Macromolecules **1997,** *30,* 2989−2996

Soluble Polymers with Laterally Attached Oligophenyl Units for Potential Use as Blue Luminescent Materials

J. K. Kallitsis,*,† K. G. Gravalos,† A. Hilberer,‡ and G. Hadziioannou‡

Department of Chemistry, University of Patras, 26500 Patras, Greece, and Department of Polymer Chemistry and Materials Science Center, University of Groningen, The Netherlands

Received September 17, 1996⊗

ABSTRACT: New blue luminescent polyethers were prepared by interfacial polymerization of 2,5-diphenyl-, 2-biphenyl-, and 2,5-bis(biphenyl)hydroquinone diacetates with α,ω- dibromides. These polymers were soluble in common solvents, show liquid crystallinity in some cases, and can be melt processed at relatively low temperatures where they are thermally stable. Moreover their solid structure and corresponding properties (e.g. optical) can be controlled by judicious choice of the monomer unit. The synthesized polyethers were characterized by viscosimetry, gel permeation chromatography, thermal analysis, mechanical analysis, and UV−vis luminescence spectroscopy. The polymers show blue photoluminescence and have relatively low liquid crystalline transition temperatures, or they are amorphous depending on the symmetry of the substitution. The photoluminescent maxima were in the range 390−407 nm depending on the monomer structure. Free standing films were casted from solutions for some polymers, and in one case the mechanical properties were examined.

Introduction

Polymer light-emitting diodes (LEDs) are a promising application for semiconducting polymers.[1−5] After the first report[1] on diodes fabricated from poly(*p*-phenylenevinylene) PPV many polymer based LEDs have been reported.[6] The limitations of synthesis, analysis and application of conjugated polymers, due to their intractability, have been solved either by the precursor route[7−12] or by substitution of the polymer backbone.[13−19]

Since conjugated polymers belong to the class of semiconducting materials, they can be used for their luminescence properties. The combination of the conjugation length and the chemical structure of the conjugated polymers used gives one the possibility of tuning the luminescence and enables one to make LEDs of different colors. Thus, copolymers bearing phenylenevinylene,[20] oligophenylene, and oligothiophene[21] moieties linked by flexible spacers have been synthesized and tested as luminescent materials.

Since the group responsible for the luminescent properties is a rigid part, the way of attachment on the polymer main chain can also control the liquid crystalline properties. Lateral attachment to the main chain has a significant effect on the reduction of the temperatures at which the liquid crystallinity appears and has also a significant effect on the increase of the solubility.[22]

In the present article we report the synthesis and characterization of soluble polyethers bearing oligophenyl units laterally attached to the main chain. The synthesized polymers show liquid crystallinity when the rigid part is symmetrically attached to the main chain, while they are amorphous in the case of the asymmetric substitution. The photoluminescence spectra demonstrate that polymers emitting blue light can be obtained using this well-defined polymerization chemistry.

Experimental Part

Materials. Chemicals were purchased from Aldrich and were used as received unless otherwise specified. 1,10-Dibromodecane and 1,12-dibromodecane were recrystallized from methanol. 2-Bromohydroquinone diacetate and 2,5-dibromohydroquinone diacetate were synthesized by bromination of the hydroquinone diacetate with 1 and 2 equiv of Br_2, respectively, in chloroform. 2-Bromohydroquinone dibenzyl ether (**3**) and 2,5-dibromohydroquinone dibenzyl ether (**6**) were obtained after reaction with benzyl bromide in alcoholic sodium hydroxide. The catalyst dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium $PdCl_2$(dppf) was synthesized according to a known procedure.[23] Tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone directly into the reaction flask.

Monomer Synthesis. 2,5-Diphenylhydroquinone Diacetate (2). 2,5-Dibromohydroquinone diacetate 14.08 g (40 mmol), phenylboronic acid, 15.2 g (120 mmol), and tetrakis(triphenylphosphine)palladium, 1.3 g, were put together in a flask which was degassed and filled with argon. Toluene (80 mL) and 2 M sodium carbonate (40 mL) were added and the mixture was refluxed under argon for 24 h. The product was extracted with toluene. The organic layer was washed with 3 N HCl and water and dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was triturated with methanol, filtered out, and dried in vacuo. Recrystallization from toluene gave 11.0 g (80%) of the desired product **2**, mp 191−193 °C.

FTIR (cm^{-1}): 3054, 1762, 1478, 1368, 1206, 1162, 1154, 1010, 932, 922, 892, 820, 760, 700.

^1H NMR ($CDCl_3$): δ 2.1 (s, CH_3, 6H), 7.2 (s, arom. CH, 2H), 7.45 (m, arom. CH, 10H).

^{13}C NMR: 20.5 (CH_3), 124.8, 127.8, 128.0, 128.5, 134.2, 136.2.

2,5-Bis(biphenyl)hydroquinone Diacetate (8). 2,5-Dibromo hydroquinone dibenzyl ether, 4.48 g (10 mmol), and $PdCl_2$ (dppf), 100 mg, were first degassed and filled with argon and then dissolved in freshly distilled THF (20 mL). The mixture was cooled to room temperature and 4-biphenyl magnesium bromide (30 mmol) in THF (20 mL) was added within 30 min. The mixture was heated at reflux for 2 days. By cooling of the mixture down to room temperature, a crystalline solid precipitated which was isolated by filtration washed with methanol and water and dried in vacuum. Recrystallization from THF gave 3.2 g (54%) of 1,4-bis-

---

† University of Patras.
‡ University of Groningen.
⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S0024-9297(96)01379-4 CCC: $14.00

Table 1. Crystal Data and Details of the Structure Determination

chem formula	$C_{34}H_{26}O_4$
fw	498.58
cryst syst	monoclinic
space group, no.	*C*2/*c*, 15
a, Å	22.470(1)
b, Å	5.614(1)
c, Å	20.154(1)
β, deg	105.724(6)
V, Å	2447.2(5)
Z	4
D_{calc}, g·cm^{-3}	1.355
F(000), electrons	1048
μ(Mo K$\bar{\alpha}$), cm^{-1}	0.88
approx cryst dimens, mm	0.05 × 0.06 × 0.56
radiation	Mo K$\bar{\alpha}$
wavelength, Å	0.710 73
monochromator	graphite
temp, K	130
final agreement factors	
$R(F) = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$ for $F_o > 4.0\,\sigma(F_o)$	0.0487
$wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2)]/\sum w(F_o^2)^2]^{1/2}$ for $F_o^2 > 0$	0.1169

(biphenyl)hydroquinone dibenzyl ether (**7**). The benzyl groups were removed by reduction of the above product in dimethylacetamide (DMA) in the presence of 0.4 g of 10% palladium on activated carbon in H_2 atmosphere at 40 °C for 24 h. The solid was precipitated with water, isolated by filtration, washed with methanol, and dried in vacuum. Recrystallization from DMA gave a white solid, which was acetylated by acetyl chloride in DMA. The product was recrystallized from DMA and 2.0 g (81%) of **8**, with mp 293−295 °C, was obtained.

FTIR (cm^{-1}): 2678, 1758, 1478, 1368, 1202, 1158, 1006, 926, 854, 768, 702.

2-Biphenylhydroquinone Diacetate (5) was synthesized from 2-bromo hydroquinone dibenzyl ether by the above described methodology. The product was isolated in 80% yield, mp 124−125 °C.

^{1}H NMR ($CDCl_3$): *δ* 2.2 (d, CH_3, 6H), 7.2 (m, CH, 3H), 7.5 (m, CH, 3H), 7.7 (s, CH, 6H).

FTIR (cm^{-1}): 3050, 2922, 1750, 1482, 1370, 1216, 1174, 1020, 932, 910, 850, 766.

Polymer Synthesis. A 2.0 mmol amount of the diacetyl derivatives (**2** or **5** or **8**), 2.0 mmol of the respective dibromide and 0.27 g (0.8 mmol) of tetrabutylammonium hydrogen sulfate were placed into a vessel equipped with magnetic stirring, an inlet/outlet, and a vacuum inlet. The flask was evacuated and filled with argon several times, and then *o*-dichlorobenzene (4 mL) and 10 N NaOH (4 mL) were added. The reaction mixture was stirred at 1100 rpm with a magnetic stirrer at 90 °C for 12 h under argon. The mixture was diluted with chloroform and the organic layer was washed with water, diluted hydrochloric acid, and water (3 times). The polymer was separated by precipitation into 4-fold excess of methanol filtration, washed with methanol, and dried in vacuo at 40 °C for 48 h. The results are shown in Table 1.

Polymer and Monomer Characterization. Intrinsic viscosities of the polymers were measured in chloroform at 30 °C with an Ubbelohde-type viscometer in a Schott Gerate AVS 310.

Molecular weight estimations were determined using a Waters 600E gel-permeation chromatography coupled with a 901 photodiode array detector at 254 nm and calibrated with monodisperse polystyrene standards through "Ultrastyragel" columns with 500, 10^4, 10^5, Å at 25 °C with tetrahydrofuran as solvent.

The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR 300 spectrometer, with [D]-chloroform as solvent and as an internal standard.

FTIR spectra were recorded using a Perkin−Elmer PC 16 instrument.

Table 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters for Non-H Atoms with Esd's in Parentheses for Atoms of the Asymmetric Unit

atom	*x*	*y*	*z*	U_{eq} (Å^2)^a
O(1)	0.05220(7)	0.7576(3)	0.11849(7)	0.0225(5)
O(2)	0.03799(12)	0.4585(4)	0.18568(10)	0.0624(9)
C(1)	0.06153(11)	0.4728(4)	0.03391(12)	0.0209(7)
C(2)	0.02465(10)	0.6250(4)	0.05909(11)	0.0199(7)
C(3)	−0.03792(10)	0.6565(4)	0.02658(11)	0.0188(7)
C(4)	−0.07923(10)	0.8104(4)	0.05457(11)	0.0189(7)
C(5)	−0.06051(11)	1.0322(4)	0.08551(12)	0.0202(7)
C(6)	−0.10140(11)	1.1688(4)	0.11003(11)	0.0204(7)
C(7)	−0.16191(11)	1.0971(4)	0.10348(11)	0.0203(7)
C(8)	−0.18034(11)	0.8752(4)	0.07281(11)	0.0206(7)
C(9)	−0.13958(11)	0.7364(4)	0.04929(11)	0.0207(7)
C(10)	−0.20625(10)	1.2506(4)	0.12632(11)	0.0201(7)
C(11)	−0.18761(12)	1.3856(4)	0.18634(12)	0.0238(8)
C(12)	−0.22910(13)	1.5357(5)	0.20557(13)	0.0286(8)
C(13)	−0.28909(13)	1.5561(5)	0.16492(14)	0.0290(8)
C(14)	−0.30828(12)	1.4233(5)	0.10531(13)	0.0274(8)
C(15)	−0.26725(11)	1.2707(5)	0.08653(13)	0.0246(8)
C(16)	0.05356(12)	0.6594(5)	0.18030(12)	0.0285(8)
C(17)	0.07678(14)	0.8340(5)	0.23672(13)	0.0311(9)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Thermal properties of the polymers were determined by differential scanning calorimetry with a Perkin−Elmer DSC-7 and a Du Pont 990 thermal analyzer equipped with a DuPont 910 DSC. Polymer samples of about 10 mg were examined under a nitrogen flow. The glass transition temperature was taken as the median value of the straight portion of the ΔC_p step observed.

UV spectra were recorded on an SLM Aminco 3000 Array spectrophotometer. Fluorescence was measured on an SLM Aminco SPF-500 spectrofluorometer. The polarizing microscopic observations were performed with a Zeiss Axiophot microscope equipped with a Mettler F82 HT hot stage and a Mettler FP 90 central processor.

The dynamic mechanical analysis data, loss tangent (tan *δ*), and complex modulus |*E**| were obtained at 110 Hz using a direct-reading viscoelastometer (Rheovibron Model DPVII-C Toyo, Baldwin). Specimen dimensions were 3.0 cm × 0.2 cm × 0.02 cm.

Crystal and Molecular Structure of Monomer 8. Suitable colorless needle-shaped crystals were obtained by recrystallization from DMA. The crystal, a parallelepiped of approximate size 0.05 × 0.06 × 0.56 mm, used for characterization and data collection was mounted on top of a glass fiber and transferred into the cold nitrogen cold stream of the low temperature unit[24] mounted on an Enrag-Nonius CAD-4P^2 diffractometer (Mo tube, 50 kV, 40 mA, monochromatic Mo Kα radiation, $\Delta\omega = 1.05 + 0.34$ tg θ), interfaced to a MSDOS computer.

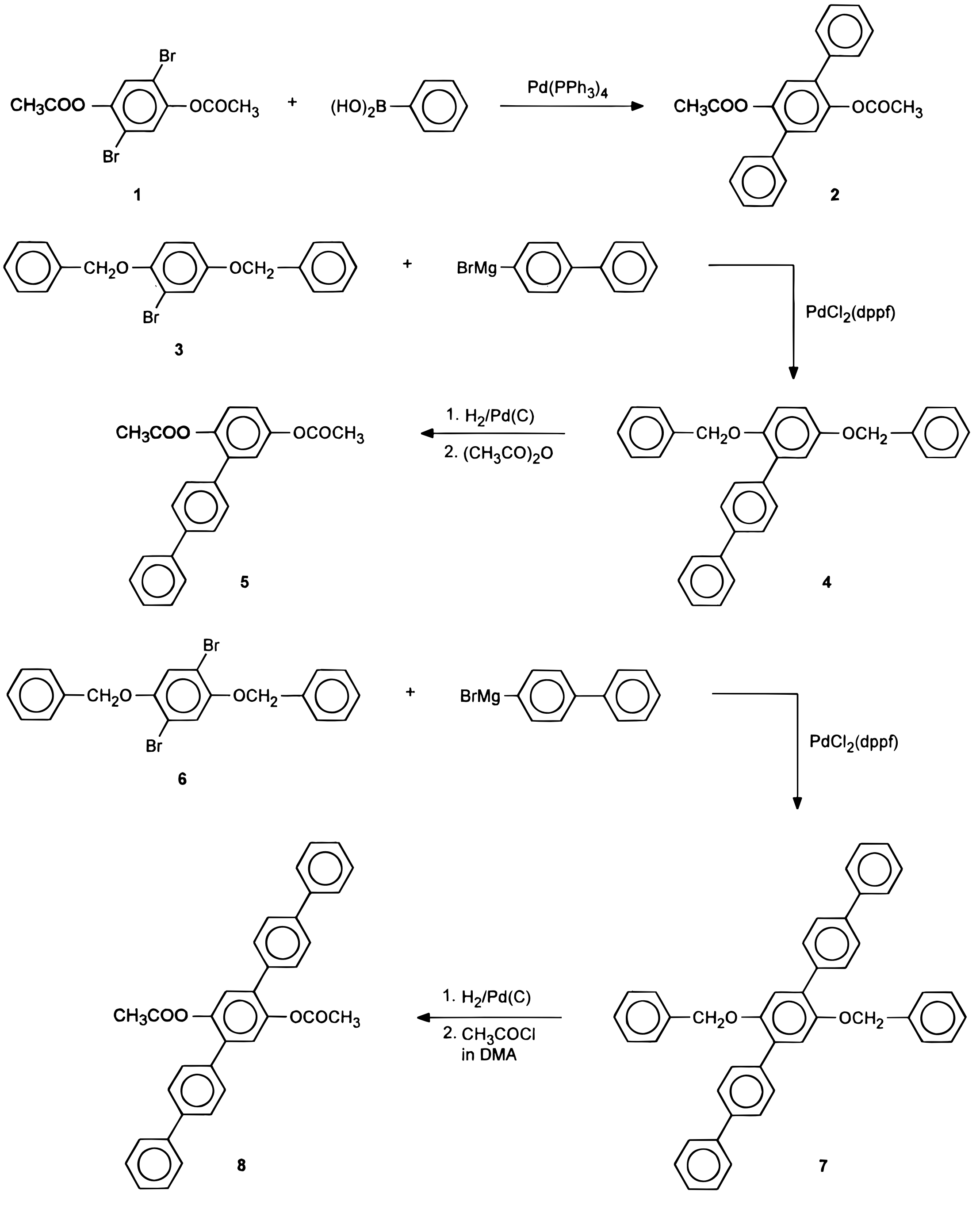
The structure was solved by direct methods with SHELX86.[25] Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates and equivalent displacements for the non-hydrogen atoms are given in Table 2.[26]

Results and Discussion

Monomer Synthesis and Crystal Structure of Monomer 8. Monomer **2** was synthesized from 2,5-dibromohydroquinone diacetate and phenylboronic acid using the Suzuki coupling[27] (Scheme 1). Monomers **5** and **8** were synthesized by the palladium-mediated coupling[28,29] of biphenyl magnesium bromide with the 2-bromo- or the 2,5-dibromohydroquinone dibenzyl ether as also shown in Scheme 1. Reduction with hydrogen in the presence of palladium on activated carbon and acetylation gave the desired products.

Crystal structure analysis of the monomer **8**, which was regarded as a model compound for the studied

Scheme 1



polymers, was performed in order to give information about the conformation of the oligophenyl part. Since it is known[30] that the distortion from the planarity in unsubstituted oligophenyls is due to the ortho-hydrogen repulsions, it is expected that the presence of the substituent will lead to a nonplanar conformation. Figure 1 shows the molecular structure of monomer **8**. The molecule has a crystallographic imposed center of inversion. Bond lengths and bond angles lie within the usual ranges. The torsion angle between the central substituted phenylene rings and the adjacent rings are about 40°, which is significantly higher than the 20° angle obtained for the unsubstituted terphenyl.[31]

The terminal phenylene ring is almost planar to the central ring, also forming a torsion angle of 38.8° with the adjacent ring, despite the absence of any substituents which could further distort the planarity. A kink is also present between the two last rings as was also found for the unsubstituted analogues[32] and shown in Figure 1 and Figure 2.

The data discussed above show that a nonplanar conformation is obtained for the monomer **8** having as result a limited conjugation between the phenylene rings.

Polymer Synthesis and Characterization. Polymerizations were carried out according to Scheme 2 using the phase transfer catalyst tetrabutylammonium hydrogen sulfate.[33] Attempts to polymerize the hydroquinone derivatives were unsuccesful. In the case of the diacetyl derivatives the reaction time was prolonged to 12 h to facilitate the elimination of the acetyl groups in this two-phase system. The polymers were obtained by dilution with $CHCl_3$, washing and precipitation in large excess of methanol.

Polymers **I**, **II**, and **III** were soluble in chloroform (except **Ia**), while **I** (with $n > 8$) and **II** were also soluble

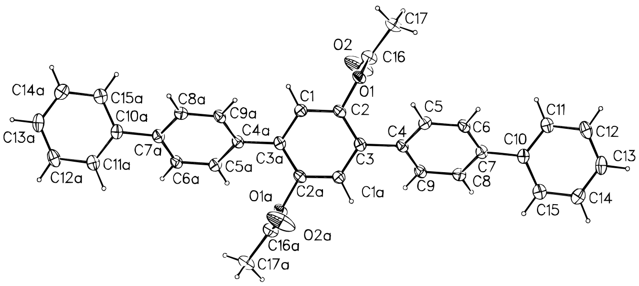


Figure 1. Molecular Structure and numbering of monomer **8**. Anisotropic displacement parameters are shown as 50% probability ellipsoids.

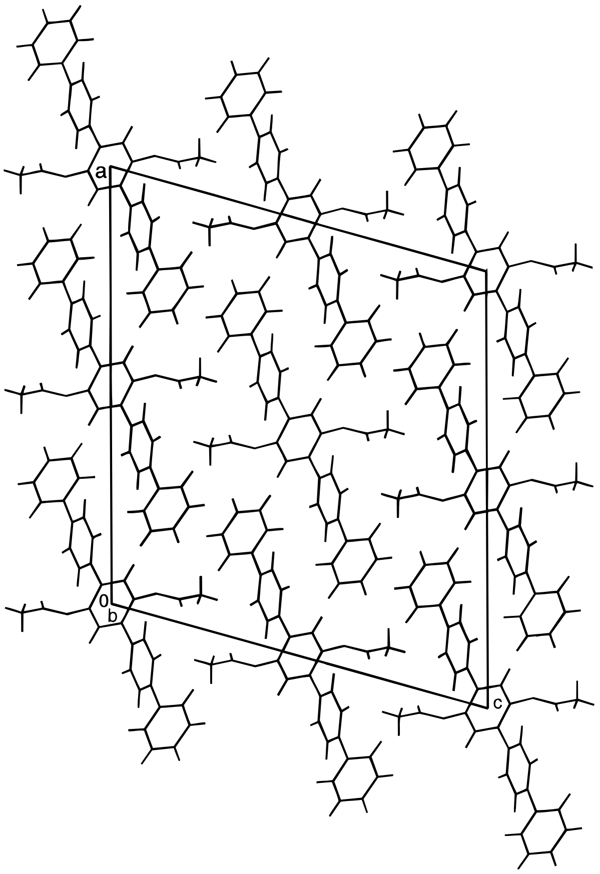


Figure 2. Projection of the crystal structure down [010].

in toluene and tetrahydrofuran. The improved solubility is obviously due to the longer aliphatic spacer and to the asymmetric attachment of the terphenyl unit in polymer **II**. In general, because of the combination of the flexible spacer and the lateral attachment of the oligophenyl unit, which acts as a substituent of the main chain, polymers with intrinsic solubility are synthesized by this method.

Some of the polymers form free standing films. The characterization of the synthesized polymers using viscosimetry and size exclusion chromatography are shown in Table 3. Medium values of intrinsic viscosities (10−50 mL/g) were obtained. Figure 3 shows the GPC traces for polymers **IIa** and **IIIa**. As shown monomodal distibutions with relatively low dispersities were obtained in some cases. Molecular weigths estimates based on calibration with polystyrene standards were in the range 6000−20 000 ($\bar{M}_n$). It should be noted that the polymerizations were not especially optimized. Fractionation of the polymers was attempted, but in the case of polymer **IIa**, only small differences were obtained as shown by GPC and viscosimetric measurements.

Structural characterization of the synthesized polymers was performed using ^{1}H and ^{13}C NMR spectra as shown in Figure 4 with the assignment of the peaks for polymers **I**, **II**, and **III**. The asymmetric attachment of the terphenyl group in polymer **II** is shown by the nonequivalent protons 9, 9* and 10, 10*.

Optical Properties in Solution. The UV−visible absorption spectra of the polymers **Ig** and **IIc** were recorded using THF solutions while for polymer **IIIa** the solution in chloroform was used. As shown in Figure 5 polymer **Ig** shows an absorption maximum at 321 nm, polymer **IIc** at 312 nm, and polymer **IIIa** at 330 nm. The solutions show **blue** fluorescence with maxima at 390, 394, and 407 nm respectively.

The observed differences on the fluorescence maxima as well as on the UV absorption maxima of the three polymers are very small. This is mainly due to the limited increase of the conjugation length from the terphenyl to the quinquephenyl caused by the twisting of the aromatic rings as supported by the crystal structure analysis. These values are in agreement with the UV absorption maximum at 340 nm recently reported for substituted poly(*p*-phenylenes).[34]

The fluorescence quantum yield was measured as $\phi = 0.34$ for polymer **Ig**, $\phi = 0.54$ for polymer **IIc**, and $\phi = 0.31$ for polymer **IIIA** (excitation at 330 nm). They are comparable with values reported in the literature[5,35] but are well below the values reported for substituted poly(*p*-phenylenes).[34,36]

Comparison of the UV-absorption spectrum of the monomer **1** with that of polymer **Ig** shows the disappearance of the absorption peak at 321 nm in the monomer. The same effect is observed for monomer **5** and polymer **III** where only the peak at 290 nm is present in the spectrum of the monomer. This can be attributed to the presence of the carbonyl group in the monomers, and it is in agreement with the observation that polyesters with similar structure[22] did not show any fluorescence as also has been observed by others.[37,38] It should be noted that aromatic aliphatic polyesters having phenylenevinylene type chromophores in the main chain were recently reported as photonic materials.[39]

Thermal Properties. The thermal properties of the studied polyethers were examined using DSC and the results are shown in Tables 4 and 5. Polymers **Id**−**g** show two endotherms during the first heating scan. By quenching at 0 °C only a T_g is obtained during the second heating except for polymer **Ie** where a crystallization exotherm followed by a double endotherm at 120 and 128 °C was observed. Plot of the melting (T_1) and the isotropization (T_2) temperatures according to the number of methylenes in the flexible spacer shows that T_2 has a significant odd−even effect but not T_1 as shown in Figure 6.

Because of the difficulty to crystallize polymers **I** they were thermally or chemically treated to induce crystallization. The results are shown in Table 5. Treatment of the melted polymers with acetone gave crystalline polymers which also showed two endotherms as can be observed in Figure 7. The melting temperatures are smaller than those obtained during the first heating scan while the isotropization temperatures are almost indentical. The T_1 dependence on the length of the spacer shows a very weak odd−even effect. The odd members of this series have very low ΔT values. For

Scheme 2

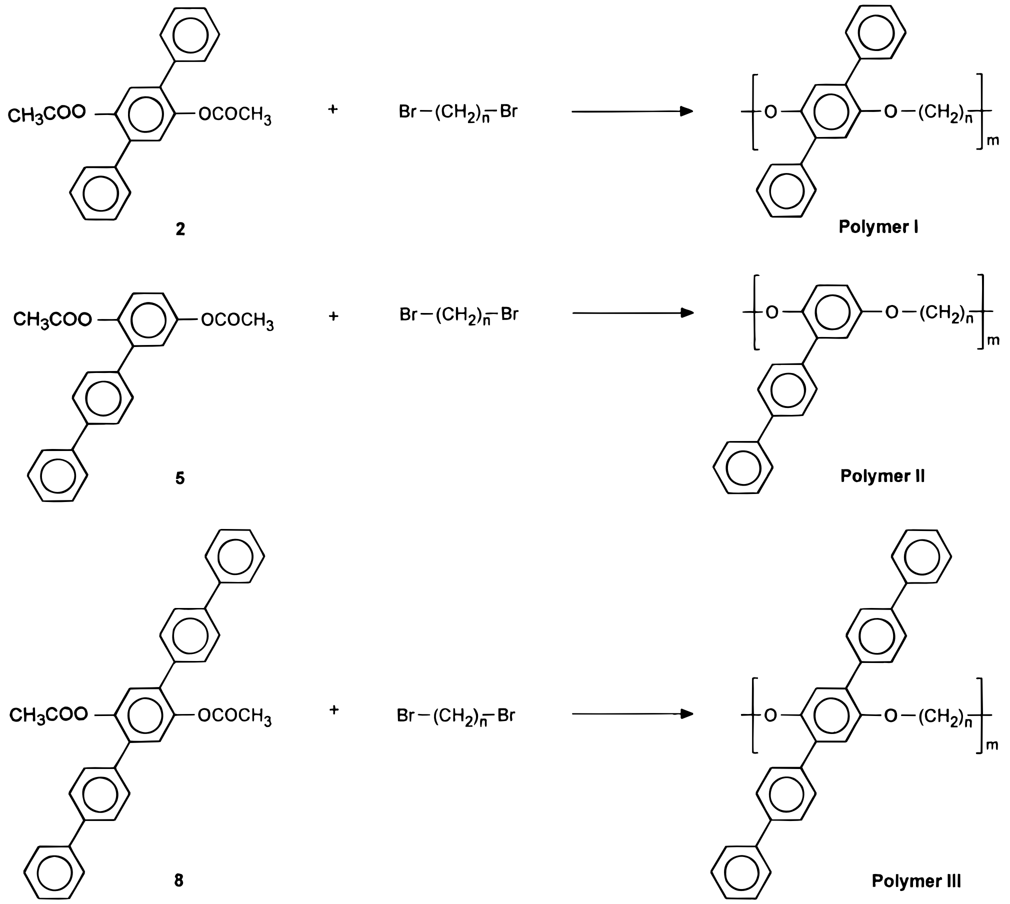


Table 3. Viscosimetric and GPC Characterization of the Synthesized Polymers

polymer	n	$[\eta]^a$ (mL/g)	$\bar{M}_n{}^b$	$\bar{M}_w{}^b$
Ia	6			
Ib	7	10	5000	7200
Ic	8	10	5000	6900
Id	9	15	6100	9500
Ie	10	21	10000	18300
If	11	12	6000	9200
Ig1	12	18	9900	21300
Ig2	12	40	16500	21200
IIa	9	35	13900	27200
IIa1	9	45	18500	27500
IIb	10	25	7800	12700
IIc	12	30	12000	21700
IIIa	12	10	6000	8200

[a] In $CHCl_3$. [b] In THF based on PS standards.

polymers **Id** and **If** (n = 9 and 11) the transition temperatures were so closely spaced that ΔH_1 and ΔH_2 values could not be obtained. The enthalpies of the two transitions are also different between the odd and even members. Polymers with odd number of methylene units show $\Delta H_1 \gg \Delta H_2$ while for polymers with even number of methylenes $\Delta H_1 \ll \Delta H_2$. These differences show that in the first case the polymers are more ordered in the crystalline state while in the second case the liquid crystalline state is more ordered. Analogous behavior was observed for polyesters derived from 4,4′-dihydroxybiphenyl and various aliphatic dibasic acids.[38]

Polymers **II** are amorphous and only a T_g was obtained from the DSC thermograms. Attemps to crystallize these materials either by thermal or by chemical treatment failed, and this is because of the asymmetric structure of these polymers.

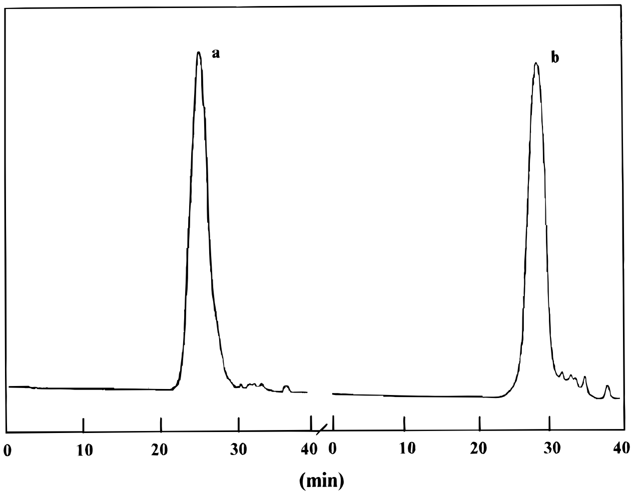


Figure 3. Size-exclusion chromatograms of polyethers **IIa1** (a) and **IIIa** (b) in THF at 25 °C.

Polymer **IIIa** showed two endotherms at 101 and 141 °C during the first heating scan. Annealing at 70 °C for 24 h gave two endotherms at 98 and 141 °C.

Microscopic examination between cross polarizers of polymers **Ia**−**g** and **IIIa** gave in all cases birefringent melts at temperatures between the two endotherms in DSC. Because of the very slow rate of crystallization, it was impossible to follow the transformation during the cooling scan. Optical textures of samples annealed at temperatures between the two endotherms e.g. at 78 °C for polymer **Id** and at 125 °C for polymer **IIIa** and cooled down to room temperature are presented in Figure 8. A more systematic examination of the formed liquid crystalline phases is in progress.

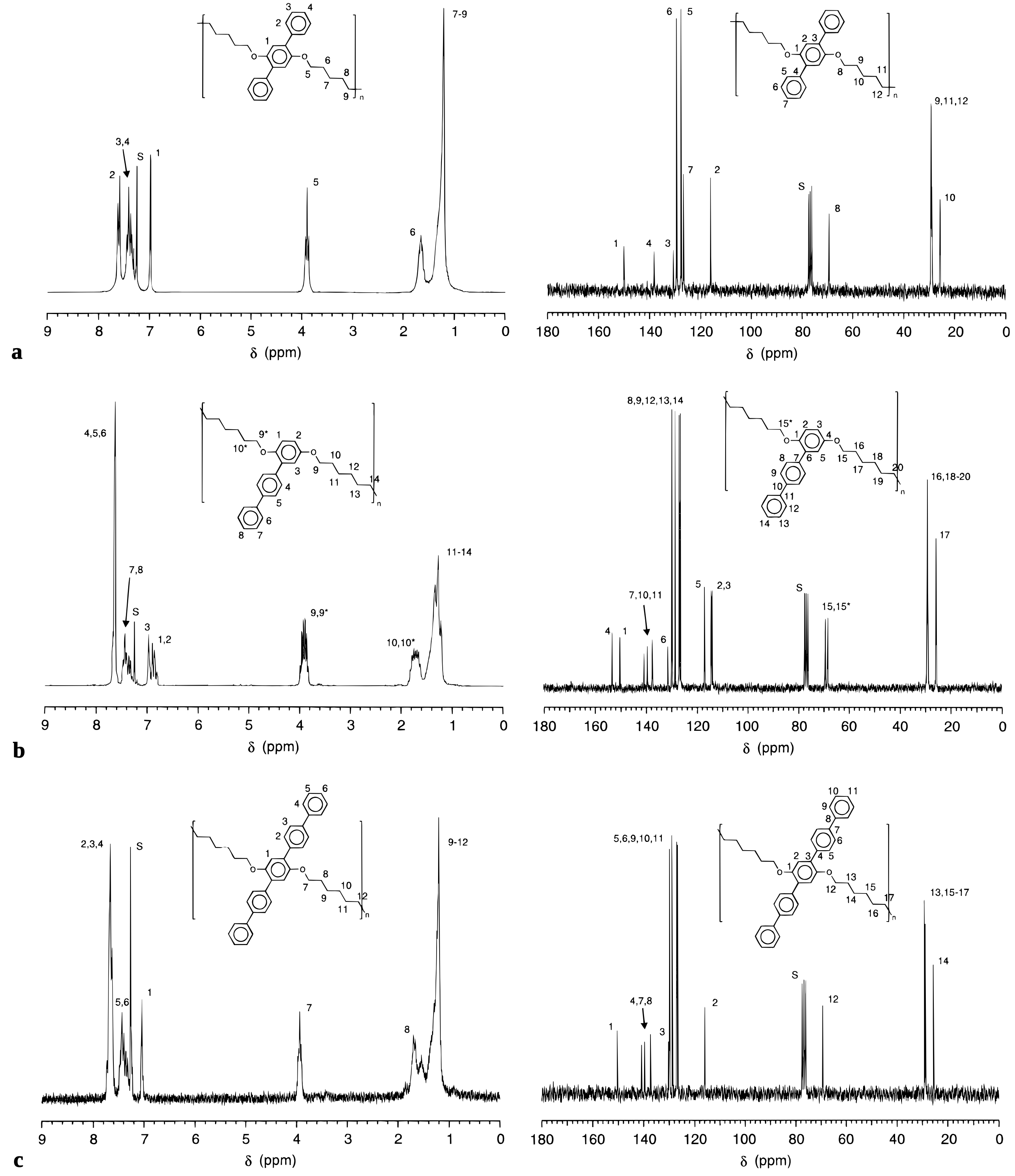


Figure 4. ^{1}H NMR and ^{13}C NMR spectra of the polyethers **Ig1** (a), **IIc** (b), and **IIIa** (c).

As shown from the thermal data liquid crystalline polymers having low transition temperatures are obtained by this method. The use of the oligophenyl units laterally attached to the main chain combines solubility and photonic properties with liquid crystallinity which appears at temperatures where the polymers are thermally stable. Using the same methodology, polymers with a phenylenevinylene segment can be synthesized, and work is in progress in this topic. The use of the lateral attachment of these units in the main chain will reduce the transition temperatures, and the cross-linking which mostly appeared for the linear counterparts at temperatures where the liquid crystalline properties exist will be overcome.[39,41]

Mechanical Properties. Polymers which form free standing films are obtained in some cases, as mentioned before. Polymers **IIa** gave transparent films after solution casting from toluene and this film was examined using dynamic mechanical analysis and tensile testing. The results in respect to the *E*′ and the *E*″ at different temperatures and frequencies are shown in

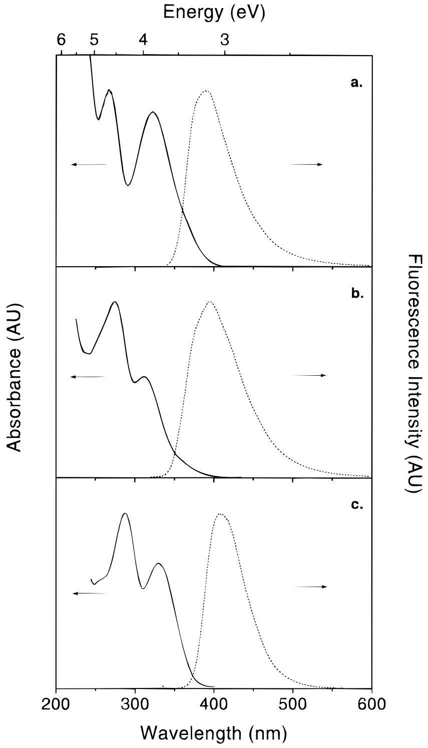


Figure 5. Absorption (—) and emission spectra (···) in THF solutions of polymer **Ig1** (a), polymer **IIc** (b), and polymer **IIIa** (c).

Table 4. DSC Data Obtained from the First Heating Scan

polymer	*n*	T_{g}[a] (°C)	T_1 (°C)	T_2 (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)
Ia	6	37	162	183	34.4	13.1
Ib	7	32	77	119	5.0	34.2
Ic	8	24	73	120	3.8	32.1
Id	9	17	67	80	*b*	*b*
Ie	10	16	65	131	10.4[c]	37.9
If	11	14	50	55		*b*
Ig	12	10	65	103	2.4	32.4
IIa	9	28				
IIb	10	25				
IIc	12	15				
IIIa	12	35	101	141		

[a] Second heating after quenching to 0 °C. [b] Peaks are overlapped. [c] An exotherm at 72 °C overlapped with this peak.

Table 5. DSC Data Obtained after Annealing or Treatment with Acetone

polymer	*n*	T_1 (°C)	T_2 (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)
Ic[a]	8	58	121	11.1	29.6
Id[a]	9	54	81	22.0	5.2
Ie[a]	10	60	124, 132	8.5	30.9
If[a]	11	48	61	26.7	2.0
Ig[a]	12	70	103	2.7	29.6
Ic[b]	8	68	121	7.0	29.2
Ie[b]	10	69, 78	131	4.3	35.5
Ig[b]	12	69, 78	103	4.3	26.0
IIIa[c]	12	98	141	5.3	25.4

[a] Crystallization after treatment with acetone for 1 day. [b] Annealing at 40 °C for 2 days. [c] Annealing at 70 °C for 1 day.

Figure 8. E'' appears a low temperature transition below −75 °C and a glass transition at 33 °C. Mechanical properties under large deformation were also examined and the results are elongation at break $\epsilon = 63\%$ and stress at break $\sigma_{\mathrm{b}} = 6.5$ MPa.

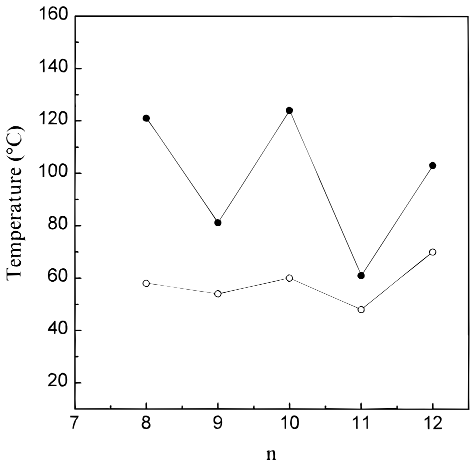


Figure 6. Variation of the first (T_1) and the second (T_2) endotherms with the number of the methylene units in polymer **I**.

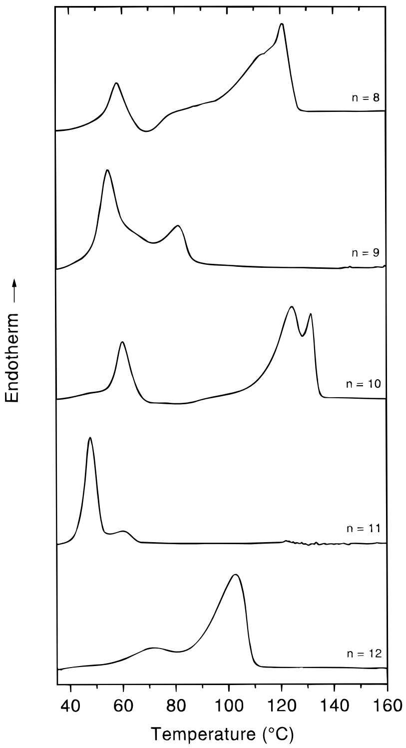


Figure 7. DSC curves of polymer **I** after treatment with acetone.

Conclusion

In conclusion aromatic polyethers having lateral oligophenyl units which combine photonic properties with liquid crystallinity can be synthesized by the reaction of the diacetyl derivatives of substituted hydroquinones with aliphatic dibromides in the presence of a phase transfer catalyst. Depending on the way of the attachment of the chromophore to the main chain, liquid crystalline or amorphous polymers are obtained. These blue light emitting polymers are intrinsically soluble because of the combination of the flexible spacer with lateral attachment of the oligophenyl unit. Due to the solubility as well as the ability to melt at relatively low temperatures these polymers are easily processable with good film forming properties. Their enhanced processability and mechanical properties greatly facilitate the fabrication of light emitting devices by spin casting or melt processing. Finally, despite the

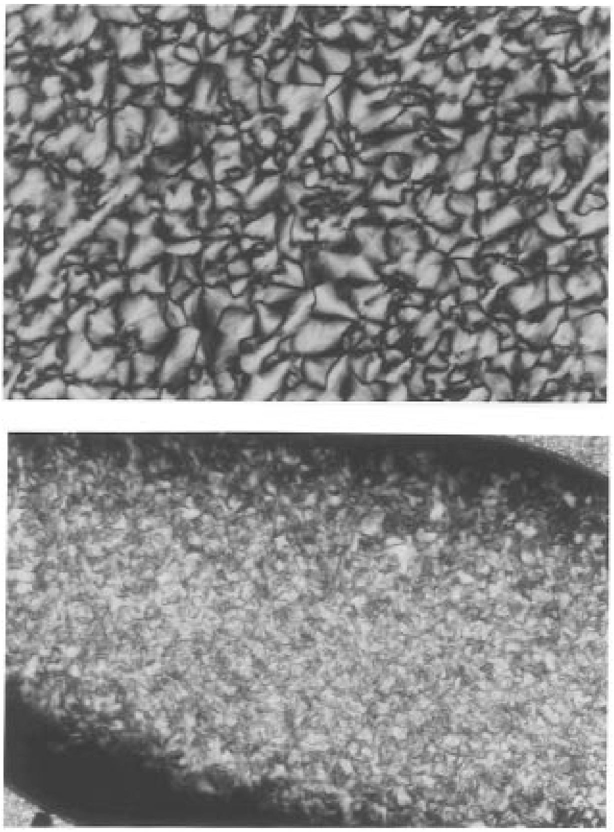


Figure 8. Optical micrographs at room temperature of polymers **Id** annealed at 78 °C for 5 h (top) and **IIIa** annealed at 125 °C for 2 h (bottom).

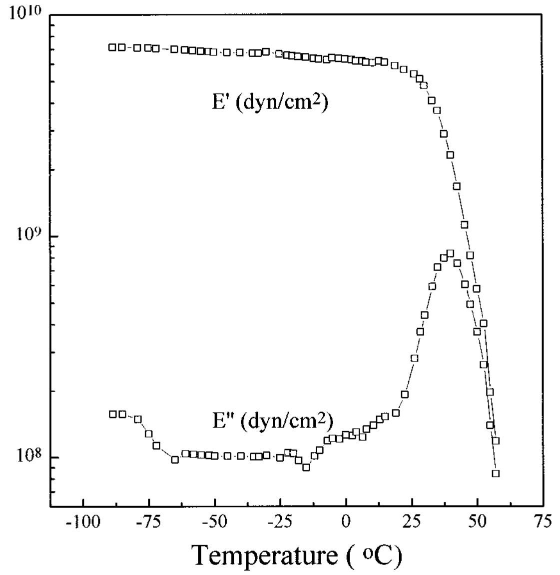


Figure 9. Temperature dependence of storage *E*′ and loss *E*″ moduli at 110 Hz of polyether **IIa1**.

increase of the conjugation length from the terphenyl to the quinquephenyl monomer unit the photoluminescence maximum shows only a small increase to higher wavelength.

Acknowledgment. The authors are indebted to Mr. G. Alberta for DSC measurements, Mr. A. Meetsma for the crystal structure determination, and the Netherlands Organization for Scientific Research (NWO) for financial support.

Supporting Information Available: Text giving experimental details and tables giving complete results of the crystal and molecular structure determination of monomer **8** (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, N.; Mackay, K.; Fried, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(2) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
(3) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.
(4) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.
(5) Hilberer, A.; Brouwer, H. J.; van der Scheer, B. J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 4525.
(6) Braun, D.; Gustafsson, G.; McBranch, D.; Heeger, A. J. *J. Appl. Phys.* **1992**, *72*, 564.
(7) Kanabe, M.; Okawara, M. *J. Polym. Sci., Part A-1* **1968**, *6*, 1058.
(8) Momii, T; Tokito, S.; Tsutsui, T.; Saito, S. *Chem. Lett.* **1988**, 1201.
(9) Iwatsuki, S.; Kubo, M.; Kumeuchi, T. *Chem. Lett.* **1991**, 1071.
(10) Conticello, V. P.; Gin, D. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 9708.
(11) Hsieh, B. R.; Antoniades, H.; Bland, D. C.; Feld, W. A. *Adv. Mater.* **1995**, *7*, 36.
(12) Zhong, X.; Francois, B. *Synth. Met.* **1989**, *29*, E35.
(13) Schlueter, A.-D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59.
(14) Pomerantz, M.; Wang, J. *Polym. Prepr.* **1994**, *35* (1), 210.
(15) Philips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Polym. Prepr.* **1994**, *35* (1), 367.
(16) McCarthy, T. F.; Witteler, H.; Pakula, T.; Wegner, G. *Macromolecules* **1995**, *28*, 8350.
(17) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.
(18) Wallow, T. I.; Novak, B. M. *Polym. Prepr.* **1993**, *34* (1), 1009.
(19) Connolly, M.; Karasz, F.; Trimmer, M. *Macromolecules* **1995**, *28*, 1872.
(20) Herrema, J. K.; van Hutten, P. F.; Gill, R. E.; Wildeman, J.; Wieringa, R. H.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 8102.
(21) Hay, M.; Klavetter, F. L. *J. Am. Chem. Soc.* **1995**, *117*, 7112.
(22) Kallitsis, J. K.; Serpi, H. S.; Tosioudi, C.; Gravalos, K. G.; Photinos, P. J.; Photinos, D. J. Presented at The 16th International Liquid Crystal Conference, Kent, OH, June 1996.
(23) Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.
(24) Bohnis, F. Van, J. *Appl. Crystallogr.* **1971**, *4*, 263.
(25) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(26) See Supporting Information paragraph.
(27) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.
(28) Katayama, T.; Umeno, M. *Chem. Lett.* **1991**, 2073.
(29) Kallitsis, J. K.; Kakali, F.; Gravalos, K. G. *Macromolecules* **1994**, *27*, 4509.
(30) Sasaki, S.; Yamamoto, T.; Kanbara, T.; Morita, A.; Yamamoto, T. *J. Polym. Sci. Polym. Phys.* **1992**, *30*, 293.
(31) Baudour, J. L.; Delugeard, Y.; Rivet, P. *Acta Crystallogr.* **1978**, *B34*, 625.
(32) Baker, K. N.; Fratini, A. V.; Resch, T.; Knachel, H. C.; Adams, W. W.; Socci, E. P.; Farmer, B. L. *Polymer* **1993**, *34*, 1571.
(33) Percec, V.; Kawasumi, M. *Macromolecules* **1993**, *26*, 3917.
(34) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.
(35) Darey, A. P.; Elliott, S.; O'Connor, O.; Beau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433.
(36) Stamplf, J.; Tasch, S.; Leising, G.; Scherf, U. *Synth. Met.* **1995**, *71*, 2125.
(37) Yan, M., Rothberg, L. J.; Papadimitracopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73*, 744.
(38) Papadimitracopoulos, F.; Konstadinidis, K.; Miller, T.; Opila, R.; Chandross, E.; Galvin, M. *Chem. Mater.* **1994**, *6*, 1563.
(39) Oberski, J.; Festag, R.; Schmidt, C.; Lüssem, G.; Wenorff, J. H.; Greiner, A.; Hopmeir, M.; Motademi, F. *Macromolecules* **1995**, *28*, 8676.
(40) Krigbaum, W. R., Watanabe, J.; Ishikawa, T. *Macromolecules* **1983**, *16*, 1271.
(41) Chan, W. K.; Yu, L. *Macromolecules* **1995**, *28*, 6410.

MA9613796