Rigid Rod Conjugated Polymers for Nonlinear Optics. 2. Synthesis and Characterization of Phenylene−Ethynylene Oligomers

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ABSTRACT: In order to make a comparison between the properties of low molecular weight poly(phenyleneethynylene) type compounds and the corresponding high molecular weight polymers, we have synthesized oligomers and model molecules of poly(phenyleneethynylene) derivatives by two different routes. This paper describes the synthesis and the X-ray and optical characterization of conjugated soluble oligomers, as well as model trimers and pentamers of the same structure in which the solubility was improved by fixing flexible alkyl chains of 10 or 12 carbons to the backbone. The electron density on the phenyl ring was also enhanced or reduced by introducing either electron-donor or electron-acceptor groups. The oligomers were synthesized by polycondensation using a palladium catalyzed coupling reaction, between a bromoaryl and an ethynylaryl unit, with HBr elimination. This method allows the insertion of a triple bond between two phenyl groups. It was initially used in our laboratory in order to obtain high molecular weight polymers. It has been adapted to favor the production of lower molecular weight compounds, by shortening the reaction time or by an important increase of the amount of catalyst. The trimers and pentamers were synthesized step by step by using a route which involves a selective protection−deprotection method, followed by the palladium coupling reaction. Model compounds and oligomers were characterized by UV−visible and Raman spectroscopies, as well as nonlinear optical measurements of the third order susceptibilities ($\chi^{(3)}$). These measurements allowed us to show the influence of the donor/acceptor groups and the chain lengths on the absorption wavelength. In addition, the nonlinear optical measurements show that the $\chi^{(3)}$ value of the pentamer (1.6×10^{-10} esu) is close to the value of the polymer (4.6×10^{-10} esu).

1. Introduction

Linear and rigid conjugated chains of polymers have attractive properties for the preparation and the study of processable materials for nonlinear optical applications.[1,2] The processing of conjugated polymers into films or fibers is crucial for the development of nonlinear materials useful in photonic applications. Unfortunately the polarizable π electrons of rigid rod conjugated polymers introduce strong intermolecular interactions, and therefore high molecular weight macromolecules are often insoluble and infusible. Conjugated polymers have also been developed in the field of conducting materials, but the electronic conductivity in molecular material requires slightly different properties than those for optical applications. High conductivities are generally obtained by doping the molecular material. In polymers, an appreciable conductivity is observed in polyacetylene, polythiophene, polyphenylene, or polyaniline and their derivatives.[3] In addition, the solubility of conjugated polymers is important for processability for nonlinear optics (NLO). In rigid rod conjugated chains the solubility is greatly increased when alkyl chains are tied on the repeating units.[4]

While polydiacetylene is one of the most studied classes of π conjugated polymers, few of them show as good solubility and high nonlinear susceptibility as p4BCMU.[5] However, the nonlinear susceptibility varies upon the conformational structure of the main chain.[6,7] Poly(*p*-phenylenevinylene) (PPV) derivatives have also been well studied and exhibit high $\chi^{(3)}$ values, in the range of 10^{-9} esu for the oriented phenyl dimethoxy substituted derivative (MO-PPV).[8,9] In contrast, the acetylene analogue of PPV, based on the phenyl−ethynyl unit, has received less attention, mainly due to the low solubility of the compound and the low molecular weight of the polymer chain.

The first synthesis of phenyl−ethynyl conjugated chains was described by Lakmikantham in 1983.[10] Oligomerization occurred via a cuprous acetylide phenyl iodide. The dry cuprous derivative was converted, by heating, to a yellow brown powder, which is a short oligomer of 10−12 phenyl−ynylene units. A more convenient method, using a palladium catalyzed polycondensation, has been applied to the synthesis of aryl−ynylene polymeric chains,[11,12] more generally known in organic synthesis as a Heck coupling.[13] A substituted diethynyl arene reacts with a disubstituted halogeno−aryl compound in the presence of a catalytic amount of a palladium complex.[14,15] During the catalytic reaction either the low solubility of the aryl−ethynyl oligomers or more likely the low solubility of the intermediate complex prevents the formation of high molecular weight chains.[16] The molecular weights of the series containing phenyl, anthryl, thienyl, or pyridyl moieties rose only to values between 1500 and 4000.[17] Recently, the possibility of increasing the solubility and simultaneously the molecular weight of such backbones was investigated by attaching flexible side chains to the rigid

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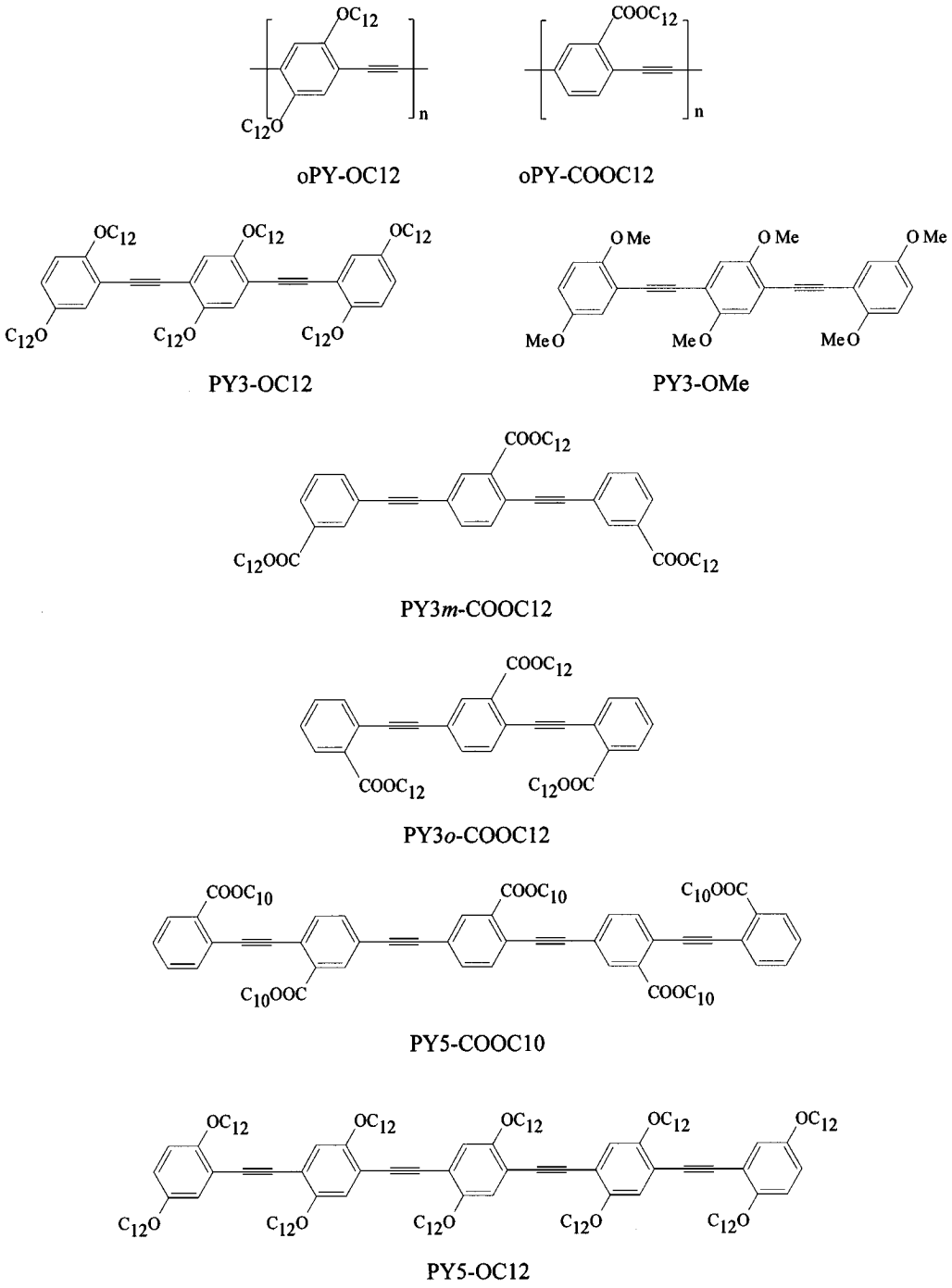

Figure 1. Oligomers and polymers synthesized in this work. The oligomers of the ether and ester series (oPY-OC12 and oPY-COOC12) are obtained by random oligomerization; PY3's and PY5's, by a step by step synthesis.

core of the main chain.[18−20] Both the alkyl side groups, which increase the chain solubility, and the use of tetrahydrofuran (THF) as cosolvent, which is well-known for its solvatation properties of metal complexes, afford high molecular weight polymers. The high molecular weights were characterized by size exclusion chromatography (SEC) and light scattering, finding average values as high as 10^5 g/mol. However, high values of optical third order susceptibilities were observed by third harmonic generation or degenerate four wave mixing.[21,22]

In the present work, we have synthesized oligomeric derivatives of the phenyl−diethynyl series in order to investigate the effect of shortening the conjugated length on the optical properties, linear absorption, and nonlinear third order susceptibilities. We will give a detailed characterization of the oligomers obtained by two synthetic routes and compare them with previous results on polymeric series.

2. Results

2.1. Synthetic Methods. 2.1.1. Synthesis of Random Distributed Oligomers. We have synthesized a series of randomly distributed oligomers with alkyl ether and alkyl ester side chains, respectively oPY-OC12 and oPY-COOC12 (Figure 1). Here the side chain ether or ester enhanced the solubility and increased or decreased the electron density respectively by electron-donor effect for OC12 or by electron-acceptor effect for COOC12. The polymerization method was already described in the literature. The reaction is shown in Scheme 1.

Scheme 1

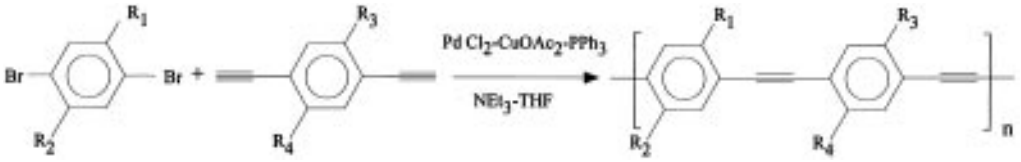

Table 1. Optical Properties of Oligomers and Corresponding Polymers in Solutions and in Solid State Thin Films, the Wavelength in THF Solutions at the Maximum of the Absorption Peak, the Molecular Absorption Coefficient (L mol^{-1}) at the Same Wavelength, the Calculated Molar Absorption Coefficient ϵ* Relative to the [Phenyl−Ethynyl] Unit Concentration, the Wavelength (nm (eV)) of the Solid Thin Film at the Absorption Peak, the Raman Scattering at Resonance ν_{vib} (C≡C) (cm^{-1}), the Half-Bandwidth of the C≡C Stretch, and the Third Order Susceptibility, $\chi^{(3)}$ (esu), Measured by Degenerate Four Wave Mixing (DFWM) at 620 nm

	solution					
oligoms and polyms	λ_{max}, nm	ϵ, 10^4 L [repetitive unit]$^{-1}$	solid films λ_{max}, nm (eV)	Raman ν_{vib} (C≡C), cm^{-1}	half-bandwidth C≡C str, cm^{-1}	$\chi^{(3)}$ (DFWM, 620 nm), 10^{-10} esu
PY3-OC12	376	1.8	378 (3.28)	2207	19	–
PY3-OMe	378	3.2	383 (3.23)	–	–	2.5
PY5-OC12	418	1.7	425 (2.92)	2200	26	1.6
oPY-OC12 f_1	400	1.3	419 (2.96)			
f_2	423	1.6	445 (2.78)			
f_3	431	1.6	452 (2.74)			
pPY-OC12	432	1.6	453 (2.73)	2196	30	4.6
PY3*m*-COOC12	333	1.6	335 (3.69)	–	–	–
PY3*o*-COOC12	344	1.9	337 (3.67)	–	–	–
PY5-COOC10	364	5.4	375 (3.30)	2204	21	
oPY-COOC12	384	1.4	403 (3.10)			
pPY-COOC12	383	3.6	405 (3.06)	2207	28	4.6

The condensation is catalyzed by the $PdCl_2-CuOAc_2-PPh_3$ complex in NEt_3−THF solvent, according to Heck conditions. R_1, R_2, R_3, and R_4 are side groups, alkyl ethers, alkyl esters, or H. The synthesis of low molecular weight oligomers implies slight modifications of the basic experimental conditions, such as the time rate of polymerization, the monomer catalyst ratio, and the solution concentration. With the primary objective being to increase the polymer initiation reaction to obtain low molecular weights, a higher catalyst to monomer ratio (10 mol %) was used than that for long polymeric chain synthesis. Oligomerization was performed during a shorter time of polymerization (6 h), using triethylamine as the solvent. No further attempts were made to study in detail the effect of polymerization conditions on conversion rate and polymerization degree. A typical example of the synthetic route for the ether derivative oPY-OC12 is given in the Experimental Section.

2.1.2. Synthesis of Model Oligomers. The model compounds, trimers PY3-OC12, PY3-OMe, PY3*m*-COOC12, and PY3*o*-COOC12 and pentamers PY5-OC12 and PY5-COOC10, were synthesized step by step (Figure 1). The trimers were obtained by the condensation of a diethynyl or a dibromoaryl with a terminal monoreactive aryl site. The pentamers were synthesized by a selective protection and deprotection method, which was already described in the literature[23] In the step by step route, the arylethynyl unit is protected on each side by trimethylsilyl and triazene groups, respectively.[24,25] Each of these protecting groups can be selectively removed in the presence of the other, and at last the coupling step increases the length of the molecule. PY5-OC12 was synthesized by coupling two monohalogened dimers, the phenyl−ethynyl−phenyl−iodide, with the corresponding bis(dodecanoxy)diethynyl−phenyl. PY5-COOC10 was synthesized by another route using a dihalogened trimer coupled with the corresponding decyl 2-ethynylbenzoate.

2.2. NMR Characterization of the Model Compounds and the Oligomers. The chemical structure and purity of trimers (PY3), pentamers (PY5), and oligomers (oPY) were checked by elemental analysis and ^{1}H and ^{13}C NMR. The relevant results of these studies are given in the Experimental Section. The spectra of the PY3 and PY5 are consistent with the expected molecular structures. The ^{1}H NMR of the PY5 and the oPY by comparison with the polymers (pPY) are very similar; all the resonances are broader, and no signal appeared in the region of the acetylenic hydrogen (3.5 ppm). In the aromatic region, the oligomer oPY as well as the polymer pPY present a weak signal (7.10 ppm) which is assigned to the phenyl end group carrying a nonreacted bromine. The spectra of PY3 and PY5 show the additive signals of the terminal hydrogens.

2.3. UV−Visible and Raman Spectroscopy. We have listed in Table 1 the results of the UV−visible and Raman scattering spectroscopies. The absorption spectra of the two oligomers (oPY-OC12 and oPY-COO12) and the model compounds (PY3-OC12 and PY3*o*-COOC12) in THF solution are given respectively in Figure 2a,b. For compounds of the same main chain length, for example, the PY3-OC12 and the PY3*m*-COOC12, it is seen that the peak absorption of the ether substituted compound (λ_{max} = 376 nm) is shifted toward longer wavelengths with respect to the ester substituted compound (λ_{max} = 333 nm). The same phenomenon is observed for the oligomers (oPY-OC12, λ_{max} = 431 nm; oPY-COO12, λ_{max} = 384 nm). This large red shift of the absorption maxima ($\delta\lambda_{max}$ = 50 nm) is induced by the donor side groups. The presence of electron-donor groups in the backbone enhances the electron delocalization through the phenyl ring, giving better conjugation along the backbone. This phenomenon has already been observed for high molecular weight poly(phenylene−ethynylene) ether and ester derivatives.[21]

We also studied the evolution of the peak absorption as a function of the length of the backbone for compounds having the same substituent, for example, the ester side group. oPY-COOC12 (λ_{max} = 384 nm) has a maximum at longer wavelength than PY3*o*-COOC12 (λ_{max} = 332 nm). The same behavior is also observed

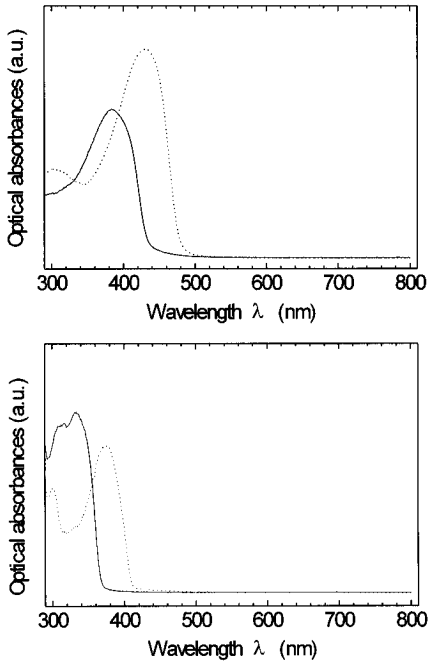

Figure 2. (a, top) UV−visible spectra of the oligomers oPY-OC12 (dotted line) and oPY-COOC12 (continuous line) in THF solution. (b, bottom) Spectra of the model compounds PY3-OC12 (dotted line) and PY3o-COOC12 (continuous line) in THF solutions.

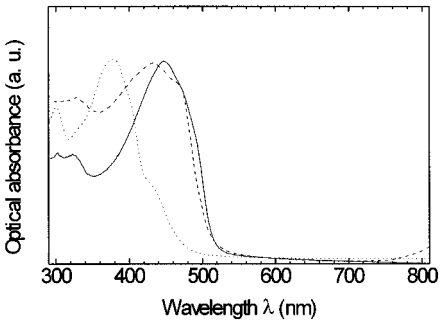

Figure 3. UV-visible spectra of solid state films of the ether series, the polymer pPY3-OC12 (continuous line) and the model compounds PY5-OC12 (dashed line) and PY3-OC12 (dotted line).

in the ether series. Figure 3 represents the UV−visible spectra of the model molecules PY3-OC12 and PY5-OC12 and that of the polymer pPY-OC12 in solid thin films. The large red shift of the absorption maxima between the trimer and polymer ($\Delta\lambda_{max} = 75$ nm) shows the dependency of the maximum absorption wavelengths with the length of the chain. In the oligomer series, where oPY-OC12 has been separated in three fractions named f_1, f_2 and f_3 by preparative SEC, the same evolution occurs. The average molecular weight of each fraction was determined by NMR *and* elemental analysis of the bromine end groups. The three fractions show absorption at three different wavelengths 400, 423, and 431 nm, corresponding to the average degree of polymerization ⟨Dpn⟩ at 13, 19, and 27, respectively. The λ_{max} vs ⟨Dpn⟩ is plotted in Figure 4 and shows that λ_{max} increases with ⟨Dpn⟩ up to a plateau value around 432 nm, obtained for the polymer pPY-OC12. This red shift of wavelengths with ⟨Dpn⟩ is associated with the increase of the π electron delocalization along the linear phenyl−ethynyl chain.

Raman scattering of vibrational modes of the unsaturated bonds is a sensitive method for the characterization of π electron delocalization in polymers and oligomers. The normal modes associated with the triple bond stretching are observed near 2210 cm^{-1}. Figure 5a shows the C≡C stretching band of the trimer PY3-OC12, the pentamer PY5-OC12, and the polymer pPY-OC12. A shift to lower frequencies is found, going from the trimer ($\Delta\nu$ = 2207 cm^{-1}), to the pentamer ($\Delta\nu$ = 2200 cm^{-1}), and to the polymer ($\Delta\nu$ = 2196 cm^{-1}). This shift is due to an increase of π electron delocalization along the chain length,[26] in addition, the electron density on the triple bond is weaker, thus resulting in a lower bond energy. The other Raman modes below 2000 cm^{-1} do not shift in frequency with the extent of conjugation. The C≡C stretching band broadens from trimer to polymer; the full width at half-maximum of the band increases from 19 cm^{-1} for PY3-OC12 to 26 cm^{-1} for PY5-OC12 and to 30 cm^{-1} for pPY-OC12, indicating that the C≡C bonds are slightly different along the conjugated chain.

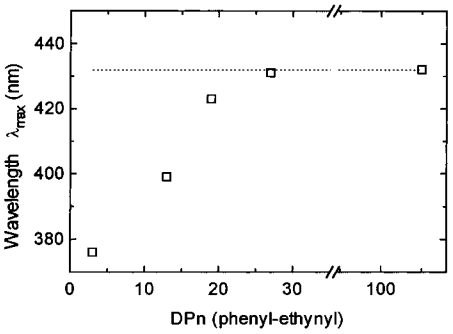

Figure 4. Plot of the wavelength at the absorption peak for separated fractions (f_1, f_2, and f_3) of oligomer ether oPY-OC12 and polymer pPY-OC12 vs the polymerization degree Dpn. The dashed line represents the asymptotic limit of the absorption maximum.

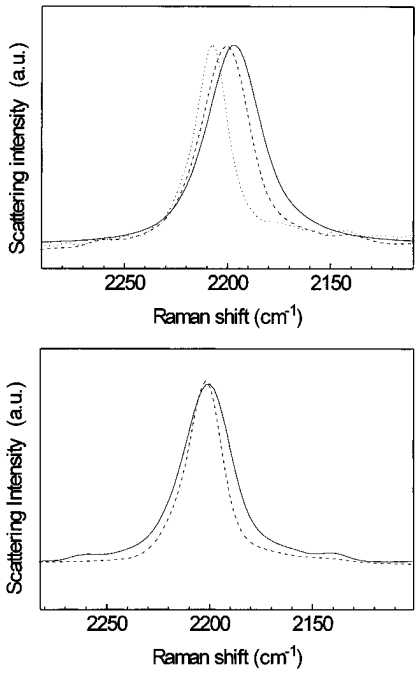

Figure 5. (a, top) Raman scattering spectra of ethers PY3-OC12 (dotted line), PY5-OC12 (dashed line), and the corresponding polymer pPY-OC12 (continuous line). (b, bottom) Raman scattering spectra of esters PY5-COOC12 (dotted line) and the corresponding polymer pPY-COOC12 (continuous line).

2.3.1. Thermal Properties. The thermal properties of the model compounds and the oligomers were ana-

Table 2. Thermal Data from DSC on Oligomer and Polymer Ethers and Esters at the Heating Rate of 10 °C min^{-1}

DSC	transition temp, °C	transition enthalpy, J/g
PY3-OC12	94	+42
PY5-OC12	51 (first peak)	+3.8
	99 (second peak)	+17.8
oPY-OC12	45 (first peak)	+4.5
	59 (second peak)	+0.3
pPY-OC12	74[a]	+10.7
PY3*o*-COOC12	9	+12
PY3*m*-COOC12	46	+30
PY5-COOC10	60	+97.4

[a] First heating. At low temperature, glass transition $T_g = -42$ °C.

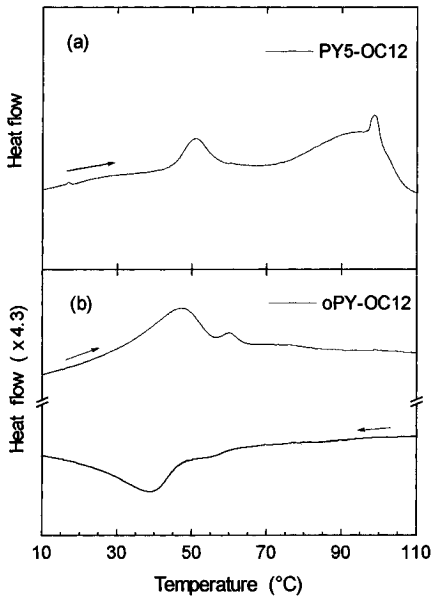

Figure 6. (a) DSC thermogram of the oligomer PY5-OC12, heating rate +10 °C min^{-1}. (b) Thermogram of the oligomer oPY-OC12, heating rate +10 °C min^{-1}, cooling rate −10 °C min^{-1}.

lyzed by differential scanning calorimetry (DSC) and polarized light optical microscopy. The most important results are listed in Table 2. The DSC thermograms for the ether substituted pentamer, PY5-OC12, and the distributed oligomer, oPY-OC12 are given in Figure 6a,b. In the case of PY3-OC12, an endothermic peak is observed at 94 °C during the heating run corresponding to an energy of 42 J/g. On cooling, the exothermic peak appears at a lower temperature (75 °C) but with a comparable energy (−42 J/g). Using polarized optical microscopy, we were able to observe that PY3-OC12 is a crystalline solid at room temperature, while at 100 °C it exhibits an isotropic phase change. These effects also occur for PY3*o*-COOC12, PY3*m*-COOC12 (melting at 46 °C, 30 J/g), and PY5-COOC10 (melting at 46 °C with an enthalpy as high as 97.4 J/g). However, the pentamer PY5-OC12 shows a very different thermogram (Figure 6a). On heating, a first transition is observed at 51 °C and a second peak at 99 °C. Using polarized light microscopy we observe a change at 51 °C from a birefringent solid to a fluid birefringent phase. An isotropic phase change is observed at 99°C. The textures observed with this technique do not reveal any specific liquid crystal phase.

In the case of the oligomer oPY-OC12 (Figure 6b), two transitions are observed. They are detected at very close temperatures on both heating and cooling, and the corresponding energy changes are very small. Using a microscope, the phase is seen to be liquid crystalline (LC) at room temperature and remains birefringent at 80 °C. oPY-COOC12 shows the same behavior. Thus, for the oligomers, there are two LC−LC transitions, which are characterized by X-ray diffraction. The LC−isotropic transition could not be observed because the sample decomposed before reaching the complete isotropic phase.

Table 3

temp for oPY-OC12, °C	small angles, Å	wide angles, Å
30	29.5	4.23
50	27.6	
80	24.5	4.43

2.3.2. X-ray Diffraction. X-ray studies were performed to obtain more detailed structural information. In the case of PY3-OC12, PY3*m*-COOC12, and PY5-COOC10 at room temperature, the diffraction pattern presents a series of fine fringes characteristic of a crystalline structure. In the case of the distributed oligomers, we observe at room temperature a broad band in the wide angle region corresponding to the alkyl chain spacing, and a thinner and more intense fringe at small angle, which corresponds to the interlamellar distance. This indicates that, for the ester derivatives, the LC properties appear for main chains longer than PY5.

Using X-ray diffraction, we also studied the evolution of the liquid crystalline properties versus temperature for the ether oligomer oPY-OC12. The relevant results of these studies are listed in Table 3. It is seen that the alkyl chain spacing increases with the temperature, while the lamellar repeat distance decreases, from 29.5 Å at 30 °C to 24.5 Å at 80 °C. Also at 80 °C, the central fringe is thinner than that observed at 30 °C, corresponding to a better ordered lamellar structure. A possible interpretation for this result is that, at 30 °C, the interlamellar spacing consists of an alkyl chain bilayer. With increasing temperature the alkyl chain becomes more mobile, resulting in a reduction of the backbone distance. This behavior has already been observed in the case of polymers having high molecular weight.

2.3.3. Nonlinear Optical Properties. The nonlinear optical measurements have been performed on thin films using degenerate four wave mixing (DFWM). The nonresonant $\chi^{(3)}$ of oligomers and polymers are reported in Table 1. The main interest of these results lies in the high values of the nonlinear susceptibility measured in the oligomers PY3 or PY5. The pentamer ether, that displays a susceptibility $\chi^{(3)} = 1.6 \times 10^{-10}$ esu, is only 3 times lower than the measured value of the corresponding polymer pPY-OC12 ($\chi^{(3)} = 4.6 \times 10^{-10}$ esu). The other interesting aspect is the high value obtained for the trimer PY3-OMe ($\chi^{(3)} = 2.5 \times 10^{-10}$ esu). In this compound the methyl substituent of phenyls induces a low dilution effect on the nonlinear susceptibility as compared to the unsaturated phenyl−ethynyl moiety. This material is also in a better ordered crystalline phase which leads to an enhanced $\chi^{(3)}$.

3. Discussion

3.1. Synthesis and Reactivity. Each of the separated fractions of oligomers was characterized by its average number of polymerization, ⟨Dpn⟩, from the number average molar mass $\langle M_n \rangle$. Both NMR and elemental analysis should be considered for $\langle M_n \rangle$ determination. No Pd traces by elemental analysis and no

terminal H on phenyl or ethynyl groups were observed by ^{1}H NMR (in particular no excess of H-phenyl relative to other H signals). The H signal of bromophenyl by NMR and the bromine percentage from elemental analysis are consistent for the molecular weight determinations of the oligomer fractions. The ⟨Dpn⟩ of each fraction, which is 3−5 times higher than in the pentamer, demonstrates that the polymerization route followed by preparative SEC, is a good alternative to the step by step route for long oligomers.

The step by step route is reported in the literature for alkyl derivatives.[23] However, this method gives low yields for alkyl ether or alkyl ester side groups on the phenyl−ethynyl protected unit. One reason is that the phenyl 1-bromo 4-triazene derivatives show poor stability in acidic conditions, such as on a silica gel column, particularly when substituted with ether side groups (**20**, yield of the step 37%). Also the purification of long side-chain oligomers is arduous. The best method for PY5-OC12 is the separation by thin layer chromatography. For PY5-COOC10 the synthesis of the triazene intermediate, 2-(3,3-diethyltriazo)-5-iododecyl benzoate (**24**), should be possible from acid unit **23**, followed by esterification. On the alkyl ester unit, the yield in triazene synthesis vanishes. The last step of the pentamer ester synthesis shows a better yield (69%) than for pentamer ether; thus the electron-attractor effect of the ester group enhances the coupling yield.

3.2. Structural Properties. By DSC thermal analysis and optical microscopy, the ether oligomers (PY5-OC12 and oPY-OC12) show LC properties. Such LC properties are characterized by a fluid birefringent phase observed by optical microscopy, and the DSC thermogram shows also a reversible transition LC ⇔ isotropic phase for oPY-OC12 near 59 °C on heating and cooling. This transition is characterized by a small enthalpy ∼0.3 J g^{-1}. The thermogram of PY5-OC12 shows a similar shape on heating, a waxy birefringent phase at 50 °C, and an isotropic phase at 100 °C. The shortest oligomers PY3-OC12 and PY3-COOC12 and the pentamer ester PY5-COOC10 show a single transition at melting from a birefringent solid phase to an isotropic liquid phase.

The X-ray diffraction confirms the thermal analysis. oPY-OC12 shows an X-ray pattern with a sharp peak at low angle and a diffuse halo at wide angle. The periodicity related to the sharp reflection is similar to the structure observed on the polymer pPY-OC12, a periodicity of 29.5 Å at 30 °C corresponding to a lamellar structure. This spacing decreases with temperature from 29.1 Å at 25 °C to 26.9 Å at 85 °C. Thus, for the polymer or oligomer ether we expected for the liquid crystalline phase an arrangement in a double layer, which is acceptable for such geometric parameters.

The pentamer ester exhibits a single endothermic transition from crystal to isotropic liquid, while the oligomer ester oPY-COOC12 and the polymer ester pPY-COOC12 show by X-ray very interesting properties. The X-ray diffraction patterns indicate clearly that the mesophase obtained at room temperature and 85 °C is a lamellar phase by the presence of a sharp reflection peak in the small angle region and a diffuse band in the wide angle region. The spacing corresponding to the sharp reflection is 25.9 Å at 25 °C and 26.4 Å at 85 °C. We expected a molecular arrangement based on a single layer of molecules with interdigited alkyl chains (see Figure 7), which could satisfy the X-ray spacings.

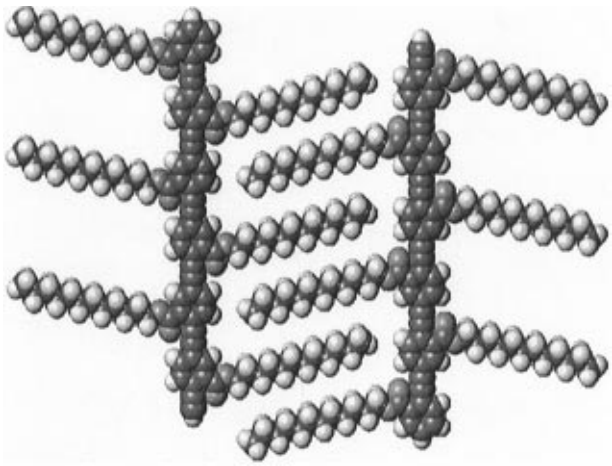

Figure 7. Molecular model of the arrangement of oPY-COOC12 oligomer deduced from X-ray diffraction.

3.3. Optical properties. The shift of the absorption peak between electron-donor and electron-acceptor side groups is observed both in model molecules and in oligomers. It is important to note that the blue shift of the absorption band between ether and ester is about the same value $\Delta\lambda \sim 40-50$ nm as that in polymers. The red shift of the absorbance maxima when the length of the oligomer occurs both in model molecules PY3 and PY5 and in distributed oligomers. The most interesting result on oligomers is that the saturation of the absorption peak shift, due to π electron delocalization, occurs at 25−30 monomer units in ether series. For pentamer ether, the absorbance maximum displays a larger red shift (418 nm) than in the oligomer fraction f_1 (400 nm for a ⟨Dpn⟩ = 13), showing the effect of the shortest molecules in the oligomer fractions. It is important to notice that, in the ester series, the saturation is already observed with the oPY-COOC12 fraction. The absorbances of the pentamer molecules indicate that the saturation in the phenyl−ethynyl chain should appear for longer chains. Unfortunately, our attempt to synthesize longer oligomers by the step by step route failed on the phenyl−ethynyl chain with electron-active side groups. Another approach in the literature[23] using a similar method has demonstrated that the multistep reaction allows one to reach the hexadecamer, on the phenyl bearing saturated grafted side chains (ethyl−heptyl). The saturation of the absorption shift appears to occur for the octamer at a value of 376 nm. This limit shows the effect of electron-donor and electron-attractor character on the wavelength shift in solution, a red shift of 49 nm for ether group, but a *red shift of 7 nm* for the ester group. This latter result confirms the great importance of charge transfers on the conjugated phenyl−ethynyl chain.

The molar absorption coefficients measured in solution depend strongly on the molecular weights of the model molecules. The absorption coefficient related to the phenyl−ethynyl repetitive units should give a better idea of the electronic absorption of a single conjugated unit. The ϵ values are very consistent in the ether series, except for the OCH_3 trimer. Its higher value shows a strong oscillator strength for this molecule. In the ester series, very high absorption coefficients are measured on the pentamer and the polymer with the trimers producing lower values. We noticed that this result occurred from the extension of the π electron system on this linear molecule. The oligomer ester, which contains an appreciable rate of very small oligomers (dimers and trimers), shows a depressed ϵ.

The nonlinear susceptibilities $\chi^{(3)}$ have been measured far from resonance (628 nm). The $\chi^{(3)}$ values (respectively 1.6×10^{-10} and 4.6×10^{-10} esu for PY5-OC12 and pPY-OC12) show that the saturation of the third order susceptibility does not occur for the pentamer. $\chi^{(3)}$ measurements on other polymers in the aryl−ethynyl series by third harmonic generation values confirm that $\chi^{(3)}$ were also obtained in the range of 10^{-10} esu.[27] The high $\chi^{(3)}$ value measured for the short oligomer PY3-OMe suggests an important effect of the donor side group on the hyperpolarizability of the conjugated molecule. This result confirms the electron-donor effect already observed on 3,8-diphenylbenzothiazol series, where the grafting of four alkyl ethers on the molecule multiplicates by 12 the molecular hyperpolarizability γ in solution.[28]

4. Conclusion

In this work we have studied the oligomer synthesis of the phenyl−ethynyl series. With the aim of searching high optical hyperpolarizabilies on soluble oligomers and polymers, we compared the properties of oligomers either produced by a step by step method or produced by random oligomerization to high molecular weight polymers. Short oligomers bearing ether or ester alkyl chains are more soluble than corresponding polymers. Their thermal properties show liquid crystalline phases, which are also very interesting for oriented materials in optoelectronic applications. The side group effects, of electron-donor or -acceptor character, induced respectively by ether and ester substituents on the phenyl rings, lead to a red shift of the peak maximum of the absorbance. Step by step synthesized oligomers clearly show a higher conjugation than the corresponding oligomers produced by random oligomerization. These results are well-correlated with the high values of third order susceptibility obtained on trimers and pentamers. The trimer ether shows $\chi^{(3)}$ value 2.5×10^{-10} esu, only half the value of the polymers having higher molecular weight. Therefore, we guess that the optimum of $\chi^{(3)}$ for the phenyl−ethynyl series should occur for long oligomers having short side chains. New attempts to ensure better condensation yield and successive protection−deprotection steps could lead to the formation of linear oligomers with electron-active side group longer than PY5.

5. Experimental Section

5.1. General Procedures. The following chemical reactives, 1-bromo-2,5-dimethoxybenzene, hydroquinone, 1,4-dibromo-2,5-dimethoxybenzene, 1-bromododecane, 3-bromobenzoic acid, 2-bromobenzoic acid, 2,5-dibromobenzoic acid, 2-amino-5-iodobenzoic acid, decanol, dodecanol, dicyclohexylcarbodiimide (DCC), (dimethylamino)pyridine (DMAP), trimethylsilylacetylene (TMSA), palladium chloride ($PdCl_2$), triphenylphosphine (TPP), tetrabutylamonium fluoride (1.1 M in THF, TBAF), copper(II) acetate ($CuOAc_2$), iodine, aluminum powder, and dichloromethane HPLC grade were obtained from Aldrich. The triethylamine, dimethylformamide, and carbon tetrachloride were obtained from Merck. The acetonitrile and tetrahydrofuran, HiPerSolv grade for HPLC, were obtained from BDH. All the chemical materials were used without further purification.

5.1.1. Synthesis of 1-Bromo-2,5-hydroquinone (1). To a two necked flask cooled at 10 °C were added aluminum powder (1.342 g, 50 mmol) and iodine (9.518 g, 75 mmol) in 50 mL of dry acetonitrile. The mixture was slowly warmed to reflux with vigorous stirring until the violet color of iodide disappeared (30 min). To the freshly prepared 1 M solution of AlI_3 (50 mmol, 50 mL), 1-bromo-2,5-dimethoxybenzene (4.34 g, 20 mmol) in 50 mL of acetonitrile was added. The mixture was refluxed for 24 h. The cooled reaction mixture was poured in 100 mL of 0.5 M HCl solution and extracted with ether. The ether fraction was then extracted with 5% aqueous sodium hydroxide solution. The aqueous fraction was acidified with concentrated HCl and then extracted with ether. The combined ether layer were dried over Na_2SO_4, the solvent was removed, and the product was chromatographed through a silica gel column using heptane/CH_2Cl_2, 1/1 as an eluent, to give 3.32 g of 1-bromo-2,5-hydroquinone (**1**); yield 78%, mp 115−117 °C. ^{1}H NMR ($CDCl_3$): δ 8.1 (s, 2H, −OH), 6.97 (d, 1H, −PhH), 6.85 (d, 1H, −PhH), 6.65 (dd, 1H, −PhH). Anal. Calcd for $C_6H_5O_2Br$: C, 38.09; H, 2.64; O, 16.93. Found: C, 38.22; H, 2.53; O, 17.02.

5.1.2. Synthesis of 1,4-Bis(dodecanoxy)benzene (2). To a solution of hydroquinone (11 g, 100 mmol) in 30 mL of dimethylformamide were added sodium hydroxyde (10 g, 250 mmol) and 1-bromododecane (52.34 g, 210 mmol). The mixture was then stirred and heated at 120 °C for 14 h, cooled, and poured into cold water. The precipitate was collected by filtration and stirred with 300 mL of warm (60 °C) ethanol for 30 min. The mixture was cooled and filtered. The precipitate was washed with cold ethanol and dried in vacuo to obtain 40.6 g pure product, yield 91%, mp 77 °C. ^{1}H NMR ($CDCl_3$): δ 6.83 (s, 4H, −PhH), 3.91 (t, 4H, $-OCH_2-$), 1.72 (q, 4H, $-CH_2-$ β ether), 1.28 (36H, $-CH_2-$), 0.89 (t, 6H, $-CH_3$). Anal. Calcd for $C_{30}H_{54}O_2$: C, 59.60; H, 8.60; O, 5.29; Found: C, 59.70, H, 8.33, O, 5.57.

5.1.3. Synthesis of 1-Bromo-2,5-bis(dodecanoxy)benzene (3). The procedure above was followed with 1-bromo-2,5-hydoquinone (**1**) (5.17 g, 27 mmol) in 20 mL of dimethylformamide, sodium hydroxyde (2.73 g, 68 mmol), and 1-bromododecane (14.99 g, 60 mmol). The crude material was purified by silica gel chromatography using heptane/CH_2Cl_2, 2/1 as eluent, to give 10.31 g of 1-bromo-2,5-didodecanoxybenzene (**3**); yield 78%, mp 51 °C. ^{1}H NMR ($CDCl_3$): δ 7.15 (d, 1H, −PhH), 7 (d, 1H, −PhH), 6.9 (dd, 1H, −PhH), 4 and 3.9 (dt, 4H, $-OCH_2-$), 1.75 (q, 4H, $-CH_2-$ β ether), 1.3 (36 H, $-CH_2-$), 0.85 (t, 6H, $-CH_3$). Anal. Calcd for $C_{30}H_{53}O_2Br$: C, 68.57; H, 10.09; O, 6.09. Found: C, 68.32; H, 10.04; O, 6.40.

5.1.4. Synthesis of 1,4-Dibromo-2,5-bis(dodecanoxy)-benzene (4). 1,4-Bis(dodecanoxy)benzene **(2)** (4.6 g, 10 mmol) and bromine (3.19 g, 1.05 mL, 20 mmol) were heated to reflux in 300 mL of carbon tetrachloride for 6 h. The solvent was removed, and the crude product was purified by chromatography (SiO_2, heptane/CH_2Cl_2, 4/1) to obtain 5.04 g product; yield 81%, mp 80 °C. ^{1}H NMR ($CDCl_3$): δ 7.11 (d, 1H, −PhH), 6.82 (m, 2H, −PhH), 3.96 (t, 2H, $-OCH_2-$), 3.89 (t, 2H, $-OCH_2-$), 1.78 (m, 4H, $-CH_2-$ β ether), 1.27 (36H, $-CH_2-$), 0.89 (t, 6H, $-CH_3$). Anal. Calcd for $C_{30}H_{52}O_2Br_2$: C, 59.60; H, 8.60; O, 5.29. Found: C, 59.70, H, 8.33, O, 5.57.

5.1.5. Synthesis of 3-Bromo Dodecyl Benzoate (5). To an ice-cooled mixture of 3-bromobenzoic acid (2.01 g, 10 mmol), dodecanol (1.863 g, 10 mmol), and DMAP (100 mg, 0.8 mmol) in 50 mL of CH_2Cl_2 was added dropwise a solution of DCC (3.094 g in 5 mL CH_2Cl_2, 15 mmol). The mixture was stirred at room temperature for 24 h. Precipitated urea was then filtered off. The filtrate was washed twice with 0.5 N HCl and saturated $NaHCO_3$ solution and then dried over Na_2SO_4. The solvent was evaporated, and the crude product was passed through a silica gel column using heptane/CH_2Cl_2, 1/1 as an eluent, to give 3.58 g of dodecyl 3-bromobenzoate (**2C**) (liquid); yield 97%. ^{1}H NMR ($CDCl_3$): δ 8.16 (t, 1H, −PhH), 7.98 and 7.94 (dt, 1H, −PhH), 7.65 (m, 1H, −PhH), 7.3 (t, 1H, −PhH), 4.3 (t, 2H, $-COOCH_2-$), 1.76 (q, 2H, $-CH_2-$ β ester), 1.26 (18H, $-CH_2-$), 0.9 (t, 6H, $-CH_3$). Anal. Calcd for $C_{19}H_{29}O_2Br$: C, 61.78; H, 7.86; O, 8.67. Found: C, 62.00; H, 8.11; O, 8.56.

5.1.6. Synthesis of 2-Dodecyl 2-Bromobenzoate (6A). The procedure above was followed with exactly the same quantities of chemicals using 2-bromobenzoic acid, to give 3.13 g of 2-bromo dodecyl benzoate **(6A)** (liquid); yield 85%. ^{1}H NMR ($CDCl_3$): δ 7.75 (m, 2H, −PhH), 7.65 (m, 2H, −PhH), 4.35 (t, 2H, $-COOCH_2-$), 1.8 (q, 2H, $-CH_2-$ β ester), 1.3 (18H, $-CH_2-$), 0.9 (t, 6H, $-CH_3$). Anal. Calcd for $C_{19}H_{28}O_2Br_2$: C, 61.78; H, 7.86; O, 8.67. Found: C, 61.81; H, 7.89; O, 8.30.

5.1.7. Synthesis of Decyl 2-Bromobenzoate (6B). The procedure above was followed using 6.2 g of 2-bromobenzoic acid, 4,01 g of decanol, 6.19 g of DCC, and 100 mg of DMAP to give 9.41 g of decyl 2-bromobenzoate **(6B)** (liquid); yield 97%. ^{1}H NMR ($CDCl_3$): δ 7.99 (dd, 1H, −PhH), 7.79 (dd, 1H, −PhH), 7.41 (td, 1H, −PhH), 7,15 (td, 1H, −PhH), 4.34 (t, 2H, $-COOCH_2-$), 1.72 (q, 2H, $-CH_2-$ β ester), 1.27 (14H, $-CH_2-$), 0.89 (t, 3H, $-CH_3$).

5.1.8. Synthesis of Dodecyl 2,5-Dibromobenzoate (7). The procedure used to obtain **5** was followed with 2,5-dibromobenzoic acid (2.8 g, 10 mmol), 1.863 g of dodecanol, 100 mg of DMAP, and 3.094 g of DCC to give 4.2 g of 2,5-dibromo dodecyl benzoate (**7**); yield 95%, mp 37−38 °C. ^{1}H NMR ($CDCl_3$): δ 7.9 (d, 1H, −PhH), 7.5 (d, 1H, −PhH), 7.43 (dd, 1H, −PhH), 4.35 (t, 2H, $-COOCH_2-$), 1.8 (q, 2H, $-CH_2-$ β ester), 1.3 (18H, $-CH_2-$), 0.9 (t, 3H, $-CH_3$). Anal. Calcd for $C_{19}H_{28}O_2Br_2$: C, 50.89; H, 6.25; O, 7.14. Found: C, 51.53; H, 6.16; O, 6.53.

5.1.9. Synthesis of 1-Ethynyl-2.5-bis(dodecanoxy)benzene (9). A deaerated solution of 1-bromo-2,5-bis(dodecanoxy)benzene (**3**) (1.575 g, 3 mmol), TPP (118 mg, 0.45 mmol), $PdCl_2$ (26.5 mg, 0.15 mmol), and $CuOAc_2$ (30 mg, 0.15 mmol) in 60 mL of anhydrous triethylamine was treated with TMSA (0.8 mL, 5.1 mmol). The mixture was heated at reflux for 24 h. After cooling, the precipitated triethylamine hydrobromide was filtered, and the solvent was evaporated. The crude material was purified on a silica gel column using heptane/CH_2Cl_2, 2/1 as an eluent, to give the silylated intermediate **8**. *Deprotection*: Compound **8** was dissolved in 20 mL of THF and TBAF (1.5 mL, 1.5 mmol) was slowly added, leading to a black solution. After 5 min, the reaction was filtered through a plug of silica gel. The solvent was evaporated, and the crude product was chromatographed through a silica gel column using heptane/CH_2Cl_2, 2/1 as an eluent, to give 1.27 g of 1-ethynyl-2,5-bis(dodecanoxy)benzene) (**9**); yield 90%, mp 48−49 °C. ^{1}H NMR ($CDCl_3$): δ 7.05 (dd, 1H, −PhH), 6.8 (m, 2H, −PhH), 4.05 et 3.95 (dt, 4H, $-OCH_2-$), 3.7 (s, 1H, −C≡CH), 1.75 (q, 4H, $-CH_2-$ β ether), 1.3 (36H, $-CH_2-$), 0.85 (t, 6H, $-CH_3$). Anal. Calcd for $C_{32}H_{54}O_2$: C, 82.76; H, 11.49; O, 6.8. Found: C, 82.04; H, 10.62; O, 6.3.

5.1.10. Synthesis of 1,4-Diethynyl-2,5-bis(dodecanoxy)benzene (11). The procedure above was followed with 1.812 g of 1,4-dibromo-2,5-bis(dodecanoxy)benzene (**4**), 53 mg of $PdCl_2$, 60 mg of $CuOAc_2$, 262 mg of TPP, and 1.5 mL of TMSA to give the silylated intermediate **10.** Compound **10** was deprotected with 3 mL of TBAF to give 1.047 g of 1,4-diethynyl-2,5 bis(dodecanoxy)benzene (**11**); yield 70%, mp 74 °C. ^{1}H NMR ($CDCl_3$): δ 6.95 (s, 2H, −PhH), 3.95 (t, 4H, $-OCH_2-$), 3.34 (s, 2H, −C≡CH), 1.8 (q, 4H, $-CH_2-$ β ether), 1.3 (36H, $-CH_2-$), 0.9 (t, 6H, $-CH_3$). Anal. Calcd for $C_{34}H_{54}O_2$: C, 82.59; H, 10.53; O, 6.47. Found: C, 82.01; H, 10.93; O, 6.61.

5.1.11. Synthesis of Dodecyl 3-Ethynylbenzoate (13). The procedure used to obtain **9** was followed with 1.07 g of dodecyl 3-bromobenzoate (**5**), 118 mg of TPP, 26.5 mg of $PdCl_2$, 30 mg of $CuOAc_2$, and 0.8 mL of TMSA to give the silylated intermediate **12**. Compound **12** was deprotected with 0.5 mL of TBAF to give 0.894 g of dodecyl 3-ethynylbenzoate (**13**); yield 95%. ^{1}H NMR ($CDCl_3$): δ 8.2 (s, 1H, −PhH), 8 (d, 1 H, −PhH), 7.65 (d, 1 H, −PhH), 7.37 (t, 1 H, −PhH), 4.3 (t, 2H, $-COOCH_2-$), 3.1 (s, 1H, −C≡CH), 1.76 (q, 2H, $-CH_2-$ β ester), 1.26 (18H, $-CH_2-$), 0.9 (t, 3H, $-CH_3$). Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.25; H, 9.55; O, 10.19. Found: C, 79.12; H, 9.69; O, 9.96.

5.1.12. Synthesis of Dodecyl 2-Ethynylbenzoate (15A). The procedure above was exactly followed with the same quantities of chemicals used for **6A**, to give 0.847 g of dodecyl 2-ethynylbenzoate (**15A**); yield 90%. ^{1}H NMR ($CDCl_3$): δ 7.93 (dd, 1 H, −PhH), 7. (dd, 1 H, −PhH), 7.45 (m, 1H, −PhH), 4.35 (t, 2H, $-COOCH_2-$), 3.4 (s, 1H, −C≡CH), 1.8 (q, 2H, $-CH_2-$ β ester), 1.3 (18H, $-CH_2-$), 0.9 (t, 3H, $-CH_3$). Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.25; H, 9.55; O, 10.19. Found: C, 79.00; H, 9.54; O, 10.38.

5.1.13. Synthesis of Decyl 2-Ethynylbenzoate (15B). The procedure above was followed using 5.05 g of **6B**, 2.8 mL of TMSA, 53 mg of $PdCl_2$, 60 mg of $CuOAc_2$, 265 mg of TPP, 30 mL of triethylamine, and 2.5 mL of TBAF to give 1.04 g of decyl 2-ethynylbenzoate (**15B**); yield 36%. ^{1}H NMR ($CDCl_3$): δ 7.96 (dd, 1H, −PhH), 7.62 (dd, 1H, −PhH), 7.41 (m, 2H, −PhH), 4.43 (t, 2H, $-COOCH_2-$), 3.39 (s, 1H, −C≡CH), 1.75 (q, 2H, $-CH_2-$ β ester), 1.29 (14H, $-CH_2-$), 0.89 (t, 3H, $-CH_3$).

5.1.14. Synthesis of Dodecyl 2,5-Diethynylbenzoate (17). The procedure used to obtain **9** was followed with 1.344 g of dodecyl 2,5-dibromobenzoate (**7**), 262 mg of TPP, 60 mg of $CuOAc_2$, 53 mg of $PdCl_2$, and 1.5 mL of TMSA to give the silylated intermediate **16**. Compound **16** was deprotected with 3 mL of TBAF to give 0.678 g of dodecyl 2,5-diethynylbenzoate; yield 67%. ^{1}H NMR ($CDCl_3$): δ 8 (s, 1H, −PhH), 7.56 (d, 2H, −PhH), 4.35 (t, 2H, $-COOCH_2-$), 3.5 (s, 1H, −C≡CH), 3.2 (s, 1H, −C≡CH), 1.75 (q, 2H, $-CH_2-$ β ester), 1.3 (18H, $-CH_2-$), 0.9 (t, 3H, $-CH_3$).

5.1.15. Trimer 2,5-Bis(dodecanoxy)phenylethyne (PY3-OC12). The procedure used to obtain **9** was followed with 3.02 g of 1,4-dibromo-2,5 bis(dodecanoxy)benzene (**4**), 4.7 g of 1-ethynyl-2,5-bis(dodecanoxy)benzene (**9**), 89 mg of $PdCl_2$, 100 mg of $CuOAc_2$, and 393 mg of TPP to give 5.2 g of yellow crude crystals (dimer + trimer). A 100 mg amount of trimer PY3-OC12 was isolated by HPLC using heptane/CH_2Cl_2, 7/3 as an eluent (retention time, 13 min); mp 92 °C. ^{1}H NMR ($CDCl_3$): δ 7.03 (2H, −PhH), 7 (2H, −PhH), 6.8 (4H, −PhH), 4 (t, 8H, $-OCH_2-$), 3.9 (t, 4H, $-OCH_2-$), 1.8 (q, 12H, $-CH_2-$ β ether), 1.27 (54H, $-CH_2-$), 0.9 (t, 18H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ 153−152 (3p, −OPh−), 118−113 (5p, −Ph−), 91.4−89.8 (4p, −C≡C−), 69.9−67.9 (4p, $-OCH_2-$), 31.9−26 (5p, $-CH_2-$), 22.7 (1p, $-CH_2CH_3$), 14 (1p, $-CH_3$). Anal. Calcd for $C_{94}H_{158}O_6$: C, 81.62; H, 11.43; O, 6,94. Found: C, 80.33; H, 11.55; O, 7.21.

5.1.16. Trimer 2,5-Methoxyphenylethyne (PY3-OCH3). The procedure used to obtain **9** was followed with 1,4-diethynyl-2,5-bis(methoxy)benzene (2 g, 10.7 mmol), 1-bromo-2,5-bis(methoxy)benzene (5.6 g, 25 mmol), $PdCl_2$ (114 mg, 0.65 mmol), $CuOAc_2$ (128 mg, 0.65 mmol), and TPP (844 mg, 0.32 mmol). The crude material was purified on a silica gel column using heptane/CH_2Cl_2, 1/1 as an eluent, to give 3.9 g of PY3-OCH3; yield 79%. ^{1}H NMR ($CDCl_3$): δ 7.13 and 6.85 (m, 8H, −PhH), 3.9 and 3.8 (s, 18H, $-OCH_3$). ^{13}C NMR ($CDCl_3$): δ 155.3 and 153.8 (3p, −OPh−), 112−119 (4p, −Ph−), 91.4 and 89.8 (2p, −C≡C−), 56.32 and 56.44 (2p, $-OCH_3$). Anal. Calcd for $C_{28}H_{26}O_6$: C, 73.36; H, 5.67; O, 20.96. Found: C, 72.85; H, 5.55; O, 20.89.

5.1.17. Ortho Trimer Dodecyl Benzoate (PY3*o*-COOC12). The procedure used to obtain **9** was followed with 2.24 g of 12,5-dibromo dodecyl benzoate **(7)**, 3.14 g of 2-ethynyl dodecyl benzoate **(15A)**, 393 mg of TPP, 89 mg of $PdCl_2$, and 100 mg of $CuOAc_2$ to give 4.52 g of yellow crude crystals (dimer + trimer). A 100 mg amount of trimer PY3*o*-COOC12 was isolated by HPLC using heptane/CH_2Cl_2, 1/1 as an eluent (retention time, 28 min); mp 25−30 °C. ^{1}H NMR ($CDCl_3$): δ 7.5 (m, 8H, −PhH); 4.35 (t, 6H, $-COOCH_2-$), 1.8 (q, 6H, $-CH_2-$ β ester), 1.3 (27H, $-CH_2-$), 0.9 (t, 9H, $-CH_3$).^{13}C NMR ($CDCl_3$): δ 166−165.5 (2p, −COO−), 134.26−123.1 (18p, −Ph−), 95.12−90.6 (4p, −C≡C−), 65.66−65.5 (3p, $-OCH_2-$), 31.9−26 (6p, $-CH_2-$), 22.6 (1p, $-CH_2CH_3$), 14.12 (1p, $-CH_3$). Anal. Calcd for $C_{61}H_{86}O_6$: C, 80.08; H, 9.4; O, 10.03; Found: C, 79.00; H, 9.5; O, 10.4.

5.1.18. Meta Trimer Dodecyl Benzoate (PY3*m*-COOC12). The procedure above was exactly followed with the same quantities of chemicals using **7** and **13** to give 4.63 g of yellow crude crystals (dimer + trimer). A 100 mg amount of the trimer PY3*m*-COOC12 was isolated by HPLC using heptane/CH_2Cl_2, 91/9 as an eluant (retention time, 21 min); mp 48−50 °C. ^{1}H NMR ($CDCl_3$): δ 8.1 (2H, −PhH), 7.7 (4H, −PhH), 7.46 (2H, −PhH), 4.39 (t, 3H, $-COOCH_2-$), 4.35 (t, 3H, $-COOCH_2-$), 1.8 (q, 6H, $-CH_2-$ β ester), 1.3 (27H, $-CH_2-$), 0.9 (t, 9H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ 165.5−165.9 (2p, −COO−), 122.94−135.76 (2p, −Ph−), 88.9−95 (3p, −C≡C−), 65.5−65.8 (2p, $-OCH_2-$), 26−31.9 (5p, $-CH_2-$), 22.67 (1p, $-CH_2CH_3$), 14.11 (1p, $-CH_3$). Anal. Calcd for $C_{61}H_{86}O_6$: C, 80.08; H, 9.40; O, 10.03. Found: C, 79.00; H, 9.52; O, 10.47.

5.2. Oligomerizations. 5.2.1. Electron-Donor Derivatives (oPY-OC12). A deaerated solution of 1,4-dibromo-2,5-bis(dodecanoxy)benzene (**4**) (1.208 g, 2 mmol), 1,4-diethynyl-2,5-bis(dodecanoxy)benzene (**11**) (0.95 g, 1.94 mmol), $PdCl_2$

(34.5 mg, 0.2 mmol), $CuOAc_2$ (40 mg, 0.2 mmol), and TPP (157.2 mg, 0.6 mmol) in 60 mL triethylamine was heated at reflux under argon for 6 h. After cooling, the mixture was filtered through silica gel and the triethylamine evaporated. The crude product was precipitated in methanol and centrifugated to give the ether substituted oligomers (oPY-OC12). These oligomers were fractionated by SEC to obtain oligomers of different lengths. ^{1}H NMR ($CDCl_3$): δ 7.13 (s, 2H, −PhBr terminal), 7.0 (s, 2H, −PhH), 4.0 (t, 4H, $-OCH_2-$), 1.8 (q, 4H, $-CH_2-$ β ether), 1.27 (36H, $-CH_2-$), 0.9 (t, 6H, $-CH_3$). Anal. Found: for f_1, C, 80.10; H, 11.20; O, 6.57; Br, 2.30. For f_2, C, 80.89 H, 10.91; O, 6.60; Br, 1.73. For f_3, C, 81.12; H, 10.88; O, 6.78; Br, 1.22.

5.2.2. Electron-Acceptor Derivatives (oPY-COO12). A deaerated solution of dodecyl 2,5-dibromobenzoate (**7**) (0.946 g, 2 mmol), dodecyl 2,5-diethynylbenzoate (**17**) (0.69 g, 1.9 mmol), $PdCl_2$ (35.3 mg, 0.2 mmol), $CuOAc_2$ (40 mg, 0.2 mmol), and TPP (156.7 mg, 0.6 mmol) in 60 mL of triethylamine was heated at reflux under argon for 3 h. After cooling, the mixture was filtered through silica gel and the triethylamine evaporated. The crude product was precipitated in methanol and centrifugated to give the ester substituted oligomers (oPY-COO12). ^{1}H NMR ($CDCl_3$): δ 8.1 (s, 1H, −PhH), 7.15 (s, 2H, −PhH), 4.32 (t, 2H, $-OCH_2-$), 1.9 (q, 2H, $-CH_2-$ β ester), 1.25 (s, 18H, $-CH_2-$), 0.9 (t, 3H, $-CH_3$). Anal. Found: C, 79.53; H, 8.60; O, 10.10; Br, 1.79.

5.2.3. 1-Bromo-2,5-bis(dodecanoxy)-4-nitrobenzene (18). Finely powdered 1-bromo-2,5-bis(dodecanoxy)benzene (**3**) (25,3 g, 48 mmol) was slowly added to a cold solution of concentated sulfuric acid (50 mL) and 65% nitric acid in water (50 mL) immersed in an ice/salt bath. The freezed mixture was stirred for 2 h. A 300 g amount of crushed ice was then added, followed by 300 mL of cold water. The precipitate was collected by filtration, and the derivative was purified by chromatography (SiO_2, CH_2Cl_2/heptane, 1/5) to obtain 17.31 g of pure product; yield 63%, mp 67 °C. ^{1}H NMR ($CDCl_3$): δ 7.41 (s, 1H, −PhH), 7.31 (s, 1H, −PhH), 4.03 (m, 4H, $-OCH_2-$), 1.78 (m, 4H, $-CH_2-$ β ether), 1.28 (36 H, $-CH_2-$), 0.88 (t, 6H, $-CH_3$). Anal. Calcd for $C_{30}H_{25}NO_4Br$: C, 63.14; H, 9.18; N, 2.45. Found: C, 63.16; H, 9.29; N, 2.27.

5.2.4. 4-Bromo-2,5-bis(dodecanoxy)aniline (19). To a stirred mixture of 1-bromo-2,5-bis(dodecanoxy)-4-nitrobenzene (**18**) (17.1 g, 30 mmol) in 60 mL of tetrahydrofuran and 30 mL of concentrated hydrochloric acid was slowly added tin powder (14.24 g, 120 mmol). The mixture was left for 14 h under stirring. Most of the solvent was evaporated (about 20 mL of liquid remaining). A 100 mL aliquot of water and 100 mL of dichloromethane were added, and the stirred mixture was neutralized with potassium carbonate. Tin salts were filtered off on celite. The organic phase was dried over Na_2SO_4, and the solvent was removed. The crude product was purified by chromatography (SiO_2, CH_2Cl_2/heptane, 1/2) to obtain 10.22 g of pure productl yield 63%. ^{1}H NMR ($CDCl_3$): δ 6.92 (s, 1H, −PhH), 6.37 (s, 1H, −PhH), 3.91 (t, 4H, $-OCH_2-$), 3.88 (br s, 2H, $-NH_2-$), 1.78 (m, 4H, $-CH_2-$ β ether), 1.27 (36 H, $-CH_2-$), 0.89 (t, 6H, $-CH_3$). Anal. Calcd for $C_{30}H_{54}NO_2Br$: C, 49.55; H, 6.47. Found: C, 49.83, H, 6.33.

5.2.5. 1-[4-Bromo-2,5-bis(dodecanoxy)phenyl]-3,3-diethyltriazene (20). 4-Bromo-2,5-bis(dodecanoxy)aniline **(19)** (4.5 g, 8.3 mmol), 10 mL of tetrahydrofuran, 2.1 mL of hydrochloric acid, and 5 mL of water were charged and stirred in a vessel freezed with an ice/salt bath. A cold solution of sodium nitrite (0.86 g, 12.5 mmol) in 5 mL was slowly added. The mixture was stirred for 30 min, keeping the temperature under 0 °C. The diazonium solution was then slowly added to a freezed mixture of potassium carbonate (1.72 g, 12.5 mmol), and diethylamine (0.914 g, 1.29 mL, 12.5 mmol) in 20 mL of water and stirred for 30 min, while the temperature was allowed to increase to room temperature. The mixture was extracted with ether. The organic fraction was washed with water, dried over Na_2SO_4, and evaporated. The crude material was purified by silica gel chromatography using heptane/CH_2Cl_2, 5/1 as eluent, to give 1.91 g of pure triazene; yield 37%. ^{1}H NMR ($CDCl_3$): δ 7.13 (s, 1H, −PhH), 6.97 (s, 1H, −PhH), 4.00 (t, 2H, $-OCH_2-$), 3.96 (t, 2H, $-OCH_2-$), 3.78 (qu, 4H, $-NCH_2-$), 1.78 (m, 4H, $-CH_2-$ β ether), 1.27 (42 H, 18 CH_2, 2 $-CH_3$), 0.89 (t, 6H, $-CH_3$). Anal. Calcd for $C_{34}H_{62}N_3O_3Br$: C, 49.55; H, 6.47. Found: C, 49.83, H, 6.33.

5.2.6. 1-[2,5-Bis(dodecanoxy)phenyl]-2-[2,5-bis(dodecanoxy)-4-(3,3-diethyltriazo)phenyl]ethyne (21). The procedure used to obtain **9** was followed with 1-ethynyl-2,5-bis(dodecanoxy)benzene **(9)** (1.2 g, 2.5 mmol), triazene **(20)** (1.56 g, 2.06 mmol), TPP (131 mg, 0.5 mmol), $PdCl_2$ (18 mg, 0.1 mmol), and $CuOAc_2$ (20 mg, 0.1 mmol). The crude product was chromatographed through a silica gel column using heptane/CH_2Cl_2, 3/1 as an eluent, to give 0.7 g of pure product; yield 36%. ^{1}H NMR ($CDCl_3$): δ 7.08 (s, 1H, −PhH), 7.03 (s, 1H, −PhH), 6.96 (s, 1H, −PhH), 6.81 (s, 2H, −PhH), 4.01 (m, 8H, $-OCH_2-$), 3.80 (qu, 4H, $-NCH_2-$), 1.80 (m, 8H, $-CH_2-$ β ether), 1.27 (78 H, 36 $-CH_2-$), 0.89 (t, 12H, $-CH_3$).

5.2.7. 1-[2,5-Bis(dodecanoxy)phenyl]-2-[2,5-bis(dodecanoxy)-4-iodophenyl]ethyne (22). The triazene **21** (0.69 g, 0.68 mmol) was charged in a vessel with sodium iodide (0.15 g, 1 mmol), trimethylchlorosilane (0.11 g, 0.12 mL, 1 mmol), 10 mL of tetrahydrofuran, and 20 mL of acetonitrile. The mixture was stirred and warmed to reflux for 30 min. The mixture was poured in 200 mL of water and extracted with dichloromethane. The organic phase was dried, and the solvent was removed. The crude material was purified by silica gel chromatography using heptane/CH_2Cl_2, 3/1 as eluent, to give 0.39 g of pure product; yield 55%. ^{1}H NMR ($CDCl_3$): δ 7.06 (d, 1H, −PhH), 6.96 (s, 1H, −PhH), 6.89 (m, 3H, −PhH), 4.01 (m, 8H, $-OCH_2-$), 1.80 (m, 8H, $-CH_2-$ β ether), 1.27 (72 H, 36 $-CH_2$), 0.89 (t, 12H, $-CH_3$).

5.2.8. Pentamer 2,5-Bis(dodecanoxy)phenylethyne (PY5-OC12). The procedure used to obtain **9** was followed with the iodotolane **(22)** (0.38 g, 0.36 mmol), 1.4-diethynyl-2.5-bis(dodecanoxy)benzene **(11)** (0.1 g, 0.2 mmol), TPP (79 mg, 0.3 mmol), palladium chloride (11 mg, 0.06 mmol), and $CuOAc_2$ (12 mg, 0.06 mmol). A 30 mL aliquot of tetrahydrofuran was added. The mixture was warmed and stirred for 48 h. The crude product was purified by preparative thin layer chromatography, using heptane/CH_2Cl_2, 3/1 as an eluent, to give 0.09 g of pure pentamer; yield 36%. ^{1}H NMR ($CDCl_3$): δ 7.06 (d, 2H, −PhH), 6.97 (m, 10H, −PhH), 3.98 (br t, 20H, $-OCH_2-$), 1.80 (m, 20H, $-CH_2-$ β ether), 1.27 (180 H, 90 $-CH_2-$), 0.89 (t, 30H, $-CH_3$). Anal. Calcd for $C_{158}H_{262}O_{10}$: C, 81.73, H, 11.37. Found: C, 82.91, H, 11.43. MW. Calcd: 2322 g/mol. Found (tonometry, CH_2Cl_2, 25 °C): 2275 g/mol.

5.2.9. 2-(3,3-Diethyltriazo)-5-iodobenzoic Acid (23). The procedure to obtain **20** was followed with 2-amino-5-iodobenzoic acid (2.63 g, 10.00 mmol), hydrochloric acid (3 mL), water (3 mL), $NaNO_2$ (0.75 g , 11 mL in 2.5 mL of water), K_2CO_3 (2.07 g, 15 mmol), and NEt_2 (1.13 g, 1.55 mL, 15 mmol in 20 mL of water). The crude product was chromatographed through a silica gel column using CH_2Cl_2 to give 1.89 g of pure product; yield 54%. ^{1}H NMR ($CDCl_3$): δ 13.80 (s, 1H, −COOH), 8.57 (d, 1H, −PhH), 7.78 (dd, 1H, −PhH), 7.46 (d, 1H, −PhH), 3.93 (qu, 2H, $-NCH_2-$), 3.79 (qu, 2H, $-NCH_2-$), 1.44 (t, 3H, $-CH_3$), 1.33 (t, 3H, $-CH_3$).

5.2.10. (3,3-Diethyltriazo)-5-iododecyl benzoate (24). The procedure used to obtain **5** was followed with triazoiodobenzoic acid **(23)** (1.89 g, 5.44 mmol), decanol (0.87 g, 5.5 mmol), DCC (1.13 g, 5.48 mmol), and DMAP (100 mg, 0.8 mmol). The crude product was chromatographed through a silica gel column using CH_2Cl_2/heptane, 3/7, to give 2.55 g of the ester (**24**); yield 84%. ^{1}H NMR ($CDCl_3$): δ 7.88 (d, 1H, −PhH), 7.67 (dd, 1H, −PhH), 7.18 (d, 1H, −Ph−), 4.25 (t, 2H, $-COOCH_2-$), 3.75 (m, 4H, $-NCH_2-$), 1.72 (q, 2H, $-CH_2-$ β ester), 1.27 (s, 20H, $-CH_3$ β amine and $-CH_2-$), 0.89 (t, 3H, $-CH_3$).

5.2.11. 2-(3,3-Diethyltriazo)-5-ethynyldecyl benzoate (26). The procedure used to obtain **9** was followed with **24** (2.2 g, 4.5 mmol), TPP (59 mg, 0.23 mmol), $PdCl_2$ (8 mg, 0.045 mmol), $CuOAc_2$ (9 mg, 0.045 mmol), and TMSA (1.2 mL, 8.55 mmol) to give the silylated intermediate **25.** Compound **25** was deprotected with 1 mL of TBAF to give 1.03 g of **26; y**ield 72%. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, 1H, −PhH), 7.48 (dd, 1H, −PhH), 7.39 (d, 1H, −PhH), 4.27 (t, 2H, $-COOCH_2-$), 3.77 (qu, 4H, $-NCH_2-$), 1.73 (q, 8H, $-CH_2-$ β ester), 1.27 (s, 20H, $-CH_3$ β amine and $-CH_2-$), 0.89 (t, 3H, $-CH_3$). Anal. Calcd

for $C_{23}H_{35}N_3O_2$: C, 71.65; H, 9.15; N, 10.9. Found: C, 71.34; H, 9.26; N, 11.31.

5.2.12. Trimer 4,4′-Bis(diethyltriazo)[(decyl benzoate)-ethyne] (27). The procedure used to obtain **9** was followed with **26** (3.25g, 8.42 mmol), **6B** (1.544 g, 3.66 mmol), $PdCl_2$ (18 mg, 0.14 mmol), $CuOAc_2$ (20 mg, 0.1 mmol), and TPP (131 mg, 0.5 mmol). The crude product was chromatographed through a silica gel column using CH_2Cl_2/heptane, 2/1, to give 2.43 g of trimer **27; y**ield 64%. ^{1}H NMR ($CDCl_3$): δ 8.12 (d, 1H, −PhH), 7.78 (m, 2H, −PhH), 7.61 (s, 2H, −PhH), 7.56 (m, 2H, −PhH), 7.45 (d, 2H, −PhH), 4.38 (t, 2H, $-COOCH_2-$), 4.29 (t, 2H, $-COOCH_2-$), 4.28 (t, 2H, $-COOCH_2-$), 3.79 (qu, 8H, $-NCH_2-$), 1.75 (m, 6H, $-CH_2-$ β ester), 1.27 (m, 54H, $-CH_3$ β amine and $-CH_2-$), 0.89 (t, 9H, $-CH_3$).

5.2.13. Trimer 4,4′-iodo[(decyl benzoate)ethyne] (28). The ditriazo trimer (**7**)(2,41 g, 2.34 mmol) was taken up in freshly distilled methyl iodide (5 mL). The solution was degassed and placed under nitrogen head space, and the tube, sealed. After heating for 24 h at 115 °C, the reaction mixture was poured into 25 mL of hexane. The precipitate was filtered off and was chromatographed through a silica gel column using CH_2Cl_2/heptane, 1/1, to give 2.46 g of diiodide trimer **28;** yield 97%. ^{1}H NMR ($CDCl_3$): δ 8.15 (s, 1H, −PhH), 7.98 (dd, 2H, −PhH), 7.95 (t, 2H, −PhH), 7.64 (s, 2H, −PhH), 7.32 (m, 2H, −PhH), 4.36 (m, 6H, $-COOCH_2-$), 1.79 (m, 6H, $-CH_2-$ β ester), 1.27 (m, 42H, $-CH_2-$), 0.88 (t, 9H, $-CH_3$).

5.2.14. Pentamer (Decyl benzoate)phenylethyne (PY5-COOC10). The procedure used to obtain **9** was followed with trimer **28** (1.56 g, 1.44 mmol), 2-ethynyldecyl benzoate **(15B)** (0.95 g, 3.31 mmol)**,** $PdCl_2$ (9 mg, 0.05 mmol), $CuOAc_2$ (10 mg, 0.05 mmol), and TPP (66 mg, 0.25 mmol). The crude product was purified by chromatography, using heptane/CH_2Cl_2, 2/1, as an eluent. Then, it was recrystallized in pentane/CH_2Cl_2, 10/1, and purified by preparative thin layer chromatography (CH_2Cl_2) to give 1.39 g of pure pentamer (PY5-COOC10); yield 69%. ^{1}H NMR ($CDCl_3$): δ 8.18 (s, 3H, −PhH), 8.02 (dd, 2H, −PhH), 7.71 (t, 8H, −PhH), 7.53 (m, 2H, −PhH), 7.42 (m, 2H, −PhH), 4.36 (m, 10H, $-COOCH_2-$), 1.76 (m, 10H, $-CH_2-$ β ester), 1.25 (m, 70H, $-CH_2-$), 0.88 (m, 15H, $-CH_3$). Anal. Calcd for $C_{93}H_{122}O_{10}$: C, 79.79; H, 8.78; O, 11.43. Found: C, 79.45; H, 8.80; O, 11.52.

5.3. Instrument and Methods. The high performance liquid chromatography (HPLC) separations were performed with a SP 8800 ternary pump, a Spherisorbe 5 μm 10 × 250 mm column, and a UV Spectra-Focus detector from Spectra Physics. SEC was performed with the same apparatus as that used for HPLC, where the Spherisorbe colomn was replaced by a P1-gel (polystyrene/divinylbenzene) 10 μm (mixed-D600 × 25 mm column. All the measurements were processed by the Focus Software from Spectra Physics.

^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with a Brücker Ac-200F spectrometer at room temperature.

The melting points were determined on an Electrothermal digital melting point apparatus or by differential scanning calorimetry (DSC). DSC was performed on a Perkin-Elmer DSC 7 at a heating or cooling rate of 10 °C/min. The observations by optical microscopy were realized with a Leitz-Orthoplan polarizing microscope connected with a Mettler Fp 82 heating stage. X-rays were measured with a Debye−Scherrer room with 900 mm of circumference. The turn anode generator was from Marconi-Avionics.

The ultraviolet and visible absorption spectra were measured with a Shimadzu UV-2101 Pc UV−visible scanning spectrophotometer or Hitachi U3000. NLO mesurements were performed on the solid thin films by the technique of DFWM. The experimental setting, which is already described in a previous paper,[29] uses 60 fs CPM pulses at 620 nm which are amplified with a 5 kHz repetition rate copper vapor laser and compressed to 10 fs with the fiber-grating prism compression technique.

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References and Notes

(1) Yu, L.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3439.
(2) Agrawal, A.; Jenekhe, S. A.; Vanheerzeele, H.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837.
(3) Garito, A.; Jen, A. K.-Y.; Lee, C. Y-C.; Dalton L. R. *Electrical, Optical and Magnetic Properties of Organic Solid State Materials. Proc. Mater. Res. Soc.* **1993**, 328.
(4) Rehahn, M.; Schlüter, A. D.; Wegner, G. *Makromol. Chem.* **1990,** *191*, 1991.
(5) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341.
(6) Rao, D. N.; Chopra, P.; Shoshal, S. K.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem.* **1986**, *84*, 7049.
(7) Aime, J. P.; Bargain, F.; Fave, J. L.; Raviso, M.; Schott, M. *J. Chem. Phys.* **1988**, *89*, 6477.
(8) Swiatkiewicz, J.; Prasad, P. N.; Karasz, F. E.; Druy, M. A.; Glatkowski, P. *Appl. Phys. Lett.* **1990**, *56*, 892.
(9) Singh, B. P.; Prasad, P. N.; Karasz, F. E. *Polymer* **1988**, *29*, 1940.
(10) Lakmikantham, M. V.; Vartikar, J.; Kwan, Y. J.; Cava, M. P.; Huang, W. S.; MacDiarmid, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*, 75.
(11) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 752.
(12) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem.* **1986**, *24*, 2311.
(13) Heck, R. F. *Palladium Reagents in Organic Syntheses;* Academic Press: New York, 1990; p 299.
(14) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.
(15) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.
(16) Brown, I. M.; Wilbur, J. M. *Macromolecules* **1988**, *21*, 1859.
(17) Giesa, R.; Schultz, R. *Makromol. Chem.* **1990**, *191*, 857.
(18) Le Moigne, J.; Moroni, M.; Coles, H.; Thierry, A.; Kajzar, F. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 65.
(19) Rutherford, D.; Stille, J. K.; Elliott, C. K.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294.
(20) Sasabe, H.; Wada, T.; Hosoda, H.; Ohkawa, H.; Yamada, A.; Garito, A. F. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 155.
(21) Moroni, M.; Le Moigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562.
(22) Moroni, M. Thèse Université Louis Pasteur, Strasbourg, 1995.
(23) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.
(24) Eastmond, R.; Walton, D. R. *Tetrahedron Lett.* **1972**, *28*, 4601.
(25) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465.
(26) Zheng, R. X.; Benner, R. E.; Vardeny, Z. E.; Baker, G. I. *Phys. Rev. B, Rapid Commun.* **1990**, *42*, 3235.
(27) Yamamoto, T.; Tagaki, M.; Kizu, K.; Kubota, K.; Kabara, H.; Kirihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797.
(28) Reinhardt, B. A. *Trends Polym. Sci.* **1993**, *1*, 4.
(29) Pham, T. A.; Daunois, A.; Merle, J. C.; Le Moigne, J.; Bigot, J. Y. *Phys. Rev. Lett.* **1995**, *74*, 904.

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