114.4, 64.7, 14.7.

2,5-Dibutoxy terephthaloyl dihydrazide (2b): (0.47 g, yield 60%). IR (solid, cm⁻¹): 3271 (N-H), 3202, 2955 (aliphatic C-H), 2870, 1620, 1589 (C=O), 1498, 1466, 1412, 1389, 1273, 1211 (C-O-C), 1119, 1065, 1026, 964, 887, 795, 772, 687, 617. ¹H-NMR (CDCl₃, ppm): δ = 9.21 (s, br, 2H), 7.86 (s, 2H), 4.22-4.08 (m, 8H), 1.93-1.83 (m, 4H), 1.59-1.45 (m, 4H), 1.02 (t, J = 7.2 Hz, 6H). ¹³C-NMR (CDCl₃, ppm): δ = 165.2, 150.7, 123.0, 115.7, 69.8, 31.4, 19.6, 14.1.

2,5-Dioctyloxy terephthaloyl dihydrazide (2c): (0.80 g, yield 72%). IR (solid, cm⁻¹): 3302 (N-H), 2916 (aliphatic C-H), 2847, 1744, 1643, 1589 (C=O), 1535, 1489, 1458, 1412, 1381, 1273, 1211 (C-O-C), 1142, 1119, 1065, 1018, 940, 910, 880, 833, 795, 725, 656. ¹H-NMR (CDCl₃, ppm): δ = 9.20 (s, br, 2H), 7.86 (s, 2H), 4.21-4.07 (m, 8H), 1.93-1.82 (m, 4H), 1.50-1.24 (m, 20H), 0.90 (t, J = 6.9 Hz, 6H). ¹³C-NMR (CDCl₃, ppm): δ = 165.1, 150.6, 123.0, 115.7, 70.0, 32.0, 29.5, 29.4, 29.4, 26.3, 22.9, 14.4.

Synthesis of Polymers. DPOD(a,m): The polymer was synthesized through the formation of a prepolymer. A flask was charged with **2a** (0.20 g, 0.71 mmol), a stoichiometric amount of isophthaloyl chloride (0.14 g, 0.71 mmol), and LiCl (10 mg). The flask was degassed and purged with N₂, and DMAc (3 mL) and pyridine (1 mL) were added at 0 °C. The reaction was carried out for 3 h at 0 °C and for 15 h at 25 °C. The prepolymer was precipitated with 150 mL of methanol, filtered, washed several times with methanol and dried for 12 h under vacuum at 100 °C. For further purification, the product was dissolved again in DMAc (5 mL) and pyridine (1 mL), precipitated with methanol, separated, and dried (0.20 g, yield 69%). IR (solid, cm⁻¹): 3472, 3271 (N-H), 2978 (aliphatic C-H), 1612 (C=O), 1450, 1396, 1296, 1227, 1196 (C-O-C), 1111, 1026, 918, 895, 818, 772, 718, 687, 633. The prepolymer **DPHZ(a,m)** was refluxed in 10 mL of POCl₃ for 12 h and then the reaction mixture was poured into 150 mL of water in order to obtain the polymer **DPOD(a,m)**. The precipitated polymer was isolated by filtering and washed with water, ethanol, and ether successively and then was dried under vacuum at 90 °C (0.05 g, yield 50%). IR (solid, cm⁻¹): 3387, 2978 (aliphatic C-H), 1721, 1628, 1551, 1458, 1389, 1288, 1219 (C-O-C), 1111, 1080, 1034, 972, 926, 880, 802, 741, 710, 687. ¹H-NMR (CDCl₃/

TFA-*d*, ppm): δ = 9.13 (s, br, 1H), 8.98-8.86 (m), 8.68-8.45 (m, 2H), 8.39-8.25 (m), 8.18-7.83 (m, 3H), 4.66-4.38 (m, br, 4H), 1.81-1.54 (m, br, 6H).

DPOD(b,m): (0.11 g, yield 81%). IR (solid, cm⁻¹): 2963 (aliphatic C-H), 1736, 1628, 1551, 1458, 1373, 1288, 1219 (C-O-C), 1088, 1026, 964, 880, 810, 741, 710, 687, 632. ¹H-NMR (CDCl₃/TFA-*d*, ppm): δ = 9.10 (s, br, 1H), 8.92-8.85 (m), 8.63-8.40 (m, 2H), 8.35-8.24 (m), 8.11-7.78 (m, 3H), 4.52-4.20 (m, br, 4H), 2.15-1.81 (m, br, 4H), 1.70-1.39 (m, br, 4H), 1.12-0.84 (m, br, 6H).

DPOD(c,m): (0.09 g, yield 62%). IR (solid, cm⁻¹): 2924 (aliphatic C-H), 2855, 1721, 1628, 1551, 1458, 1389, 1288, 1219 (C-O-C), 1080, 1026, 972, 910, 880, 802, 741, 710, 687. ¹H-NMR (CDCl₃/TFA-*d*, ppm): δ = 9.14 (s, br, 1H), 8.94-8.88 (m), 8.59-8.43 (m, br, 2H), 8.38-8.32 (m), 8.13-7.84 (m, br, 3H), 4.49-4.33 (m, br, 4H), 1.63-1.49 (m, br, 4H), 1.48-1.18 (m, br, 20H), 0.94-0.79 (m, br, 6H).

DPOD(a,p): (0.06 g, yield 54%). IR (solid, cm⁻¹): 3448, 2986 (aliphatic C-H), 1628, 1551, 1458, 1396, 1335, 1288, 1219 (C-O-C), 1111, 1080, 1034, 972, 926, 856, 795, 748, 710. ¹H-NMR (CDCl₃/TFA-*d*, ppm): δ = 8.55 (s, br, 4H), 8.50-8.12 (m), 8.01-7.93 (br, 2H), 4.65-4.40 (m, br, 4H), 1.82-1.56 (m, br, 6H).

DPOD(b,p): (0.07 g, yield 76%). IR (solid, cm⁻¹): 2955 (aliphatic C-H), 1697, 1628, 1551, 1450, 1389, 1335, 1288, 1219 (C-O-C), 1119, 1065, 1018, 972, 880, 856, 802, 741, 710. ¹H-NMR (CDCl₃/TFA-*d*, ppm): δ = 8.45 (s, br, 4H), 8.46-7.95 (m), 7.94-7.82 (br, 2H), 4.49-4.24 (m, br, 4H), 2.16-1.86 (m, br, 4H), 1.71-1.48 (m, br, 4H), 1.16-0.91 (m, br, 6H).

DPOD(c,p): (0.11 g, yield 78%). IR (solid, cm⁻¹): 2924 (aliphatic C-H), 2855, 1728, 1628, 1551, 1450, 1389, 1335, 1288, 1219 (C-O-C), 1080, 1018, 964, 880, 849, 802, 741, 710. ¹H-NMR (CDCl₃/TFA-*d*, ppm): δ = 8.54 (s, br, 4H), 7.94 (s, br, 2H), 4.53-4.30 (br, 4H), 2.10-1.94 (br, 4H), 1.66-1.15 (m, br, 20H), 0.95-0.78 (br, 6H).

Results and Discussion

Preparation of Materials. The synthetic routes of monomers and relating polymers are described in Figure 1. Monomer preparation was started from **1a**, which was obtained from the alkylation of diethyl 2,5-dihydroxy terephthalate by iodoethane in the presence of potassium carbonate. Reaction of **1a** with hydrazine afforded monomer **2a**. Other monomers with butyl and octyl substituents (**2b** and **2c**) were obtained in the same way. Alkyl groups of the resultant monomers were identified by ¹H-NMR and ¹³C-HMR and the hydrazide functionality was confirmed by the presence of a broad absorption at 3350 cm⁻¹ in the IR spectrum.

Polymers (DPODs) were synthesized through two steps containing polycondensation and subsequent cyclodehydration as previously described.[12,13,18,19] Polycondensation of dihydrazides and dichlorides occurred to afford the prepolymers, **DPHZs**, in DMAc/pyridine containing lithium chloride (5 wt%). Prepolymer cyclodehydration was performed at a high temperature (130 °C) using phosphorus oxychlo-
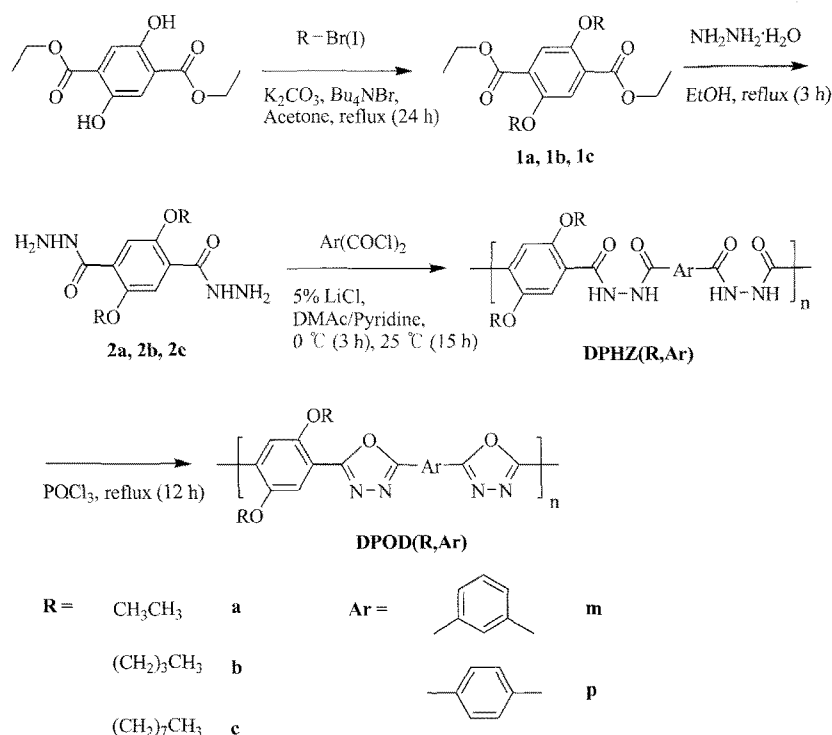

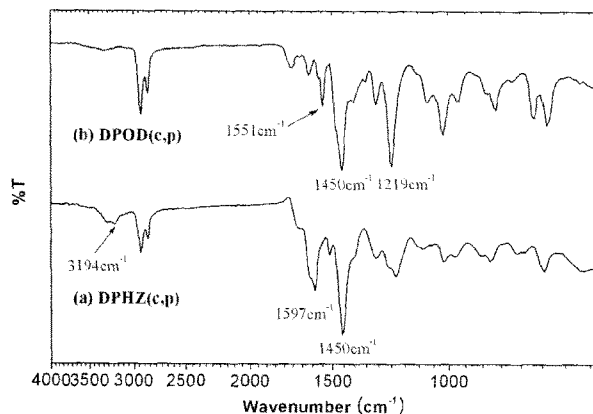**Figure 1.** Synthetic procedure of monomers and polymers.

Figure 2. FT-IR spectra of DPHZ(c,p) and DPOD(c,p).

ride. The temperature was adjusted to minimize a side reaction such as alkoxy group decomposition. Depending on *meta*-dichloride (isophthaloyl chloride) and *para*-dichloride (terephthaloyl chloride) as an adopted counter monomer, prepolymer cyclodehydration produced *meta*-polymers [DPOD(R,m)] and *para*-polymers [DPOD(R,p)], respectively. Several polymers with different alkyl chain lengths were prepared in the same way.

Polymer conversion of the prepolymer was monitored by IR analysis. Intensive absorption bands around 1597 cm^{-1} (arising from the carbonyl groups of the prepolymer) disappeared after cyclodehydration occurred. No NH-band was observed at 3100-3400 cm^{-1} for the **DPOD** polymers produced. Moreover, characteristic absorptions of the oxadiazole ring at 1551 cm^{-1} (C=N stretching) and at 1219 cm^{-1} (=C-O-C= stretching) appeared, which were used as an indication of successful cyclodehydration as shown in Figure 2.

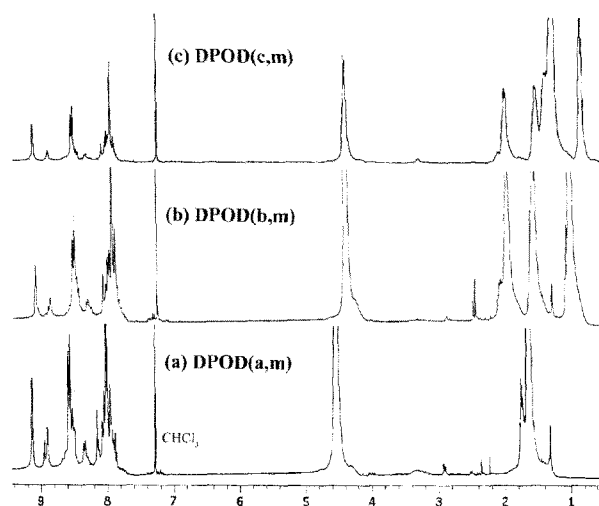Polymer structures were also defined by ^{1}H-NMR. Polymers were dissolved in deuteriochloroform containing deu-

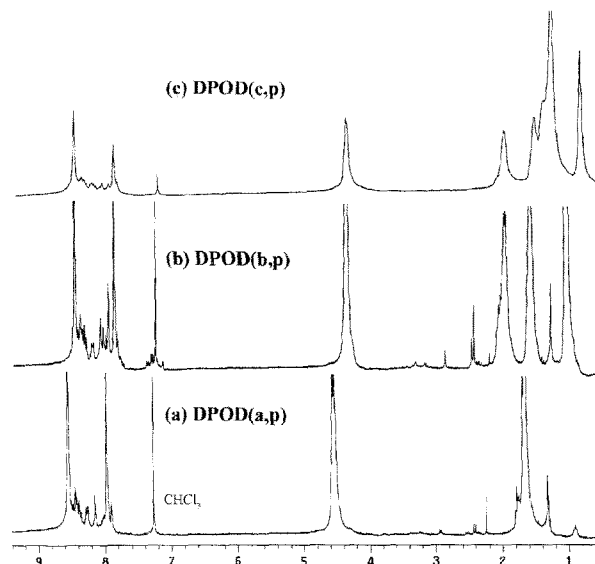**Figure 3.** ^{1}H-NMR spectra of DPOD(a,m), DPOD(b,m), and DPOD(c,m).

Figure 4. ^{1}H-NMR spectra of DPOD(a,p), DPOD(b,p) and DPOD(c,p).

teriotrifluoroacetic acid and the observed spectra of *meta*- and *para*-polymers were compared in Figure 3 and Figure 4. All the polymers produced an alkoxy methylene peak at 4.5 ppm and an aromatic proton multiplex at 8.5 ppm due to dialkoxy phenylene.[20] A singlet peak at 9.1 ppm in *meta*-polymers was assigned to unsubstituted phenylene protons. Integration of the aliphatic hydrocarbon region (0.5-2.2 ppm) well agreed with the expected alkyl lengths of the pendant alkoxy polymers.

Solubilities. Solubility findings of **DPOD**s are presented in Table I. All the polymers were completely insoluble in toluene and in dimethylformamide (DMF) but were partially soluble in chloroform and in tetrahydrofuran (THF). However, adding a small amount of a strong organic acid such as trifluoroacetic acid (TFA) allowed us to prepare clear polymer solutions. Solvent ratios (chloroform to TFA: 4/1-10/1) were adjusted to enable complete dissolution of *meta*- and *para*-polymers. Greater TFA levels were required

Table I. Polymer Solubility in Several Organic Solvents

Polymer	Solubility^{a}				
	CHCl$_3$/TFA	CHCl$_3$	THF	DMF	Toluene
DPOD(a,m)	+ +^{b}	+ -	+ -	-	-
DPOD(b,m)	+ +^{c}	+ -	+ -	-	-
DPOD(c,m)	+ +^{d}	+ -	+ -	-	-
DPOD(a,p)	+^{b}	+ -	+ -	-	-
DPOD(b,p)	+^{c}	+ -	+ -	-	-
DPOD(c,p)	+^{d}	+ -	+ -	-	-

^{a}(++) soluble, (+,+-) partially soluble, (-) insoluble. Volume ratio of chloroform and trifluoroacetic acid: 4/1^{b}, 6/1^{c}, 10/1^{d}. Polymer concentration is 35 mg/mL in solvent.

Table II. Thermal Stability of DPHZ and DPODs[a]

Polymer	T_d (°C)[b]	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Char Yield (wt%)[c]
DPHZ(c,m)	352	367	430	18
DPOD(c,m)	386	399	436	24
DPOD(c,p)	408	417	442	21

[a]Thermal gravimetric analysis (TGA). [b]Temperature of 5% weight loss. [c]Residue at 600 °C.
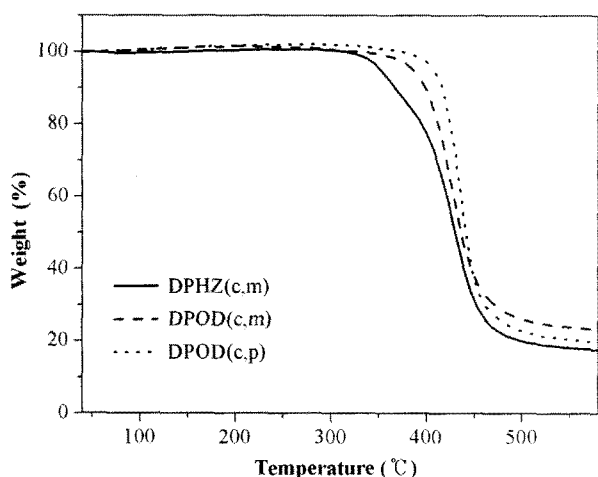
Figure 5. TGA thermograms of DPHZ(c,m), DPOD(c,m), and DPOD(c,p).

to dissolve polymers with shorter alkyl chains. *Meta-* and *para-*polymers showed similar solubility trend with respect to alkyl chain length but *para-*polymers were less soluble. Solubility tests were performed with a maximum polymer concentration of 35 mg/mL.

Thermal and Optical Properties. Thermal gravimetric analysis of the polymers was performed and showed no weight loss up to 320 °C under nitrogen. Degradation temperature (T_d) was defined as the temperature at a weight loss of 5% and the char yield was measured at 600 °C in Table II. The TGA curve of a prepolymer [DPHZ(c,m)] exhibited an interesting behavior (Figure 5). **DPHZ(c,m)** prepolymer showed an initial weight loss at *ca.* 350 °C, which was attributed to the loss of water due to the cyclodehydration of hydrazide groups during heating. A second weight loss was detected at *ca.* 380 °C due to the decomposition of alkyl groups, as previously reported.[19] However, similar first weight loss was not observed for polyoxadiazoles, which were stable to 380 °C. Furthermore, *para-*polymers were observed somewhat more stable (higher T_d) than *meta-*polymers, which concurred the previous findings,[21] as thermal stability depends on adjacent monomer structures in order: *ortho-ortho* < *meta-meta* < *meta-para* < *para-para*.

The optical characterization of the conjugated polymers was performed with UV-Vis absorption spectra of both solution and thin film. All orange colored solutions pro-

Table III. UV-Vis Absorption Features of Polymers (DPODs)

Polymer	Film (nm)[a]		Solution (nm)[b]	
	λ_{max}	$\lambda_{cut\text{-}off}$	λ_{max}	$\lambda_{cut\text{-}off}$
DPOD(a,m)	315, 385	478	310, 398	455
DPOD(b,m)	315, 384	448	307, 395	450
DPOD(c,m)	323, 384	465	307, 395	450
DPOD(a,p)	337, 401	475	324, 403	465
DPOD(b,p)	341, 397	455	321, 394	475
DPOD(c,p)	337, 401	475	320, 395	475

[a]Thin film was spin-coated on a fused glass. [b]Polymers were dissolved in a co-solvent of chloroform and trifluoroacetic acid (2/1, v/v).
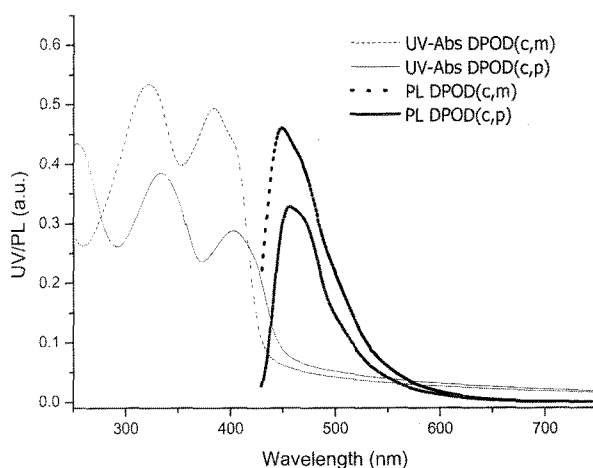
Figure 6. UV-Vis absorption and photoluminescence spectra of DPOD(c,m) and DPOD (c,p).

vided two distinctive absorption peaks with a shoulder at 300-450 nm and maximum absorption wavelengths were summarized in Table III. For film measurement, polymer films were spin-coated on a quartz substrate using chloroform and trifluoroacetic acid (2:1 v/v). A significant spectral change was not observed with the alkyl chain length. However, the spectral difference between the *meta-*polymers and the *para-*polymers was obviously detected with a red-shift by ca. 15 nm for the *para-*polymers. Figure 6 shows emission spectra of polymer DPOD(c,m) and DPOD(c,p) films under 400 nm irradiation which emit maximum wavelengths of 449 and 457 nm, respectively.

X-ray Diffraction Analysis. The solid geometries of the prepared polymers were investigated by XRD analysis. M. Gillo *et al.* previously described the layered structure of poly(phenylene oxadiazole), in which alkoxy side chains are arranged in planar extended conformations.[19]

As shown in Figure 7, the powder diffractograms of all **DPODs** contained two sharp peaks and one broad diffraction peak. Using the formula $n \lambda = 2 d \sin\theta$ (n : integer, λ : X-wavelength, d : spacing, θ : incident angle), we calcu-
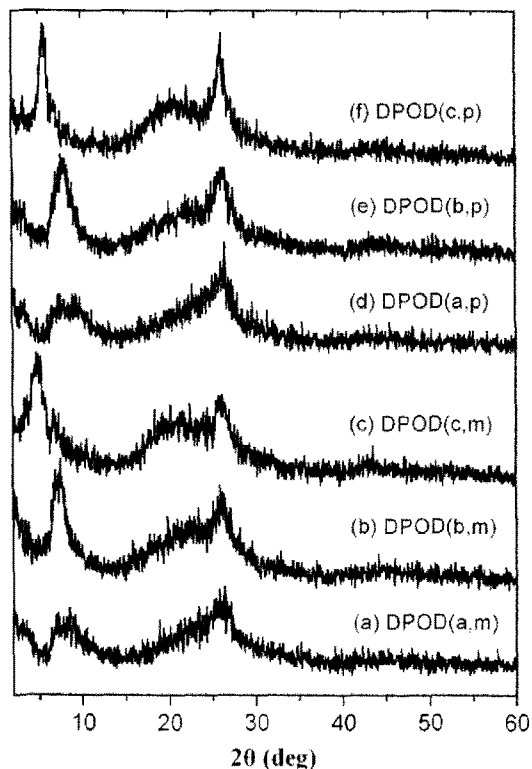
Figure 7. X-ray powder pattern of DPODs at room temperature.

**Table IV. X-ray Data for DPODs**

Polymer	2θ (deg)	d_{hkl} (Å)
DPOD(a,m)	8.25 ± 0.05	10.70 ± 0.07
	22.95 ± 0.05	3.87 ± 0.01
	25.75 ± 0.05	3.46 ± 0.01
DPOD(b,m)	7.30 ± 0.05	12.10 ± 0.08
	22.35 ± 0.05	3.97 ± 0.01
	25.95 ± 0.05	3.43 ± 0.01
DPOD(c,m)	4.85 ± 0.05	18.20 ± 0.19
	21.15 ± 0.05	4.20 ± 0.01
	25.95 ± 0.05	3.43 ± 0.01
DPOD(a,p)	9.15 ± 0.05	9.65 ± 0.05
	24.65 ± 0.05	3.61 ± 0.01
	26.20 ± 0.05	3.40 ± 0.01
DPOD(b,p)	7.90 ± 0.05	11.18 ± 0.07
	21.80 ± 0.05	4.07 ± 0.01
	25.95 ± 0.05	3.43 ± 0.01
DPOD(c,p)	5.65 ± 0.05	15.62 ± 0.14
	20.35 ± 0.05	4.36 ± 0.01
	26.00 ± 0.05	3.42 ± 0.01

lated several molecular distances between side chains, between main chains, and between polymer layers. These are tabulated with X-ray diffraction data in Table IV. It was

found that the diffraction peak at *ca.* 26° (2θ) observed for all the polymers, represented a d spacing of 3.4 Å. In terms of the layered packing model, this represents the distance between stacked polymer layers (layer thickness) in Figure 8 and agrees with previously reported results for poly(*p*-phenylene 1,3,4-oxdiazole)s.[18,19] Moreover, this distance is identical to the typical distance observed between the aromatic planes in aromatic systems (e.g., graphite). The broad peak at *ca.* 22° (2θ) corresponded to a spacing of 3.6-4.4 Å

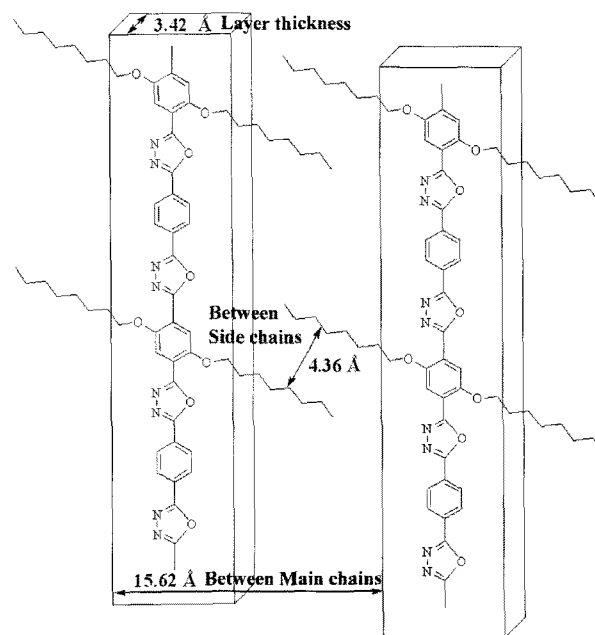*Meta*-polymer DPOD(c,m)
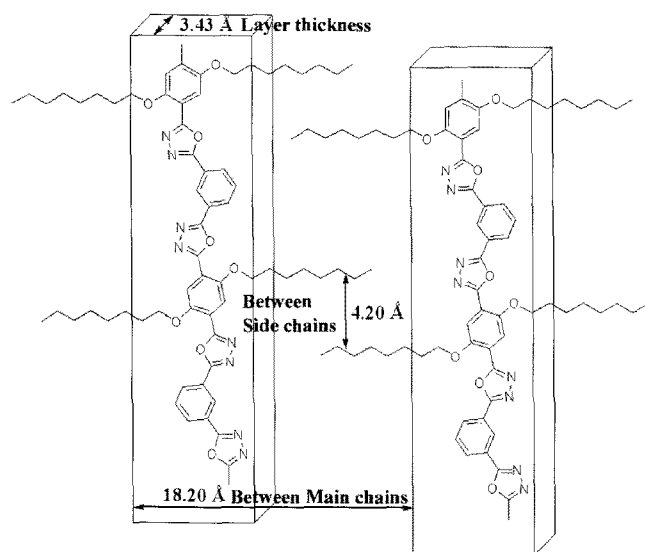
Para-polymer DPOD(c,p)

Figure 8. Molecular layer packing of DPOD(c,m) and DPOD(c,p).
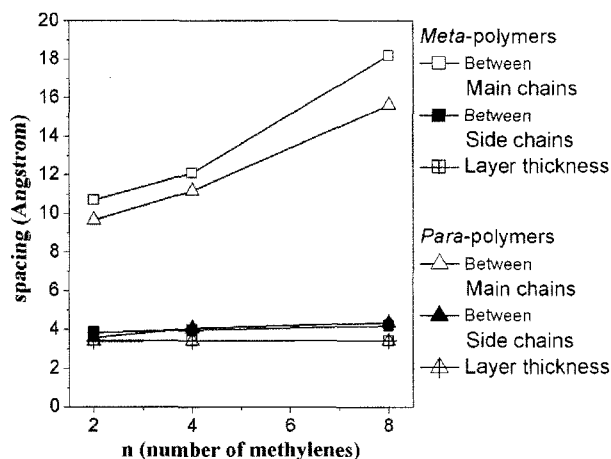
Figure 9. *d* spacing vs. the number of methylenes (*n*) of the alkoxy side chain for *meta/para*-polymers.

and was observed for all DPODs. It was attributed to spacing between adjacent alkoxy side chains. Noticeable shifts in the broad peak occurred when side chain length was altered in both *meta*- and *para*-polymers. Distances between side chains in ethyl substituted polymers were shorter than in corresponding butyl and octyl substituted polymers.

The intense diffraction peak observed at a range of 4.9-9.2 was attributed to the distance between adjacent main chains within a layer. This peak shifted to smaller angle as side chain length was increased. It indicates that increased side chain length causes proportional increment in distances between polymer main chains. The distances increased by 7.50 Å on going from **DPOD(a,m)** to **DPOD(c,m)** and by 5.97 Å on going from **DPOD(a,p)** to **DPOD(c,p)**, as shown in Figure 9. Spacing increment of 1.25 and 1.00 Å corresponds to one methylene unit in alkyl chain length of *meta*-polymers and *para*-polymers, respectively. Typically, the distance between main chains was greater for *meta*-polymers than *para*-polymers at a same alkyl chain length.

Conclusions

In this research, we designed novel poly(dialkoxyphenylene 1,3,4-oxadiazole)s with three different alkyl substituents and regio-isomeric structures. The polymer structures were defined by ¹H-NMR and FT-IR analyses. All synthesized polymers were soluble in co-solvents of chloroform and trifluoroacetic acid and relative solubility was found to depend on alkyl chain length. *Meta*-polymers were more soluble than *para*-polymers. All polymers showed good thermal stability in nitrogen up to 320 °C. Wide-angle X-ray diffractograms revealed that polymers adopted a stacked planar conformation. Layer-to-layer thickness was 3.4 Å for all polymers, but within a layer side chain-to-side chain and main chain-to-main chain distances increased with alkyl

chain length. The chain-to-chain distances of *meta*-polymers were greater than those of equivalent *para*-polymers.

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