Rigid Rod Conjugated Polymers for Nonlinear Optics. 3. Intramolecular H Bond Effects on Poly(phenyleneethynylene) Chains

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ABSTRACT: This paper describes the synthesis and the X-ray and the optical characterization of conjugated soluble polymers in which the planarity of the backbone has been improved by intramolecular H bonds. The solubility of the polymers was enhanced by increasing the number of alkyl chains on the aryl group. The electron density on the phenyl ring was also modified by the amino and ester groups, introducing electron-donor or electron-acceptor groups, which also increase the polarizability. The polymers have been 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 to obtain oligomers or high molecular weight polymers, having important nonlinear susceptibilities. The new polymers have been 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 H bonds between the aryl groups on the absorption wavelength. In addition, the nonlinear optical measurements show that the $\chi^{(3)}$ value of the pPY (6.8×10^{-10} esu) is close to the highest values obtained in acetylenic polymers such as polydiacetylenes.

Introduction

Fully conjugated polymers represent an attractive class of materials for a large number of applications in electronic conductivity and optoelectronics. Recently, the application of poly(phenylenevinylenes) (PPV) to light-emitting diodes stimulated the investigations in the domain of poly(aryl) derivatives. In the past years, the acetylene analogues of PPV, based on the phenylethynyl unit, the poly(phenylynylenes) (hereafter abbreviated pPY) received an increasing attention, mainly due to their conjugated rigid rod like character and to their optical properties. In a former publication,[1] we reported the synthesis and the characterization of various homo- and copolymers based on the *p*-phenyleneethynylene system. These compounds display high conjugation and appreciable $\chi^{(3)}$, exceeding 10^{-10} esu.[2] We have also pointed out the effect of electron-donor and electron-acceptor groups on the enhancement of the nonlinear properties. Another main characteristic of these polymers is their intense fluorescence yield which make them attractive for applications in the domain of light-emitting diodes.[3] At the same time, some of these oligomers and polymers present a weak solubility in solvents, mainly the polymers, where the aryl units are polyaromatic such as anthracenyl.

The aim of this work is to improve the solubility of the pPYs for a better use of these polymer solutions in thin film elaboration. At the same time, they are designed to improve the nonlinear susceptibilities. The higher solubility of the pPY derivatives with respect to the previous polymers is achieved by attaching a higher number of alkyl side chains via amine functions on the phenyl unit. A particular interest has been devoted to the anthracene copolymer. We also emphasize the high nonlinear susceptibilities of pPYs bearing electroactive side groups. Finally, we introduce a new kind of pPYs, which present both electroactive groups and intramolecular H bonds in order to increase the planarity of the main chain. Indeed, due to lateral H bonds between successive amino and ester substituents on the aryl unit, the number of rotation conformers is reduced, therefore improving the planarity of the backbone. In addition, due to the better π orbital overlapping of sp^1-ar, between C≡C and a phenyl group, an enhancement of the hyperpolarizability of the pPY chain is obtained.

Results

Synthetic Methods. The phenyleneethynylene polymers were synthesized by a condensation method in the presence of a catalytic amount of a palladium complex.[4−6] The polycondensation method was carried out in a mixture of triethylamine and tetrahydrofuran at 85 °C using $PdCl_2$, PPh_3, and $CuAc_2$ as catalysts. THF, used as a cosolvent during the reaction, is well-known for its good solvation properties for both metal complexes and highly polarizable polymer chains. These experimental conditions have contributed to a drastic increase of the molecular weights of the pPYs.[1]

Two different ways have been explored in order to modify the regioregularity of the main chain.

(1) First, a symmetric substituted diethynylarene reacted with a disubstituted halogenoaryl compound. The general route is described in Scheme 1, with R_1, R_2, R_3, and R_4 being the same or different. Depending on the aryl units, homo- or copolymers have been synthesized. The molecular structures are given in Figure 1a. The condensation is catalyzed by the $PdCl_2$−$CuOAc_2$−PPh_3 complex in NEt_3−THF solvent, according to Heck conditions. The polycondensation of an aryl diethynyl on an aryl dibromo unit proceeds by random addition along the chain, head to head or head to tail (see Figure 2a). This method was previously used to obtain long polymer chains of a pPY series, in particular alkyl ether groups, $pPYOC_{12}$, which has been extensively studied in the previous paper. In the present

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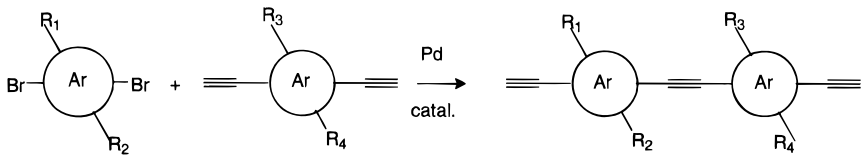
Scheme 1



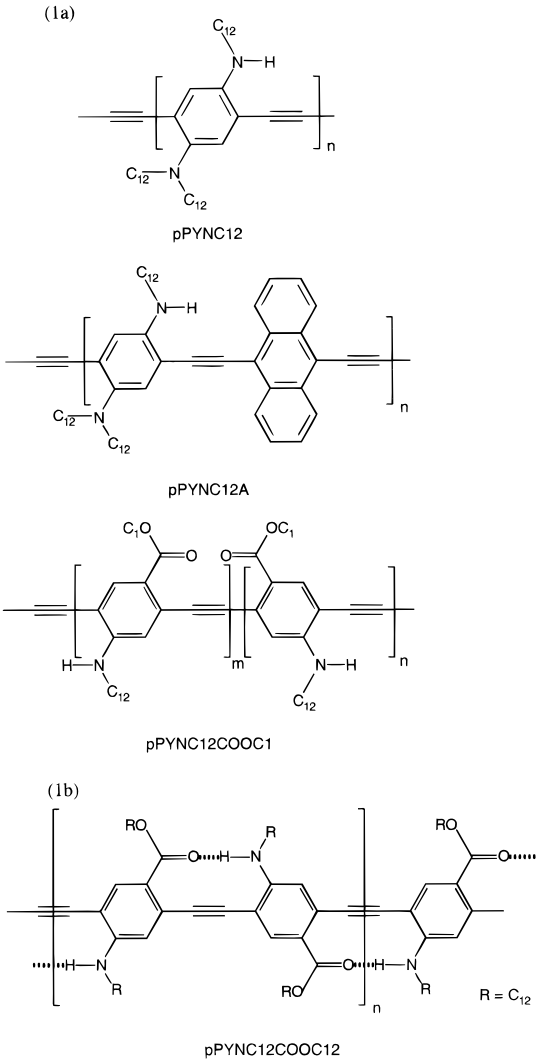


Figure 1. Polymers pPY based on alkylamine side groups synthesized in this work: (a) Homopolymer $pPYNC_{12}$ and copolymer $cpPYNC_{12}A$, bearing three alkyl chains per phenyl group, improve the solubility; the H bonds between sites on $pPYNC_{12}COOC_1$ are randomly distributed between the proximate ester and amine neighbor. (b) Scheme of the regular $pPYNC_{12}COOC_{12}$; the H bonds between proximate sites are periodically disposed between each phenyl unit.

work, the new polymers based on two different alkylamine $pPYNC_{12}$ units ($cpPYNC_{12}A$ and $pPYNC_{12}COOC_1$) have been synthesized following the procedure detailed in the Experimental Section.

(2) The second procedure allows us to reach a regular and well-ordered polymer. It is obtained by polycondensation of a single asymmetric bifunctional unit, such as an ethynyl halogeno aryl derivative (Scheme 2).

The interesting feature of this route is a strict control of the head to tail configuration of the chain (see Figure 2b). It has recently been proposed by Schumm et al.[7] The same step by step route allowed us to prepare well-defined oligomers.[8] The synthesis of the ethynyl halogeno aryl derivative required the addition of a halogen to the phenyl ring after the ethynyl group. The preparation of the ethynyl iodo aryl monomer was much more difficult than the diethyl compound. It has been obtained through a triazene intermediate. The regular polymer $pPYNC_{12}COOC_{12}$, represented in Figure 1b, was synthesized by homopolymerization of the iodoethynylaryl monomer, **19**, and purified from short oligomers by preparative size exclusion chromatography (SEC). Following this route, an ester and an alkyl amino side group were periodically introduced between phenyl moieties, inducing intramolecular H bonds *parallel to the main chain*. The expected properties of this new polymer are based on the ladder-like rigidity and a better π electron delocalization along the main chain.

Physical Properties of the Polymers. These polymers are deep-colored solids, from orange to purple red, except $pPYNC_{12}$, which is a strongly viscous oil at room temperature. They also present an intense, green to red fluorescence in solution or in the solid state. The two polymers $pPYNC_{12}$ and $cpPYNC_{12}A$ are very soluble in solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, or xylene. The random $pPYNC_{12}COOC_1$ and the alternated $pPYNC_{12}COOC_{12}$ show poorer solubilities, except for hot toluene and hot xylene.

Polymer Characterization in Solution. (A) NMR Spectroscopy. The ^1H NMR spectra of the polymers have been performed in $CDCl_3$. They are slightly different from those of the monomers. All resonances are broader, and in all cases no signal has been detected in the near 3.5 ppm region of the acetylenic proton. This shows that, after the polycondensation reaction, the polymer separation removes all traces of nonreacted monomer or short oligomers with acetylenic H.

(B) Molecular Weight. The molecular weights measurements have been performed by SEC in eluent THF using the coupled on-line light-scattering technique. With this method the molecular weights of the rigid rod polymers can be obtained vs the elution volume. High molecular weights have been detected, 1.1×10^6 for $pPYNC_{12}$ and 4.2×10^5 g/mol for $cpPYNC_{12}A$. The molecular weight distribution is quite broad for $pPYNC_{12}$ ($M_w/M_n = 4.7$), while surprisingly a very narrow distribution ($M_w/M_n \simeq 1.1$) has been obtained for the copolymer $cpPYNC_{12}A$. For $pPYNC_{12}COOC_1$ and $pPYNC_{12}COOC_{12}$, their low solubility prevents measurements of their molecular weights by light-scattering or SEC methods.

(C) Optical Properties: UV−Visible Spectra. In Table 1 we have reported the absorption maxima and the molecular extinction coefficients for the polymer solution and their corresponding thin solid films. Figure 3 shows the solid state UV−visible spectra of thin films for the homopolymer $pPYNC_{12}$ and the anthracene copolymer $cpPYNC_{12}A$. A broad absorption band shows up in the visible range, with a maximum at 491 nm for $cpPYNC_{12}A$, and a wide absorption for $pPYNC_{12}$ with no sharp peak but with an edge near 450 nm. The spectra are similar in solution, except for a blue shift of the main absorption band of ~18 and 5 nm, for $pPYNC_{12}$ and $cpPYNC_{12}A$ respectively.

For comparison, Figure 4a shows the UV−visible absorption spectra in CCl_4 solution of the other polymers. The maxima of the absorption bands λ_{max} occur at 461 and 468 nm, for $pPYNC_{12}COOC_1$ and $pPYNC_{12}$-

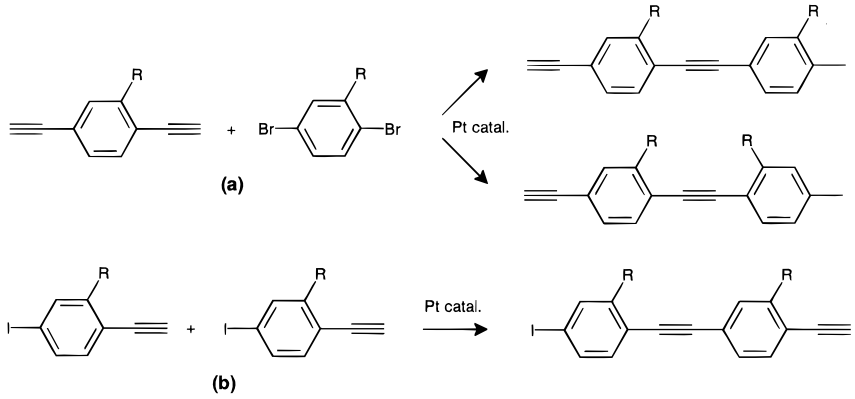


Figure 2. Two routes leading to homopolymers and copolymers.

Scheme 2

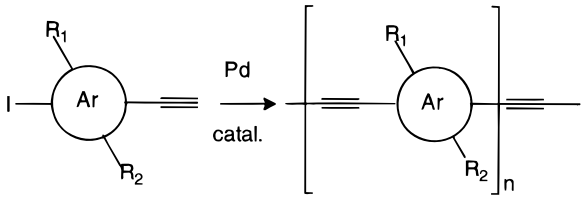


Table 1. UV−Visible Absorption Maxima and Coefficients of the Polymers

polymers	λ_{max} solution[a] (nm)	ϵ solution, THF ($L \cdot mol^{-1} \cdot cm^{-1}$)	λ_{max} film[a] (nm)
$pPYNC_{12}$	432*,[b]	1.06×10^4	450*
$cpPYNC_{12}A$	485[b]	0.71×10^4	491
$pPYNC_{12}COOC_1$	461[a] 462[b] 412[c]	1.51×10^4	442
$pPYNC_{12}COOC_{12}$	468[a] 469[b] 446[c]	1.57×10^4	470
$pPYOC_{12}$	425[b]	1.63×10^4	453

[a] The asterisk (*) corresponds to the shoulder in the visible range; the letter in superscript gives the solvent: (a) CCl_4, (b) THF, (c) DMF.

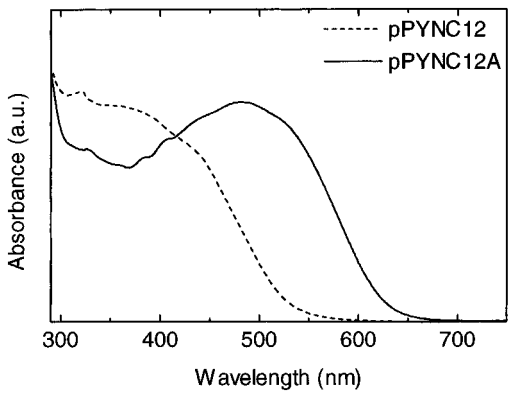


Figure 3. Solid state UV−visible spectra of $pPYNC_{12}$ and $cpPYNC_{12}A$.

$COOC_{12}$, respectively. Bearing H bonds, these polymers are strongly sensitive to protic conditions in solution. For the two polymers dissolved in dimethylformamide, λ_{max} shifts to 412 and 446 nm, while they are almost unchanged in THF.

Infrared and Raman Spectroscopies. The infrared (IR) and Raman spectra have been obtained at room temperature on cast films of the polymers. The Raman measurements were carried out with a 1064 nm excitation wavelength in order to avoid the strong luminescence of these samples in the visible region. One of the most important Raman peak of pPY polymers is associated to the C≡C stretching vibration. The corresponding Raman shift occurs near 1990 cm^{-1}. The most characteristic IR peaks are N−H and C═O. The stretching frequencies of the N−H bond for $pPYNC_{12}$ and $pPYNC_{12}A$ occur at 3391 and 3368 cm^{-1}. These are close values with respect to N−H bonds of secondary aromatic amines. For $pPYNC_{12}COOC_1$ and $pPYNC_{12}COOC_{12}$, the N−H stretch occurs at 3336 and 3332 cm^{-1}. This lowering of the N−H bond energy is consistent with the H linking between the primary alkylamine and the alkyl ester side groups. The asymmetrical vibrational stretching of the C≡C bond is weak in IR, particularly for $pPYNC_{12}$ and $pPYNC_{12}A$. These data are summarized in Table 2. The values of the ether polymer $pPYOC_{12}$ are also reported as a reference.

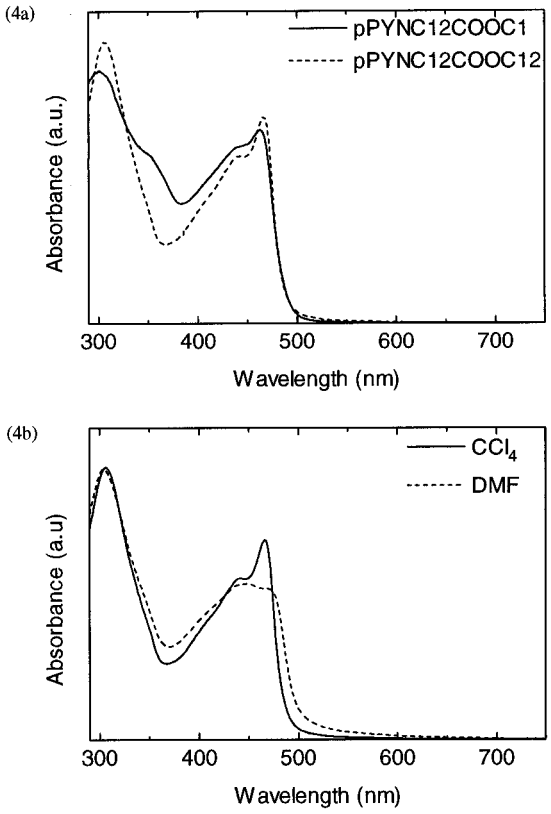


Figure 4. (a) UV−visible spectra in CCl_4 of $pPYNC_{12}COOC_1$ and $pPYNC_{12}COOC_{12}$. (b) UV−visible spectra of $pPYNC_{12}$-$COOC_{12}$ in CCl_4 and DMF solution.

Nonlinear Optical Properties. The nonlinear optical measurements have been performed on thin films using degenerated four wave mixing (DFWM) at 620 nm (see Experimental Section for details). The nonresonant

Table 2. Infrared and Raman Spectroscopic Data of $pPYNC_{12}$, $cpPYNC_{12}A$, $pPYNC_{12}COOC_1$, $pPYNC_{12}COOC_{12}$, and $pPYOC_{12}$

	IR (cm^{-1})				
polymers	$\nu_{stretch}$ N−H	$\nu_{stretch}$ C=O	$\nu_{stretch}$ C≡C	Raman (cm^{-1}) $\nu_{stretch}$ C≡C	$\chi^{(3)}$ DFWM (esu × 10^{-10})
$pPYNC_{12}$	3391		2194	2190	4.4 ± 0.9
$cpPYNC_{12}A$	3368		2190	2190	
$pPYNC_{12}COOC_1$	3336	1707	2192		2.1 ± 0.4
$pPYNC_{12}COOC_{12}$	3332	1699	2188	2183	6.8 ± 1.4
$pPYOC_{12}$			2199	2196	4.6 ± 0.9

third-order susceptibility $\chi^{(3)}$ of these polymers are reported in Table 2. The main interest of these measurements lies in the high values of the nonlinear susceptibility measured in $pPYNC_{12}COOC_{12}$. Its $\chi^{(3)} = (6.8 \pm 1.4) \times 10^{-10}$ esu and is higher than the measured value of $pPYOC_{12}$ ($\chi^{(3)} = (4.6 \pm 0.9) \times 10^{-10}$ esu). In contrast a lower value is obtained for the random derivative $pPYNC_{12}COOC_1$, i.e. $\chi^{(3)} = (2.1 \pm 0.4) \times 10^{-1}0$ esu, which is much lower than the regioregular copolymer.

(D) Molecular Ordering. Thin solid films are obtained by casting concentrated solutions of the polymers on glass slides. Observed under polarized light, the films exhibit a strong birefringence after rubbing the surface or shearing the melt. For $pPYNC_{12}$, which is a strongly viscous oil at room temperature, a weak birefringence is observed. At 70 °C, the fluidity of the polymers $cpPYNC_{12}A$, $pPYNC_{12}COOC_1$, and $pPYNC_{12}COOC_{12}$ increases, the samples remaining highly birefringent up to 150 °C. At higher temperatures, greater than 150 °C, the polymers start to decompose. The textures observed in the liquid crystalline phases do not reveal any characteristic smectic or nematic mesophase.

The polymers have also been studied by X-ray scattering. They exhibit a diffuse Bragg reflection at large angles and a sharper band at small angles at 25 and 85 °C. The shape of these patterns, often observed for a rigid-rod polymer having a flexible side chain,[9] is characteristic of a lamellar molecular stacking. For each polymer, at 25 and 85 °C, the broad band observed at wide angle corresponds to a periodicity of 4.5 Å. The diffractogram of $pPYNC_{12}COOC_1$ (Figure 5a) presents a sharp band at small angle, revealing an *ordered structure*. The X-ray patterns of $pPYNC_{12}$, $cpPYNC_{12}A$, and $pPYNC_{12}COOC_{12}$ (Figure 5b) show broader bands at small angles, corresponding to a less ordered molecular organization. The spacing, calculated for $pPYNC_{12}$, $cpPYNC_{12}A$, and $pPYNC_{12}COOC_{12}$ from the small angle diffraction peak at 85 °C are respectively 21.6, 22.3, and 27.9 Å. These periodicities are consistent with the calculated lengths based on lateral groups in an extended conformation. The spacing calculated from the $pPYNC_{12}COOC_1$ diffraction pattern at small angle is 27.1 Å.

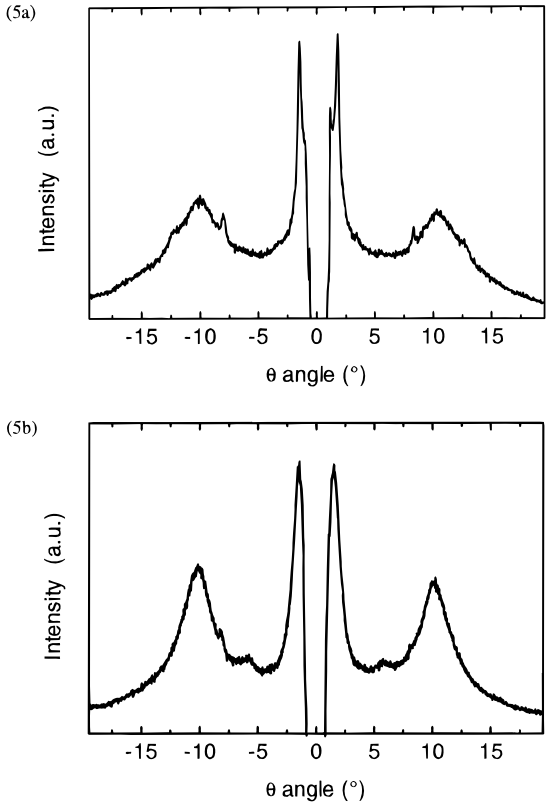


Figure 5. (a) X-ray diffraction diagram for $pPYNC_{12}COOC_1$ at 25 °C. (b) X-ray diffraction diagram for $pPYNC_{12}COOC_{12}$ at 25 °C.

Discussion

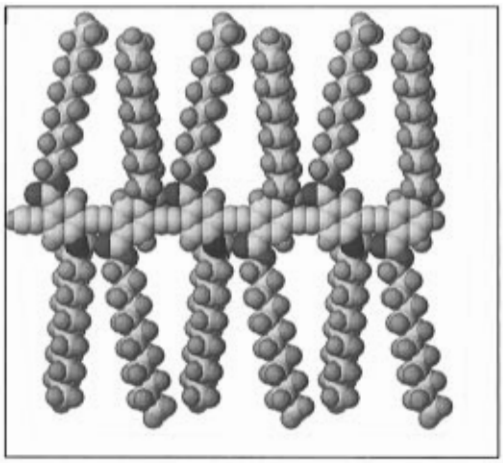
Polymer Chain Characterization. The polycondensation of symmetrical diethynyl aryl and dibromo aryl derivatives by a Pd-coupling method affords to synthesize a class of rigid and conjugated polymers. The pPY may also be prepared by a dissymmetrical polycondensation using an ethynyl halogeno aryl, which is also used in a step by step synthesis, that allows a strict head to tail alternation. Both routes lead to high molecular weights.

The solubility of the polymers depends on the number and length of alkyl chains on the aryl groups. The $pPYNC_{12}$ and $cpPYNC_{12}A$, based on a monomer unit bearing three C_{12} side chains, display higher solubilities than the equivalent derivatives with only two alkyl chains per phenyl. The $cpPYOC_{12}A$ described in paper 1, having only two side chains on the phenyl group, had a poor solubility. On the other hand, H bonds between the phenyl substituents reduce drastically the polymer solubility that excludes the possibility to analyze its molecular weight distribution by SEC and light scattering.

The light-scattering molecular weight (LS M_w) measurements, already described in previous papers, confirms here its utility. This method gives the weight average molecular mass of the very rigid chains, which cannot be simply deduced from PS calibration method. We found one distribution peak centered at 10^6 for $pPYNC_{12}$ and 4×10^5 for $cpPYNC_{12}A$. Their degrees of polymerization, higher than 1000, are higher also than for previous pPYs ($M_w \sim 10^5$ for $pPYOC_{12}$). Particularly long polymer chains have been detected by SEC in $pPYNC_{12}$. The very high molecular weight obtained on this polymer and its broad distribution may be explained by its high solubility and/or by aggregation of pPY chains. A better characterization by light scattering and neutron diffraction are in progress. During polymerization the polymer remains perfectly soluble, even for a very long chain, in the polymerization mixture (NEt_3, THF). For the other polymers, the lower solubility induces the precipitation of the long chains, leading to shorter polymers as well as narrower distributions.

Structural Properties. The X-ray diffraction performed on these polymers confirms the observations by optical microscopy of a liquid crystal phases. For all of them, the diffraction patterns show the same shape with a sharp peak at low angle (broad for $pPYNC_{12}$, very sharp for $pPYNC_{12}COOC_1$) and a diffuse halo at wide angles. From the small angle diffraction peaks of

(6a)



(6b)

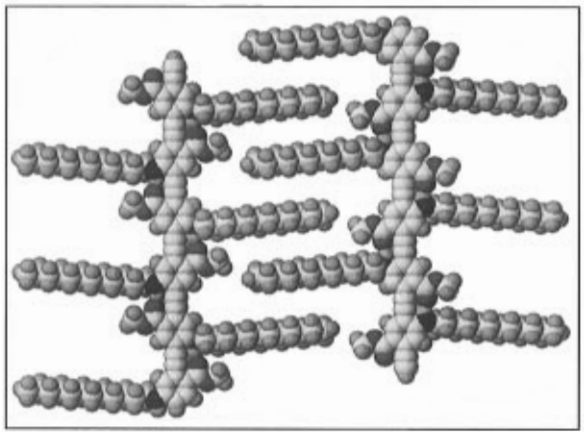


Figure 6. Molecular models deduced from X-ray diffraction of (a) $pPYNC_{12}COOC_{12}$ and (b) $pPYNC_{12}COOC_1$.

$pPYNC_{12}$ and $cpPYNC_{12}A$ we calculated (vide supra) a periodicity of about 22 Å. These dimensions are not consistent with an extended side chains model where the evaluated distance is about 30 Å. $pPYNC_{12}$ and $cpPYNC_{12}A$ bear three paraffinic side chains on each repeating unit. These bulky substituents prevent a planar molecular arrangement. A model of tubes, placed in a hexagonal organization, might be more accurate for these two polymers. It would give a distance of about 21 Å, which is close to the experimental dimensions. This possible stacking of the molecules may also explain the weakly ordered mesophases of $pPYNC_{12}$ and its viscous, nonsolid texture at room temperature.

For $pPYNC_{12}COOC_{12}$, the periodicity is significantly different (~28 Å). Figure 6a shows a possible molecular configuration of a single chain for $pPYNC_{12}COOC_{12}$, where H bonds between the carboxyl and alkylamine side groups are represented between the nearest neighbors. According to this model the presence of intramolecular H bonds implies a good planar configuration of phenyl residues in the main chain. In addition it leads to slightly different orientations of alkyl side chains, which could explain the lateral disorder of chains in extended conformation.

In contrast to $pPYNC_{12}COOC_{12}$, $pPYNC_{12}COOC_1$ has only one long side chain on each repeating unit. The spacing calculated from the very sharp X-ray diffraction band in bulk gives a layer periodicity of 27.1 Å (Figure 5b). Since we *expect, for the liquid crystalline phase, an arrangement in a single layer*, this value is consistent with the evaluated distance on the structural model of $pPYNC_{12}COOC_1$ represented in Figure 6b. This ideal molecular configuration displays a periodicity of 27 Å between the phenylethynyl chains organized in a layered structure of interdigited side chains. The interdigitation of aliphatic chains occurs without steric effect.

Optical Properties. The absorption spectra of the polymer solutions present an absorption band in the visible range 400−500 nm, which has already been described for substituted pPYs. We notice that the substituents having a mesomeric effect, donor or acceptor, induce a red shift of this absorption band in comparison to the pure alkyl side chains.[8,10] The $pPYNC_{12}$, in spite of its orange color, presents no maximum of absorption in the visible range but a rather wide band with a cutoff near ~550 nm. This is attributed to a large distribution of rotational conformers, related to the nonplanar arrangement of the molecules. The numerous paraffinic side chains, three for each repeating unit, prevent a good organization for this polymer which is a weakly ordered liquid crystal at room temperature. By comparing the UV−visible spectra of $pPYNC_{12}$ and $cpPYNC_{12}A$, in solution or in the solid state, we can infer that the introduction of anthracenyl groups in the backbone shifts the absorption of 40−50 nm to the longer wavelengths. In addition, the spectra corresponding to the solid state phase are shifted to the red, indicating a better ordering and higher conjugated conformations than in solution.

The shape of the UV−visible spectra of $pPYNC_{12}COOC_1$ and $pPYNC_{12}COOC_{12}$ is quite sharp. But in both cases, the absorption band in the visible range displays two peaks, near 440 and 470 nm (Figure 4a). The last one is much more pronounced in the case of the regular polymer. It is probably related to well-planar conformations of the backbone. This behavior is manifested both in the solid state and in solution using nonprotic solvents, such as CCl_4 and THF. When these two polymers are dissolved in a protic solvent (DMF), their UV−visible spectra are drastically altered (Figure 4b), and a large blue shift of the λ_{max} is observed, 22 nm for the regular polymer and 39 nm for the other one (Table 1). The ester substituents of the regular $pPYNC_{12}COOC_{12}$ are much more bulky than those of $pPYNC_{12}COOC_1$, and the solvation by the DMF could be more efficient for $pPYNC_{12}COOC_1$. It is also important to notice that in each case, in solid state or in solution, the absorption of the regular polymer displays a red shift corresponding to an increased electron delocalization.

The Raman spectra of the polymers (Table 2) display maxima at 2190, 2190, and 2183 cm^{-1} for the bands assigned to C≡C stretching modes. These values indicate a high delocalization, which seems to be slightly improved in comparison with the $pPYOC_{12}$ polymer (2196 cm^{-1}). The infrared spectroscopy gives consistent results. The C≡C stretching bands appear at lower frequencies, but are weaker, particularly for $pPYNC_{12}$ and $pPYNC_{12}A$.

The H-bonded polymers show the typical IR bands for the N−H and the C═O bonds. In the case of the regular $pPYNC_{12}COOC_{12}$, the stretching frequencies of the C≡C, N−H, and C═O bonds are systematically shifted to lower frequencies. These weaker bonds for the regular polymer are the result of a higher ratio of intramolecular H bonding. The resulting more planar conformations favorizes a higher conjugation, which is consistent with the red shift observed in UV visible

spectrometry for $pPYNC_{12}COOC_{12}$ as compared to $pPYNC_{12}COOC_1$.

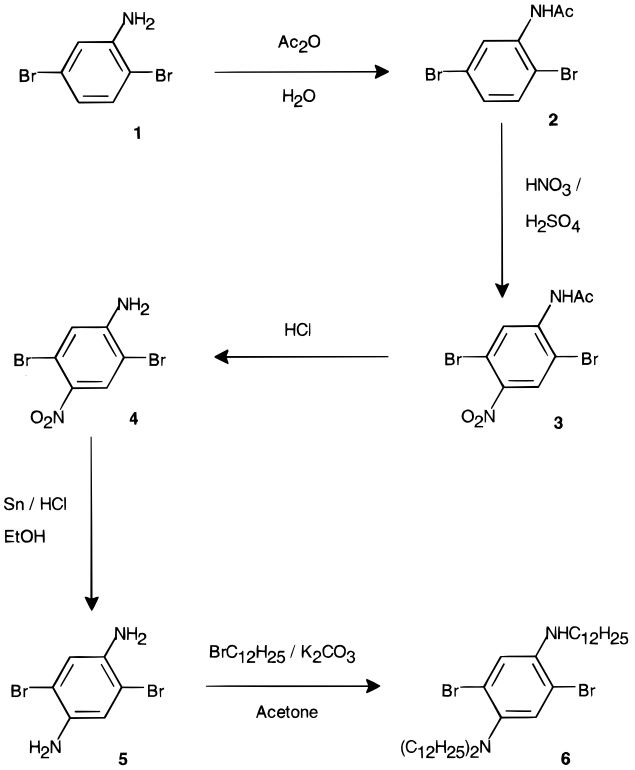
The nonlinear optical susceptibilities $\chi^{(3)}$ have been measured by degenerated four wave mixing (DFWM) with 60 fs pulses, using the self-diffraction two beams configuration. The pulses are obtained from an amplified colliding pulse mode-locked laser at 620 nm. The low repetition rate of the laser (5 kHz) allows us to exclude any thermal contribution to the nonlinear susceptibility. The central wavelength of the 60 fs pulses is off resonant for the samples studied here. In some cases, however, a small resonant contribution due to a long absorption tail in the visible is present, for $pPYNC_{12}COOC_{12}$ in particular. This contribution is estimated to alter the $\chi^{(3)}$ values about 30%. This is deduced by fitting the absorption line with an exponential, which is then included as a resonant contribution in the nonlinear susceptibility. This resonant part is substracted from the measured $\chi^{(3)}$. In the case of $cpPYNC_{12}A$, however, the residual absorption at 620 nm (see Figure 3) is too large to estimate the correct nonresonant $\chi^{(3)}$. It is important to mention that all measurements are performed in the same experimental conditions (laser fluence, spot diameter, optical alignment after the sample and detecting conditions). In addition the DFWM signal was measured as a function of the time delay between the two incident pulses. In each case, the signal decays faster than the pulse duration and has no time independent thermal background. On this time scale only electronic processes take place. This is consistent with previous well-known observations.[11] The fast decay times indicate ultrashort dephasing dynamics ($T_2 < 40$ fs) as expected for off-resonance excitations. The fact that the decay is faster than the pulse duration is simply related to the nonlinear process involved. DFWM is a third-order process whereas the pulses are measured with the standard second harmonic autocorrelation. The important information here is the amplitude of the DFWM signals which allows us to deduce $\chi^{(3)}$. The DFWM measurements lead to the following conclusion. In the smaller band gap polymer series, $pPYNC_{12}$, $pPYNC_{12}COOC_{12}$, and $pPYNC_{12}COOC_1$, we expected larger values of nonresonant $\chi^{(3)}$ than for the first ether derivative[1] or oligomers series.[8] The $\chi^{(3)}$ values (respectively $(4.4 \pm 0.9) \times 10^{-10}$, $(2.1 \pm 0.4) \times 10^{-10}$, and $(6.8 \pm 1.4) \times 10^{-10}$ esu for $pPYNC_{12}$, $pPYNC_{12}COOC_1$, and $pPYNC_{12}COOC_{12}$) show that the third-order susceptibility is higher for $pPYNC_{12}COOC_{12}$ than for the other polymers. It confirms an interesting approach of inducing a strong conformational order between phenyl groups in the main chain in order to enhance the third-order susceptibility. Therefore, we demonstrate also a novel interest of introducing intramolecular H bonds in the molecular engineering of polymers for NLO, which was first observed on polydiacetylene chains such as pnBCMU.[12]

Conclusions

In this work we have been able to prepare a new series of rigid rod pPY conjugated polymers. The polymer solubilities have been increased by adding a higher number of lateral substituents, which allowed us to prepare a well soluble anthracenyl copolymer. The characterization by size exclusion chromatography of the polymer and the copolymer substituted with dodecylamine chains on the phenyl group display the highest average molecular weight ever synthesized on this type of homopolymer, with values up to 10^6 g/mol.

A new approach, which we have used on this pPY system, is to increase the planarity of the backbone by means of intramolecular H bonds. A regular and a random polymer, able to form H bonds between consecutive amine and ester substituents, has been prepared via two different synthetic routes. The X-ray patterns of these two polymers show very different molecular organizations. The solid state stacking of the random polymer does not favor the intramolecular H bonds and planar conformation of the backbone. The linear spectroscopy properties in solution clearly demonstrate the formation and the removal of the H bonds in nonprotic and protic solvents. On the other hand, the infrared and the UV−visible measurements, in solution and solid films, reveal an increased number of H bonds and a more efficient electronic delocalization for the regular polymer. The other interesting aspect is the high solubility of the $pPYNC_{12}$ for preparation of thin films by means of a spin-coating method, which make them attractive for nonlinear optical studies.

Scheme 3



Experimental Section

Materials. The 2,5-dibromoaniline, the 2,5-dibromo-4-fluorotoluene (**7**), iodine, bromoalkanes, dicyclohexylcarbodiimide (DCCI), (trimethylsilyl)acetylene (TMSA), palladium(II) chloride ($PdCl_2$), triphenylphosphine (PPh_3), potassium carbonate (K_2CO_3), and sodium iodide (NaI) were obtained from Lancaster. The 4-fluoro-2-nitrobenzoic acid (**12**), (dimethylamino)pyridine (DMAP), tin, copper(II) acetate ($CuAc_2$), methylene chloride (CH_2Cl_2) HPLC grade, and tetrabutylammonium fluoride (TBAF) 1.1 M in THF were obtained from Aldrich and used without further purification. Triethylamine (Aldrich) was distilled from KOH before use. THF was distilled from sodium and kept under nitrogen.

Synthesis Methods. The Dibromoaryls: Synthesis of the 2,5-Dibromo-4-(didodecylamino)-*N*-dodecylaniline (6, Scheme 3). 2,5-Dibromoacetanilide (2). In a vessel were placed the dibromoaniline (13.8 g, 55 mmol), 50 mL of acetic anhydride, and 50 mL of water. The mixture was warmed up to reflux with stirring for 4 h and then poured in 500 mL of water. The precipitate was collected by filtration and washed with water to obtain 3.304 g of pure product **2**. Yield: 93%. ^{1}H NMR ($CDCl_3$): δ 8.32 (d, 1H, Ph H), 7.71 (s, 1H, NHAc), 7.03 (d, 1H, Ph H), 6.75 (dd, 1H, Ph H), 2.21 (s, 3H, $NCOCH_3$).

2,5-Dibromo-4-nitroacetanilide (3). To a cooled mixture (ice/salt bath) of 50 mL of concentrated H_2SO_4 and 50 mL of concentrated HNO_3 was added the dibromoacetanilide **2** (14.65 g, 50 mmol). The mixture was stirred for 2 h while the temperature was kept under 10 °C. Then 300 g of crushed ice was added. The precipitate was collected by filtration and then purified on a silica gel column using heptane/CH_2Cl_2, 1/1, as an eluent to give 3.9 g of pure nitro derivative **3**. Yield: 70%. Mp: 204−205 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.97 (s, 1H, Ph H), 8.20 (s, 1H, Ph H), 7.77 (s, 1H, NHAc), 2.32 (s, 3H, $NCOCH_3$). Anal. Calcd for $C_8H_6N_2O_3Br_2$: C, 28.43; H, 1.79; N, 8.29; O, 14.20. Found: C, 28.36; H, 1.91; N, 8.45; O, 14.56.

2,5-Dibromo-4-nitroaniline (4). 2,5-Dibromo-4-nitroacetanilide (**3**) (11.49 g, 34 mmol) was refluxed for 16 h in 50 mL of 1 M HCl. The cooled solution was poured in 200 mL of water, washed with 50 mL of methylene chloride, and then neutralized with potassium carbonate. The precipitate was collected by filtration, washed with water, and dried to obtain 9.77 g of dibromonitroaniline (**4**). Yield: 97%. ^{1}H NMR ($CDCl_3$): δ 8.22 (s, 1H, Ph H), 7.23 (s, 1H, Ph H), 6.28 (s, 2H, NH_2).

2,5-Dibromo-4-aminoaniline (5). The 2,5-dibromo-4-nitroaniline (**4**) (9.5 g, 32.1 mmol) was dissolved in 60 mL of ethanol. Then 30 mL of concentrated HCl was poured, and tin powder (15.43 g, 130 mmol) was added in small amounts. The mixture was stirred for 6 h and then concentrated under reduce pressure to save 20 mL of liquid. Next, 100 mL of water and 100 mL of ethyl ether were added. The stirred mixture was neutralized by potassium carbonate. The Sn salts were filtered off on Celite. The aqueous fraction was extracted three times with 100 mL of ether. The combined organic fractions were dried on sodium sulfate, and the solvent was evaporated. After chromatography (silica gel, NEt_3/CH_2Cl_2, 1/19) 4.11 g of pure dibromoaminoaniline was obtained **5**. Yield: 48%. ^{1}H NMR (acetone-d_6): δ 6.94 (s, 2H, Ph H), 6.28 (s, 4H, NH_2). This compound is air and light sensitive (oxidation).

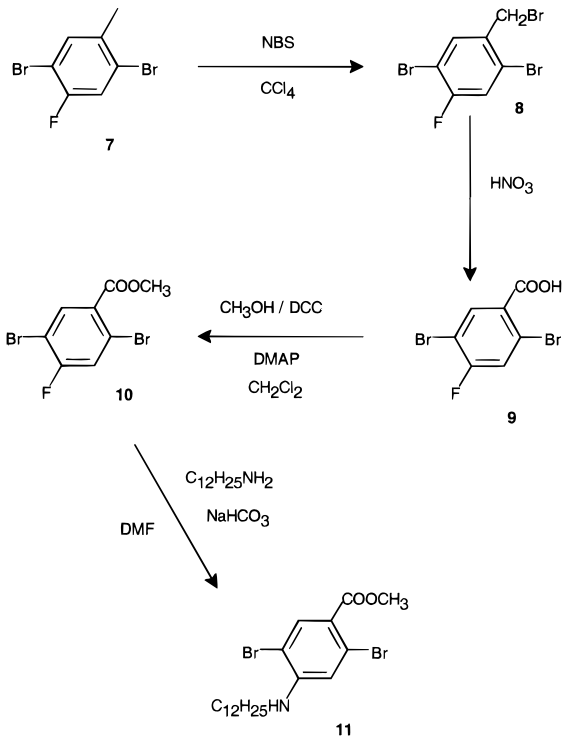
2,5-Dibromo-4-(didodecylamino)-*N*-dodecylaniline (6). To a solution of dibromoaminoaniline (**5**) (3.99 g, 15 mmol) in 50 mL of acetone were added 1-bromododecane (14.24 g, 60 mmol) and potassium carbonate (4.15 g, 30 mmol). The mixture was stirred for 16 h. The cooled mixture was poured in 200 mL of cold water and stirred for 1 h. The precipitate was collected by filtration and then purified by chromatography (silica gel, heptane/CH_2Cl_2, 2/1) to obtain 7.17 g of trialkyl derivative **6**. Yield: 62%. ^{1}H NMR ($CDCl_3$): δ 7.19 (s, 1H, Ph H), 6.82 (s, 1H, Ph H), 4.08 (s, 1H, NH), 3.10 (qu, 2H, CH_2 α NH), 2.89 (t, 4H, $N(CH_2)_2$), 1.68 (m, 6H, CH_2 β amines), 1.28 (s, 54H, CH_2), 0.89 (t, 9H, CH_3). Anal. Calcd for $C_{42}H_{78}Br_2N_2$: C, 65.43; H, 10.20; N, 3.63. Found: C, 65.73; H, 10.37; N, 3.46.

Synthesis of the Methyl 2,5-Dibromo-4-(*N*-dodecylamino)benzoate (11, Scheme 4). α,2,5-Tribromo-4-fluorotoluene (8). To a solution of 2,5-dibromo-4-fluorotoluene (26.79 g, 100 mmol) in 150 mL of CCl_4 were added bromosuccinimide (17.8 g, 100 mmol) and benzoyl peroxide (170 mg, 0,7 mmol). The stirred mixture was heated to reflux for 16 h, and then cooled. The precipitate was filtered off, and the solvent was evaporated. To the crude product was added a solution of CH_2Cl_2/pentane, 1/5, and the succinimide crystals were filtered off. The solvent was removed to give 25.31 g of tribromofluorotoluene **8**. Yield: 73%. ^{1}H NMR ($CDCl_3$): δ 7.67 (d, 1H, Ph H), 7.38 (d, 1H, Ph H), 4.53 (s, 2H, CH_2Br).

2,5-Dibromo-4-fluorobenzoic Acid (9). The tribromofluorotoluene **8** (12.49 g, 36 mmol) was stirred and heated to reflux for 16 h in a solution of 15 mL of 65% nitric acid and 20 mL of water. The cooled mixture was extracted twice with 50 mL of ether. The organic phase was extracted three times with 50 mL of a 5% aqueous sodium hydroxide solution. The aqueous phase was acidified to pH = 2 with concentrated hydrochloric acid and extracted three times with 100 mL of ether. The organic solution was dried on sodium sulfate, and the solvent was removed to give 6.11 g of acid **9**. Yield: 57%. Mp: 148−149 °C. ^{1}H NMR ($CDCl_3$): δ 8.29 (d, 1H, Ph H), 7.51 (d, 1H, Ph H), 6.95 (s, 1H, COOH). Anal. Calcd for $C_7H_3O_2Br_2F$: C, 28.22; H, 1.02. Found: C, 28.45; H, 1.04.

Methyl 2,5-Dibromo-4-fluorobenzoate (10). Dibromofluorobenzoic acid **9** (5.95 g, 20 mmol), methanol (0.79 g, 1 mL, 24.7 mmol), DCCI (4.15, 20.1 mmol), DMAP (100 mg, 0.82 mmol), and 50 mL of CH_2Cl_2 were charged in a single-necked flask topped with a calcium chloride guard tube, refluxed, and stirred for 15 h. Urea was filtered off, and the filtrate was washed with a 0.5 M HCl solution and then with a saturated $NaHCO_3$ solution. The solution was dried on Na_2SO_4, the solvent was removed, and the crude product was chromatographed (SiO_2, CH_2Cl_2/heptane, 1/1) to obtain 6.64 g of ester **10**. Yield: 92%. Mp: 198−200 °C. ^{1}H NMR ($CDCl_3$): δ 8.17 (d, 1H, Ph H), 7.46 (d, 1H, Ph H), 3.96 (s, 3H, $COOCH_3$).

Scheme 4



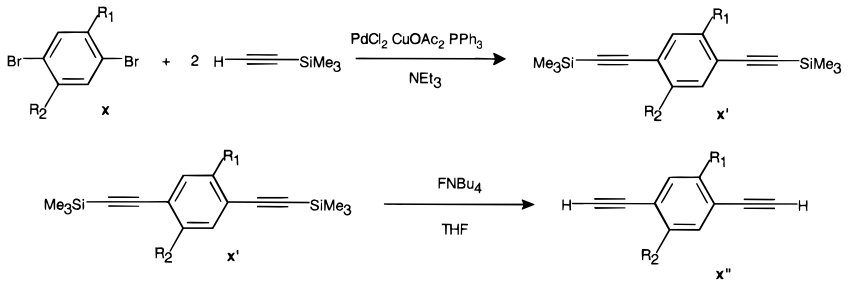
Methyl 2,5-Dibromo-4-(*N*-dodecylamino)benzoate (11). To a solution of the fluoroaryl **10** (6.50 g, 18 mmol) and dodecylamine (3.74 g, 20.2 mmol) in 10 mL of DMSO was added $NaHCO_3$ (1.52 g, 18.1 mmol). The mixture was heated at 60 °C and stirred for 3 days. The cooled mixture was poured in 200 mL of water and then filtered. The precipitate was collected and chromatographed (SiO_2, CH_2Cl_2/heptane, 1/4) to obtain 6.82 g of pure product **11**. Yield: 72%. Mp: 58−60 °C. ^{1}H NMR ($CDCl_3$): δ 8.06 (s, 1H, Ph H), 6.83 (s, 1H, Ph H), 4.70 (t, 1H, NH), 3.87 (s, 3H, $COOCH_3$), 3.18 (qu, 2H, NCH_2), 1.69 (q, 2H, CH_2 β amine), 1.27 (s, 18H, CH_2), 0.89 (t, 3H, CH_3). Anal. Calcd for $C_{24}H_{31}N$: C, 50.33; H, 6.55; N, 2.93. Found: C, 50.63; H, 6.75; N, 2.76.

1,4-Diethynylaryls 6″ and 11″ (Scheme 5). Coupling. Palladium chloride (53 mg, 0.30 mmol), copper acetate (60 mg, 0.3 mmol), triphenylphosphine (262 mg, 1.0 mmol) and the dibromoaryl (**6** or **11**) (3.2 mmol) were charged under nitrogen in a two-necked flask with dry and degassed triethylamine (100 mL). (Trimethylsilyl)acetylene (1.5 mL, 10.6 mmol) was added, and the reaction mixture was stirred and heated at 85 °C under nitrogen for 8 h. After being cooled to room temperature, the mixture was filtered to eliminate the ammonium salt and the triethylamine was removed. The soiled residue was dissolved in dichloromethane, recrystallized in methanol, and then purified by chromatography (SiO_2, CH_2Cl_2/heptane, 1/1).

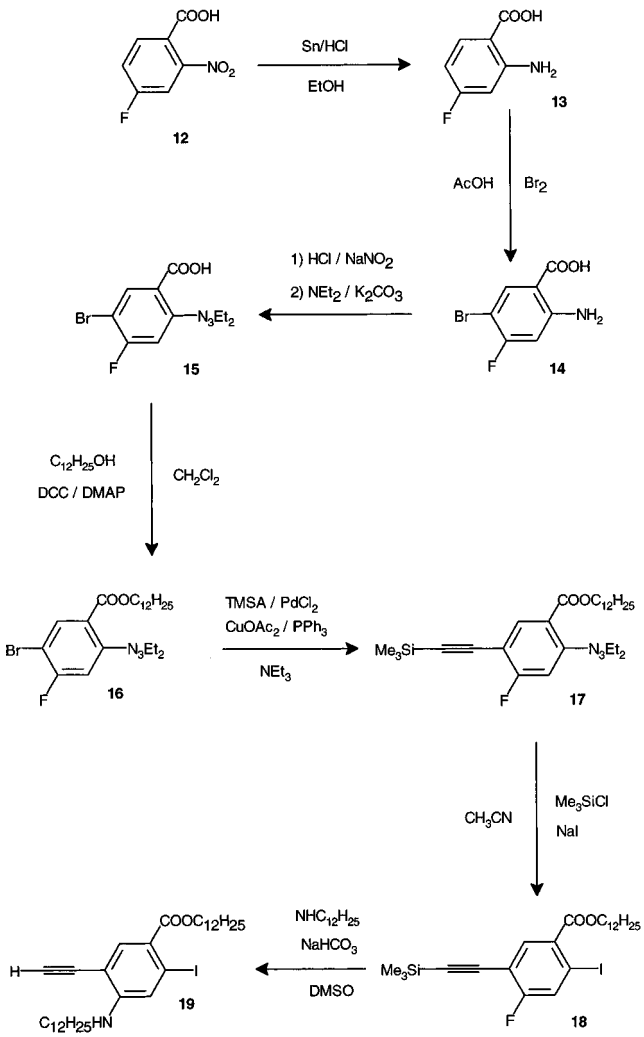
Deprotection. The bis[(trimethylsilyl)ethynyl]aryl was dissolved in 50 mL of tetrahydrofuran, and a solution of tetrabutylammonium fluoride (1.1 M, $^1/_2$ equiv) was added. After being stirred for 5 min at ambient temperature, the mixture was chromatographed on a small silica gel column using tetrahydrofuran as eluent. The solvent was removed, and the crude product was recrystallized in methanol and dried in vacuum.

2,5-Diethynyl-4-(didodecylamino)-*N*-dodecylaniline (6″). Yield: 38%. NMR ($CDCl_3$): δ 7.03 (s, 1H, Ph H), 6.70 (s, 1H,

Scheme 5



Scheme 6



Ph H), 4.33 (s, 1H, NH), 3.10 (qu, 2H, CH_2 α NH), 3.02 (t, 4H, $N(CH_2)_2$), 3.46 (s, 1H, C≡CH), 3.43 (s, 1H, NCH), 1.65 (m, 6H, CH_2 β amines), 1.28 (s, 54H, CH_2), 0.89 (t, 9H, CH_3). Anal. Calcd for $C_{46}H_{80}N_2$: C, 83.57; H, 12.20; N, 4.24. Found: C, 83.71; H, 11.89; N, 3.97.

Methyl 2,5-Diethynyl-4-(*N*-dodecylamino)benzoate (11″). Yield: 58%. Mp: 52−55 °C. ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 1H, Ph H), 6.83 (s, 1H, Ph H), 4.16 (t, 1H, NH), 3.82 (s, 3H, $COOCH_3$), 3.61 (s, 1H, CCH), 3.17 (s, 1H, C≡CH), 3.13 (qu, 2H, NCH_2), 1.71 (q, 2H, CH_2 β amine), 1.28 (s, 18H, CH_2), 0.90 (t, 3H, CH_3). Anal. Calcd for $C_{24}H_{33}NO_2$: C, 78.43; H, 9.05; N, 3.81; O, 8.71. Found: C, 77.86; H, 9.24; N, 3.57; O, 8.53.

The ethynyl iodoaryl monomer 19 was synthesized as shown in Scheme 6.

2-Amino-4-fluorobenzoic Acid (13). The synthetic way was the same as for **4**. The required chemicals were the 4-fluoro-2-nitrobenzoic acid (3.50 g, 16 mmol), tin (7.60 g, 64 mmol), 30 mL of ethanol, and 15 mL of hydrochloric acid; 2.41 g of product **13** was obtained. Yield: 82%. ^{1}H NMR (acetone-d_6): δ 7.88 (qu, 1H, Ph H), 6.68 (s, 3H, COOH and NH_2), 6.52 (qu, 1H, Ph H), 6.32 (h, 1H, Ph H).

2-Amino-5-bromo-4-fluorobenzoic Acid (14). To a solution of aryl **13** (2.40 g, 15.5 mmol) in 20 mL of acetic acid was added the bromine (2.50 g, 0.8 mL, 15.6 mmol). The solution was stirred at room temperature for 15 h. The acetic acid was evaporated. The bulk was dissolved in 10 mL of ethanol and poured in 200 mL of water. The precipitate was collected by filtration and dried to give 3.11 g of acid **14**. Yield: 86%. ^{1}H NMR (acetone-d_6): δ 8.02 (d, 1H, Ph H), 6.80 (s, 3H, COOH and NH_2), 6.70 (d, 1H, Ph H).

5-Bromo-2-(3,3-diethyltriazo)-4-fluorobenzoic Acid (15). The aminoaryl **14** (4.5 g, 8.3 mmol), 3 mL of hydrochloric acid, and 3 mL of water were charged and stirred in a vessel cooled with an ice−salt bath. A cold solution of sodium nitrite (1.11 g, 16 mmol) in 5 mL of water 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 cooled mixture of potassium carbonate (2.76 g, 20 mmol) and diethylamine (1.46 g, 2 mL, 20 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 CH_2Cl_2 as eluent to give 2.55 g of pure triazene **15**. Yield: 61%. ^{1}H NMR ($CDCl_3$): δ 13.93 (s, 1H, COOH), 8.41 (d, 1H, Ph H), 7.43 (d, 1H, Ph H), 3.94 (qu, 2H, NCH_2), 3.80 (qu, 2H, NCH_2), 1.44 (t, 3H, CH_3), 1.32 (t, 3H, CH_3).

Dodecyl 5-Bromo-2-(3,3-diethyltriazo)-4-fluorobenzoate (16). The substituted benzoic acid **15** (2.5 g, 7.86 mmol) dodecanol (1.49 g, 8 mmol), DCCI (1.65, 8 mmol), DMAP (150 mg, 1.22 mmol), and 50 mL of CH_2Cl_2 were charged in a single-necked flask topped with a calcium chloride guard tube, refluxed, and stirred for 15 h. Urea was filtered off, and the filtrate was washed with a 0.5 M HCl solution and then with a saturated $NaHCO_3$ solution. The solution was dried on Na_2SO_4, the solvent was removed, and the crude product was chromatographed (SiO_2, CH_2Cl_2/heptane, 1/1) to obtain 2.55 g of ester **16**. Yield: 89%. ^{1}H NMR ($CDCl_3$): δ 7.83 (d, 1H, Ph H), 7.23 (d, 1H, Ph H), 4.26 (t, 2H, $COOCH_2$), 3.76 (m, 4H, NCH_2), 1.73 (q, 2H, CH_2 β ester), 1.27 (s, 24H, CH_3 β amine and CH_2), 0.90 (t, 3H, CH_3).

Dodecyl 2-(3,3-diethyltriazo)-4-fluoro-5-[(trimethylsilyl)ethynyl]benzoate (17). The same method was used then for **6″** and **11″**. The reagents were bromoaryl **16** (3.39 g, 7 mmol), $PdCl_2$ (25 mg, 0.14 mmol), $CuOAc_2$ (28 mg, 0.14 mmol), PPh_3 (120 mg, 0.46 mmol), 30 mL of NEt_3, and finally TMSA (1.05 g, 1.5 mL, 10.6 mmol). After purification by column chromatography (SiO_2, CH_2Cl_2/heptane, 1/2), 3.31 g of the (trimethylsilyl)ethynyl derivative **17** was obtained. Yield: 94%. ^{1}H NMR ($CDCl_3$): δ 7.75 (d, 1H, Ph H), 7.18 (d, 1H, Ph H), 4.26 (t, 2H, $COOCH_2$), 3.78 (m, 4H, NCH_2), 1.72 (q, 2H, CH_2 β ester), 1.27 (s, 24H, CH_3 β amine and CH_2), 0.90 (t, 3H, CH_3), 0.27 (s, 9H, $SiCH_3$).

Dodecyl 4-Fluoro-2-iodo-5-[(trimethylsilyl)ethynyl]-benzoate (18). In a cooled and dry vessel topped with a cooler and a $CaCl_2$ guard tube were charged triazene **17** (3.30 g, 6.54 mmol), NaI (1.35 g, 9 mmol), 15 mL of CH_3CN, and trimethylsilyl chloride (1.81 g, 2 mL, 16.7 mmol). The mixture was stirred and heated at 60 °C for 45 min. The cooled mixture was poured in 100 mL of a $NaHCO_3$ saturated aqueous solution and then acidified to pH = 2 with concentrated hydrochloric acid. The mixture was extracted twice with 100 mL of ether. The combined organic fractions were washed with water and then dried on Na_2SO_4, and the solvent was

removed. The crude product was chromatographed (SiO_2, CH_2Cl_2/heptane, 1/4) to obtain 2.28 g of iodoaryl **18**. Yield: 66%. ^1H NMR ($CDCl_3$): δ 7.92 (d, 1H, Ph H), 7.72 (d, 1H, Ph H), 4.32 (t, 2H, $COOCH_2$), 1.78 (q, 2H, CH_2 β ester), 1.27 (s, 18H, CH_2), 0.89 (t, 3H, CH_3).

Dodecyl 4-(*N*-Dodecylamino)-5-ethynyl-2-iodobenzoate (19). The fluoro[(trimethylsilyl)ethynyl]aryl **18** (2.20 g, 4.14 mmol), dodecylamine (1.11 g, 6 mmol), and $NaHCO_3$ (0.7 g, 8.33 mmol) were charged with 10 mL of DMSO in a vessel. The mixture was stirred and heated to 80 °C for 24 h. The cooled mixture was then poured in cold water and stirred for 1 h. The precipitate was collected by filtration, and the derivative was purified by chromatography (SiO_2, CH_2Cl_2) to obtain 2.35 g of pure monomer **19**. Yield: 91%. Mp: 58−61 °C. ^1H NMR ($CDCl_3$): δ 7.93 (s, 1H, Ph H), 7.19 (s, 1H, Ph H), 4.91 (t, 1H, NH), 4.25 (t, 2H, $COOCH_2$), 3.46 (s, 1H, C≡CH), 3.18 (qu, 2H, NCH_2), 1.71 (m, 4H, CH_2 β ester and amine), 1.27 (s, 36H, CH_2), 0.89 (t, 6H, CH_3). Anal. Calcd for $C_{33}H_{54}NO_2I$: C, 63.55; H, 8.73; N, 2.25. Found: C, 63.57; H, 8.80; N, 2.09.

Polymerization. The A-ϕ-A + B-ϕ-B copolymerization was performed by Heck coupling, using a palladium complex as catalyst.

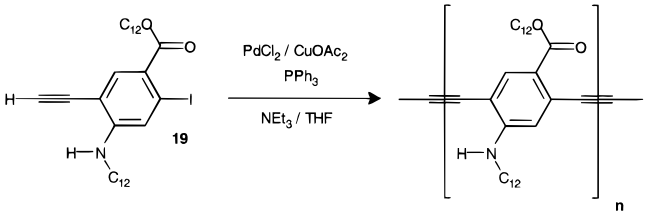
The monomers (1.8 mmol of each), palladium chloride (35 mg, 0.2 mmol), copper acetate (6 mg, 0.03 mmol), triphenylphosphine (210 mg, 0.8 mmol), triethylamine (50 mL), and tetrahydrofuran (50 mL), all dry and degassed, were put under nitrogen in a two-necked 250 mL flask equipped with a magnetic stirrer and a reflux condenser. The degassed reaction mixture was heated at 85 °C and stirred under nitrogen for 3 days. The precipitated ammonium salt was filtered off and washed with THF, keeping the organic phases together. The solvents were removed, and the residue was dissolved in 5 mL of hot THF, poured in 200 mL of cold methanol to precipitate, centrifuged, and then dried in vacuum. The remaining monomers and smallest oligomers were removed by preparative SEC to obtain the polymer.

pPYNC$_{12}$. Yield: 81%. ^1H NMR ($CDCl_3$): δ 6.9 (m, 2H, Ph H), 4.3 (m, 1H, NH), 3.1 (m, 6H, $N(CH_2)$, 1.8 (m, 6H, CH_2 β amines), 1.3 (m, 54H, CH_2), 0.9 (m, 9H, CH_3). Anal. Calcd: C, 78.28; H, 11.65; N, 4.15. Found: C, 76.50; H, 11.04; N, 3.98; Br, 4.21.

cpPYNC$_{12}$A. Yield: 87%. Very bad resolution for NMR spectra. Anal. Calcd: C, 82.20; H, 9.89; N, 3.19. Found: C, 80.93; H, 9.26; N, 2.98; Br, 4.72.

pPYNC$_{12}$COOC$_1$. Yield: 58%. ^1H NMR ($CDCl_3$): δ 8.2 (m, 1H, Ph H), 6.8 (m, 1H, Ph H), 4.0 (m, 3H, $COOCH_3$), 3.6 (m, 1H, NH), 3.2 (m, 2H, NCH_2), 1.8 (m, 2H, CH_2 β amine), 1.3 (m, 18H, CH_2), 0.9 (m, 3H, CH_3). Anal. Calcd: C, 73.84; H, 8.73; N, 3.91; O, 8.94. Found: C, 74.01; H, 8.99; N, 3.29; O, 9.34; Br, 4.57.

The A-ϕ-B homopolymerization of the iodoethynylaryl monomer was also performed by Heck coupling, using the following mechanism:



pPYNC$_{12}$COOC$_{12}$. The same polymerization method was used then for the other polymers, with the iodoethynylaryl (2.25 g, 3.6 mmol), $PdCl_2$ (35 mg, 0.2 mmol), $CuAc_2$ (6 mg, 0.3 mmol), PPh_3 (210 mg, 0.8 mmol), 30 mL of dry NEt_3, and 30 mL of dry THF. After precipitation and purification by SEC, 1.09 g of polymer was obtain. Yield: 61%. ^1H NMR ($CDCl_3$): δ 8.2 (m, 1H, Ph H), 6.9 (m, 1H; Ph H), 4.3 (m, 2H, $COOCH_2$), 3.6 (m, 1H, NH), 3.2 (m, 2H, NCH_2), 1.8 (m, 4H, CH_2 β amine and ester), 1.3 (m, 36H, CH_2), 0.9 (m, 6H, CH_3). Anal. Calcd: C, 76.42; H, 10.29; N, 2.71. Found: C, 75.24; H, 9.78; N, 2.32; I, 4.41.

Instruments and Characterization Methods. The polymer molecular weights have been obtained by size exclusion chromatography (SEC) in eluent THF with the coupled detection of refractive index and light scattering on a previously described apparatus.[13] The infrared spectra of thin solid films deposited on KBr plates were recorded on a Perkin-Elmer 983 infrared spectrophotometer. The ultraviolet absorption spectra were measured in THF solution or in cast solid films on quartz substrates, with a Shimadzu UV-2101PC UV−vis or a Hitachi U3000 UV−vis scanning spectrophotometer. Fluorescent measurements have been performed on a Hitachi F-4010 scanning spectrophotometer. Raman scattering measurement were made with a 1061 nm Nd−Yag laser line and a Brüker FTIR spectrometer (IFS 66 and FRA 106), which have has described elsewhere.[8]

The nonlinear optical measurements were performed on thin films using degenerated four wave mixing (DFWM). The experimental setup, which is already described in a previous paper,[14] uses 60 fs CPM pulses at 620 nm which are amplified with a 5 kHz repetition rate copper vapor laser.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7. The melting points were determined with an electrothermal digital melting point apparatus or by DSC.

^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ with a Brüker AC-200F spectrometer at room temperature or with a variable-temperature probe.

The molecular modeling was performed using software Sybyl from Tripos, running on an Indigo 2 work station from Silicon Graphics.

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