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Poly[3-(alkoxyphenyl)thiophenes]: Synthesis and Linear and Nonlinear Optical Properties

Lucie Robitaille and Mario Leclerc[*]

Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada

Claire L. Callender

Communications Research Center, P.O. Box 11490, Station H,
Ottawa, Ontario, K2H 8S2, Canada

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Poly[3-(alkoxyphenyl)thiophene] derivatives were chemically and electrochemically synthesized. It has not been possible to obtain soluble, highly conjugated poly[3-(methoxyphenyl)-thiophenes] while chemically prepared poly[3-((octyloxy)phenyl)thiophenes] were found to be completely soluble in common organic solvents. Temperature-dependent UV–visible absorption measurements on these polymers have revealed that the chemical structure as well as the nature and the position of the alkoxy chain on the phenyl ring have a strong influence on the linear optical properties. Third harmonic generation measurements at 1.053 μm were carried out on spin-coated films of poly[3-(4′-(octyloxy)phenyl)thiophene] and poly[3-(2′-(octyloxy)phenyl)-thiophene]. $\chi^{(3)}$ values of about 10^{-12} esu were obtained which are similar as those obtained with other polythiophene derivatives.

Introduction

Nonlinear optical materials have attracted great attention because of their potential applications in ultrafast and highly efficient devices for optical communication, information processing, storage, and computing.[1-4] During the past few years, it has been demonstrated that organic materials possess many advantages over existing inorganic materials, for example, ease of processing, good chemical, and thermal stability, versatility of synthesis, and fast optical nonlinear responses.[5,6]

Earlier studies by Hermann et al.[7] and theoretical work by Rustagi and Ducuing[8] have established the importance of an extended π-system in increasing the third-order nonlinear susceptibilities ($\chi^{(3)}$). Conjugated polymers, because of the π-electron delocalization along the polymer backbone, are expected to show large third-order nonlinear properties. Indeed, relatively large optical nonlinearities (10^{-12}–10^{-9} esu) have been observed by several research groups in neutral π-systems such as polyacetylenes,[9-12] polythiophenes,[13-19] polyanilines,[20,21] poly(*p*-phenylenevinylenes)[22,23] and other aromatic polymers.[24-26]

Recently, Prasad and Reinhardt[27] have measured the third-order nonlinear optical susceptibilities of a large number of aromatic model compounds. They have found that (1) a thiophene ring in a conjugated structure is more efficient than any other heteroaromatic ring in increasing optical nonlinearity, (2) the presence of an aromatic group in the side chain produces a two-dimensional π-conjugation that also increases the optical nonlinearity, and (3) the presence of an alkoxy pendant group on an aromatic ring enhances $\chi^{(3)}$ values.

To test these observations, Callender et al.[13] have performed third harmonic generation measurements on a series of alkyl- and alkoxy-substituted polythiophenes. They have observed only a small effect of these substituents on the $\chi^{(3)}$ values.

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[*] To whom correspondence should be addressed.

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Following the concepts developed by Prasad and Reinhardt,[27] another possibility to enhance the nonlinear optical effects could be the introduction of an aromatic side group on a polythiophene backbone. In this regard, Sato et al.[28] have recently reported the synthesis of poly(3-phenylthiophene), but this polymer has been found to be insoluble and infusible. However, it is well-known that the addition of long flexible side chains on the conjugated backbone enhances the solubility of the polymer.[29–33] For example, Pei et al.[34,35] have reported the synthesis and characterization of a processable poly[3-(4′-octylphenyl)thiophene].

Moreover, the linear optical properties of conjugated polymers can also exhibit very interesting features for applications in some optical devices. For example, some polythiophene derivatives undergo some thermally induced conformational transitions which give rise to thermochromic properties.[36–40] Indeed, there is a strong coupling between the electronic structure and the backbone conformation of conjugated polymers,[41] which explains why conformational changes are accompanied by spectral changes (chromism).

Therefore, to develop novel well-defined processable polythiophenes with interesting linear and nonlinear optical properties, chemical and/or electrochemical synthesis of ortho, meta, and para derivatives of 3-(alkoxyphenyl)thiophenes was carried out. The linear optical properties of poly[3-(*o*-,*m*-,*p*-methoxyphenyl)thiophenes] and poly[3-(*o*-,*m*-,*p*-(octyloxy)phenyl)thiophenes] were analyzed as well as the nonlinear optical properties of spin-coated films of poly[3-(4′-(octyloxy)phenyl)thiophene] and poly[3-(2′-(octyloxy)phenyl)thiophene].

Results and Discussion

Polymer Characterization. The oxidation potential of the monomers are listed in Tables I and II. Since the substituents are electron-donating groups, values of oxidation potentials lower than the value of the unsubstituted thiophene (E_{ox} = 2.06 V vs SCE[42]) were effectively expected. However, it is important to note that the strength of the electron-donating effect of the substituent is highly dependent upon the position of the alkoxy group on the phenyl ring.

Table I. Summary of Properties of Chemically and Electrochemically Prepared Poly[3-phenylthiophene] and Poly[3-(methoxyphenyl)thiophenes]

			λ_{max} (nm)	
polymer	E_{ox},[c] (V vs SCE)	E_{ox}[d] (V vs SCE)	in the solid state	CHCl$_3$ solution
poly[3-(4′-methoxyphenyl)thiophene][a]	1.30	1.06 2.06	412	404
poly[3-(3′-methoxyphenyl)thiophene][a]	1.70	1.09 1.95	368	358
poly[3-(2′-methoxyphenyl)thiophene][a]	1.80	0.93 1.93	424	418
poly[3-phenylthiophene][b]	1.66	1.38	520	
poly[3-(4′-methoxyphenyl)thiophene][b]	1.30	0.95 1.83	520	
poly[3-(3′-methoxyphenyl)thiophene][b]	1.70	1.23 1.98	<300	
poly[3-(2′-methoxyphenyl)thiophene][b]	1.80	0.97 1.95	512	

[a] Chemically prepared polymers. [b] Electrochemically prepared polymers. [c] Oxidation potential of the monomer. [d] Oxidation potential of the polymer.

Table II. Summary of Properties of Chemically Prepared Poly[3-((octyloxy)phenyl)thiophenes]

			λ_{max} (nm)	
polymer	E_{ox}[a] (V vs SCE)	E_{ox}[b] (V vs SCE)	in the solid state	CHCl$_3$ solution
poly[3-(4′-(octyloxy)phenyl)thiophene]	1.34	1.14 1.92	400	396
poly[3-(3′-(octyloxy)phenyl)thiophene]	1.46	1.03 1.90	362	364
poly[3-(2′-(octyloxy)phenyl)thiophene]	1.67	0.95 1.90	422 542 (sh) 588 (sh)	448

[a] Oxidation potential of the monomer. [b] Oxidation potential of the polymer.

The chemical polymerization of the (methoxyphenyl)thiophenes gave polymers that are only partially soluble (≈40–50%) in common organic solvents. These results are not particularly surprising since only poly(3-alkylthiophenes) with side chains larger than the propyl group are completely soluble.[29] The soluble neutral para and ortho polymers exhibit an absorption maximum slightly above 400 nm in solution and in the solid state (Table I). The meta derivative is less conjugated with an absorption maximum for the soluble fraction at 358 nm in solution and at 368 nm in the solid state. These polymers are electroactive, and the soluble fractions exhibit an oxidative peak around 1 V vs SCE. The oxidation peak of the phenyl groups, which are more difficult to oxidize, appears around 2 V. Therefore, the neutral form of these polymers is very stable in air.

The electropolymerized poly[3-(methoxyphenyl)thiophenes] are completely insoluble in common organic solvents. With the exception of the meta derivative, the electropolymerized polymers have better conjugation length (their absorption maxima are higher than 500 nm) and lower oxidation potentials than the corresponding chemically prepared polymers (Table I). Their better properties and lower solubility could be related to a more regulated structure.

As expected, chemical oxidation of the 3-((octyloxy)phenyl)thiophenes gave polymers that are completely soluble in common organic solvents such as chloroform, dichloromethane, and tetrahydrofuran. Once again, poor properties have been observed for the meta derivative

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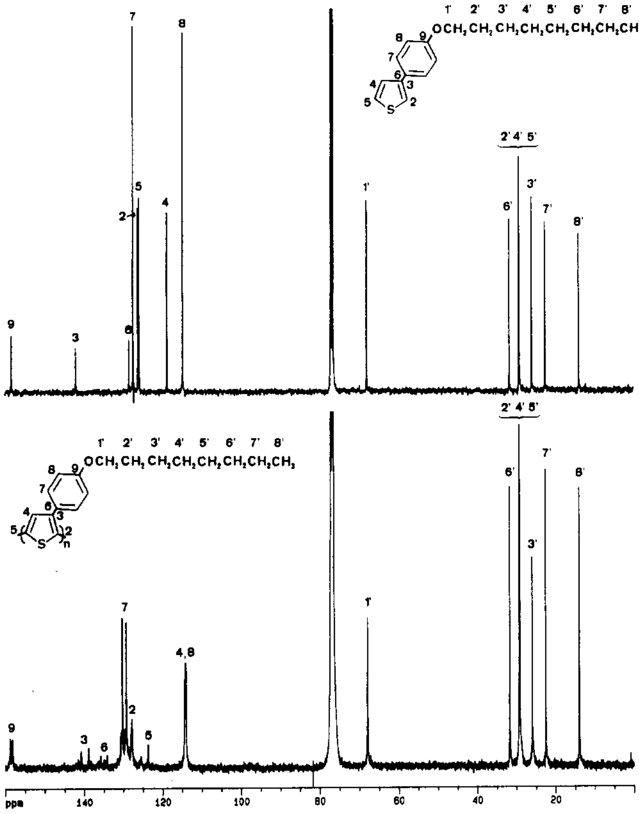

Figure 1. ^{13}C NMR spectra of 3-(4'-(octyloxy)phenyl)thiophene (top) and poly[3-(4'-(octyloxy)phenyl)thiophene] (bottom) in $CDCl_3$.

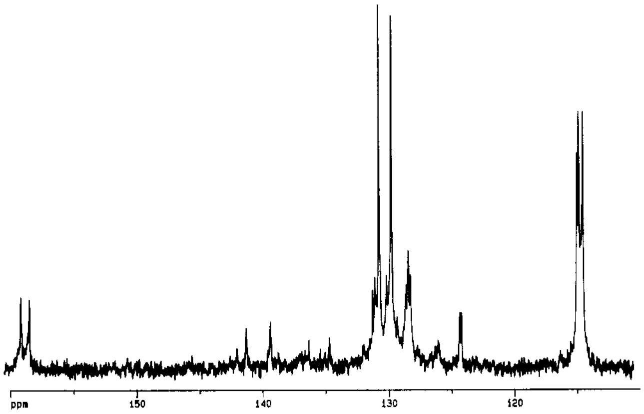

Figure 2. Aromatic area of the ^{13}C NMR spectrum of poly[3-(4'-(octyloxy)phenyl)thiophene].

(Table II). Furthermore, it has been impossible to get clear information about its chemical structure from NMR and IR spectroscopies. Indeed, it seems that the polymerization of the meta-substituted derivative does not lead to a regular and conjugated material. Poly[3-(4'-(octyloxy)phenyl)thiophene] has a short conjugation length apparently due to the poor regioregularity of the polymer as can be observed by NMR spectroscopy. The ^{13}C NMR spectra of [3-(4'-(octyloxy)phenyl)thiophene] and the corresponding polymer are presented in Figures 1 and 2. Assignments were done following previous results reported by Pei et al.[35] and Ueda et al.[43] Clearly, many carbon atoms in the spectrum of the polymer give rise to two peaks of comparable intensity. On the basis of previous

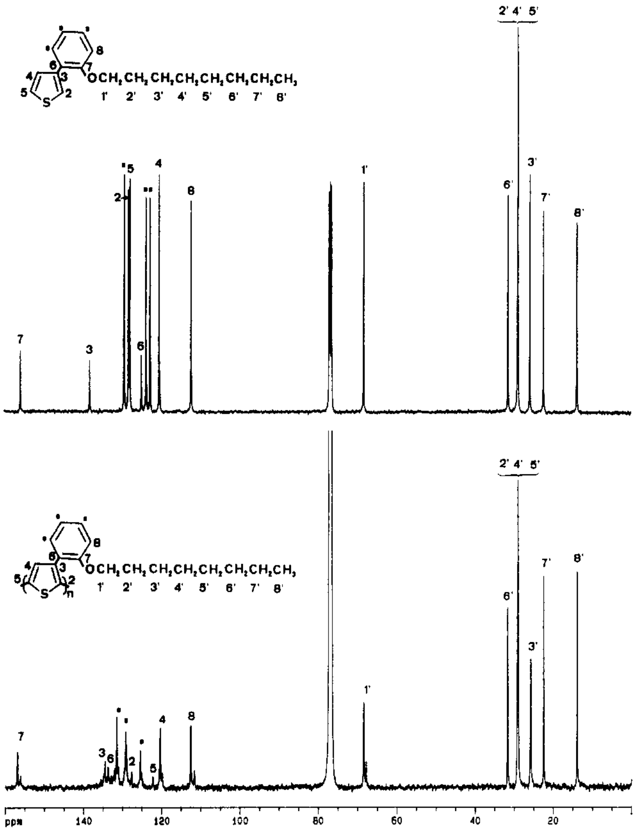

Figure 3. ^{13}C NMR spectra of 3-(2'-(octyloxy)phenyl)thiophene (top) and poly[3-(2'-(octyloxy)phenyl)thiophene (bottom) in $CDCl_3$.

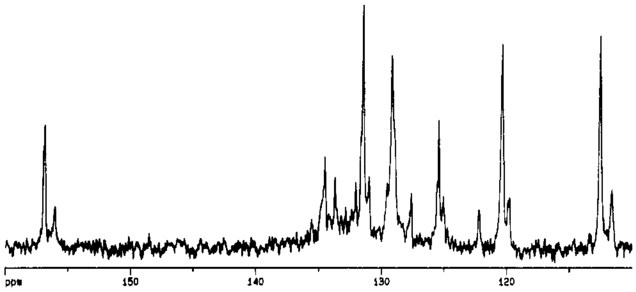

Figure 4. Aromatic area of the ^{13}C NMR spectrum of poly[2'-(octyloxy)phenyl thiophene].

results obtained with other alkyl- and phenyl-substituted polythiophenes,[31,32,43–45] it is believed that these two signals can be related to different types of linkage in the polymer. It has been proposed that one signal could be related to head-to-head couplings and the other one to head-to-tail couplings. The intensity of signals in ^{13}C NMR spectroscopy is usually dependent upon the relaxation time of the atoms, and thus it cannot be used for quantitative analysis. However, in this case, it can be assumed that these two different types of coupling should not have a strong influence on the relaxation time. Consequently, a peak ratio of 1:1 should indicate a totally random polymer, i.e., 50% of the linkages are of the head-to-head type and 50% are of the head-to-tail type.[43,44] Since head-to-head linkages, especially with a phenyl group on the side chain, can cause rotational defects along the polymer back-

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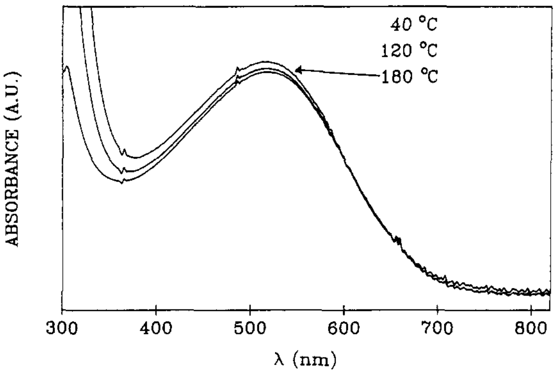

Figure 5. Temperature-dependent UV–visible absorption spectra of poly[3-phenylthiophene] in the solid state.

bone,[45–47] the high proportion of these linkages in poly[3-(4′-(octyloxy)phenyl)thiophene] contributes to the observed short conjugation length and relatively high oxidation potential.

As shown in Figures 3 and 4, similar splittings were also observed for poly[3-(2′-(octyloxy)phenyl)thiophene]. However, in this case, the peak ratio is about 3:1. Since the properties discussed above are better for this polymer than for the former, it is possible to assume that 75% of the linkages are of the head-to-tail type. It seems that the alkoxy side chain in the ortho position on the phenyl group creates more steric hindrance, increasing the selectivity for head-to-tail linkages. In agreement with the NMR results which have revealed a distribution of two types of coupling, poly[3-(4′-(octyloxy)phenyl)thiophene] and poly[3-(2′-(octyloxy)phenyl)thiophene] have been found to be amorphous with a glass transition at 22 and 20 °C, respectively.

The electropolymerization of the 3-((octyloxy)phenyl)thiophenes were unsuccessful. Since the monomers were insoluble in propylene carbonate, an attempt was made to electropolymerize in nitrobenzene or mixtures of nitrobenzene and propylene carbonate, on platinum, ITO or graphite electrodes, at various temperatures between 5 °C and room temperature and using different current densities. In all conditions, it was impossible to obtain polymers on the electrode.

It is also interesting to note that the intermediate 3-(hydroxyphenyl)thiophenes cannot be polymerized either chemically or electrochemically, in the experimental conditions that we have used for the methoxy and octyloxy derivatives.

Linear Optical Properties. Temperature-dependent UV–visible absorption measurements of these materials were also carried out, and some of these results are shown in Figures 5–7.

It has been shown that the nature and the length of the substituents has a strong influence on the optical properties of polythiophenes in the solid state.[40] Moreover, interesting thermochromic properties have been reported for some polythiophenes which have been attributed to a conformational transition of the backbone from a planar structure to a nonplanar form.[36–40] This transition seems to be related to an increase of the disorder in the side chains which then induces the twisting of the main polymer chain.[39,40]

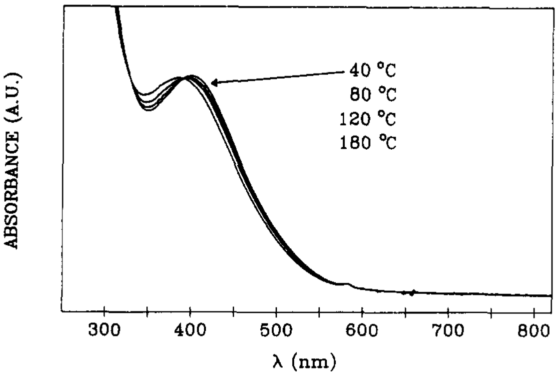

Figure 6. Temperature-dependent UV–visible absorption spectra of poly[3-(4′-(octyloxy)phenyl)thiophene] in the solid state.

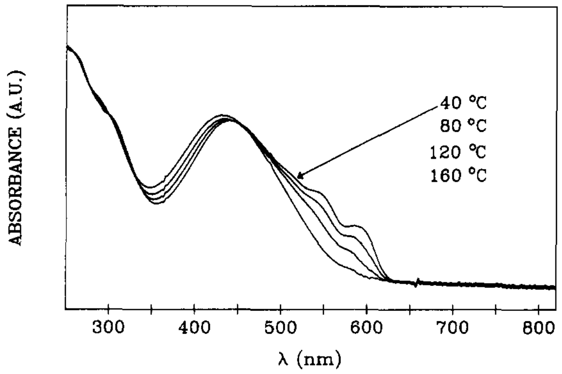

Figure 7. Temperature-dependent UV–visible absorption spectra of poly[3-(2′-(octyloxy)phenyl)thiopene] in the solid state.

Poly[3-phenylthiophene] (Figure 5) and all poly[3-(methoxyphenyl)thiophenes] did not show any thermochromic effect. Their respective maximum absorptions (λ_{max}) remain the same between 40 and 180 °C. Only a small increase of the absorption upon heating is observed and can be attributed to an increase of the absorption of the phenyl group in the UV range (i.e., 286 nm). It therefore seems that the presence of the methoxy group on the phenyl ring does not create enough disorder to give rise to a conformational transition of the main polymer chain when heated up to 180 °C.

However, if the size of the alkoxy substituent on the phenyl ring is increased, the polymers then exhibit different behavior (Figures 6 and 7). As mentioned above, due to its large proportion of head-to-head linkages, poly[3-(4′-(octyloxy)phenyl)thiophene] shows an absorption maximum at a relatively short wavelength. When the polymer is heated from 40 to 180 °C, its maximum of absorption shifts from 400 (3.10 eV) to 386 nm (3.21 eV) (Figure 6). According to the work of Roux et al.[40] on alkyl- and alkoxy-substituted polythiophenes, poly[3-(4′-(octyloxy)phenyl)thiophene] seems to have a twisted conformation at room temperature that can progressively undergo some localized modifications in its torsional angles leading to the observed small decrease of the conjugation length.

In contrast, poly[3-(2′-(octyloxy)phenyl)thiophene] exhibits an absorption maximum at 440 nm (2.82 eV) and two other absorption peaks at 542 (2.29 eV) and 588 nm (2.11 eV) at 40 °C (Figure 7). These two last peaks are believed to be associated with a relatively planar conformation of the main polymer chain. Indeed, the proportion of head-to-tail couplings is high enough to allow the formation of sequences of high conjugation length in this

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Table III. Refractive Indexes for Poly[3-((octyloxy)phenyl)thiophenes]

	n	
polymer	1053 nm	351 nm
poly[3-(4′-(octyloxy)phenyl)thiophene]	1.71	1.55
poly[3-(2′-(octyloxy)phenyl)thiophene]	1.71	1.54

Table IV. Magnitude ($\chi^{(3)}$ (-3ω; ω,ω,ω)) and Phase (Φ) of the Third-Order Nonlinear Susceptibilities for Poly[3-((octyloxy)phenyl)thiophenes]

polymer	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ (esu)	phase Φ (deg)
poly[3-(4′-(octyloxy)phenyl)thiophene]	0.75×10^{-12}	210 ± 25
poly[3-(2′-(octyloxy)phenyl)thiophene]	1.4×10^{-12}	240 ● 25

polymer, while the first maximum absorption at 422 nm should correspond to sequences with a higher content of head-to-head linkages. Upon heating, the absorption around 440 nm increases, while the absorption in the range 500–630 nm decreases. The presence of an isosbectic point during the transition indicates the coexistence of two distinct forms in the polymer, the observed transition being a variation of the ratio of these two phases. Upon heating, it is then assumed that the disorder created in the alkoxy side chain increases the steric hindrance which then forces the backbone to adopt a twisted structure. This conformational structure should be similar to that one occurring at low temperatures where the content of head-to-head couplings is important. This thermally induced transition of the backbone modifies also the refractive index (the absorption spectrum) of the material and could be therefore useful for some optical applications.

However, from these results, it is then obvious that a complete description of the thermochromic properties must take into account the structure of the polymer. For example, without any structural characterization and possible presence of ortho isomer,[35] Pei et al.[34] have mentioned that poly[3-(4′-octylphenyl)thiophene] is not thermochromic because the flexible alkyl chain, which is believed to be the driving force of the conformational transition, is too far from the conjugated backbone. On the other hand, Roux et al.[40] have shown that head-to-tail coupled poly[3-alkylthiophenes] are thermochromic, while head-to-head coupled poly[3-alkylthiophenes] are not. Moreover, it has been shown that poly[3-(2′-(octyloxy)phenyl)thiophene] with a high content of head-to-tail linkages can exhibit a thermochromic behavior. It is then not clear whether a perfectly head-to-tail coupled poly[3-(4′-alkylphenyl)thiophene] or poly[3-(4′-alkoxyphenyl)thiophene] would be thermochromic or not. Unfortunately, attempts to prepare such polymers in our laboratory have not yet been successful.

Nonlinear Optical Properties. Third harmonic generation measurements at 1.053 μm were carried out for poly[3-(4′-(octyloxy)phenyl)thiophene] and poly[3-(2′-(octyloxy)phenyl)thiophene]. The values of the refractive indices at 351 and 1053 nm for each polymer are given in Table III. The dispersion of the refractive indices was determined by a Kramers–Kronig analysis of the absorption data.

The magnitude, $\chi^{(3)}$, and phase, Φ, of third-order nonlinear susceptibilities have been determined for each polymer. Values are presented in Table IV. The magnitude for the $\chi^{(3)}$ values for poly[3-(4′-(octyloxy)phenyl)thiophene] and poly[3-(2′-(octyloxy)phenyl)thiophene] are 0.75×10^{-12} and 1.4×10^{-12} esu, respectively. The uncertainties in $\chi^{(3)}$ are estimated to be ±10%. The values of the phase of $\chi^{(3)}$ are in good agreement with previous data on this class of polymers[13,14,19] and are consistent with contributions to $\chi^{(3)}$ from two-photon resonances. The $\chi^{(3)}$ values are slightly lower than those determined for alkyl and alkoxy-substituted polythiophenes (i.e., 10^{-12}–10^{-11} esu).[13] However, it must be mentioned that alkyl- and alkoxy-substituted polythiophenes are known to be highly head-to-tail coupled (over 80%) and the synthesis of poly[3-((octyloxy)phenyl)thiophene] with a larger head-to-tail content would probably result in an increase in λ_{max} and a resultant increase in $\chi^{(3)}$. But it is likely that the $\chi^{(3)}$ values will still be in the same order of magnitude as the values obtained for poly(alkylthiophenes). Consequently, the presence of an aryl substituent does not seem to result in a significant enhancement of the magnitude of third-order nonlinear susceptibilities in polythiophenes. Indeed, third-order nonlinear properties of this class of materials seem to be predominantly dependent on the inherent electronic structure of the polymer backbones.[48] However, a possibility of enhancement of $\chi^{(3)}$ values could be the preparation of oriented materials.[22,49,50]

Conclusion

Novel aryl derivatives of polythiophene have been chemically and electrochemically synthesized. In the case of poly[3-(methoxyphenyl)thiophenes], electrochemical polymerization has led to polymers with better properties than the chemically prepared polymers. However, it has not been possible to obtain soluble, highly conjugated poly[3-(methoxyphenyl)thiophenes. Chemical polymerization of [3-((octyloxy)phenyl)thiophenes] has given polymers which are completely soluble in common organic solvents. ^{13}C NMR spectroscopy has shown that chemically prepared poly[3-(4′-(octyloxy)phenyl)thiophene] and poly[3-(2′-(octyloxy)phenyl)thiophene] have head-to-tail content of about 50% and 75%, respectively. UV–visible spectra have revealed that, at room temperature, the high head-to-head content in poly[3-(4′-(octyloxy)phenyl)thiophene] induces important steric interactions which force the main polymer chain to adopt a twisted conformation. On the other hand, due to its higher proportion of head-to-tail couplings, poly[3-(2′-(octyloxy)phenyl)thiophene] shows the presence of highly conjugated sequences. Temperature-dependent UV–visible absorption measurements have shown that the already twisted backbone of poly[3-(4′-(octyloxy)phenyl)thiophene] can undergo only some thermally induced localized fluctuations in its torsional angles leading to a small decrease of its conjugation length. On the other hand, poly[3-(2′-(octyloxy)phenyl)thiophene] has exhibited interesting thermochromic properties which are related to a conformational transition of the polymer backbone. These properties could be interesting to thermally modify the refractive index of this polymer. Finally, third harmonic generation measurements have indicated that the presence of aryl substituents does not increase the $\chi^{(3)}$ values of polythiophenes. Future improvements in third-order nonlinear materials may result from new polymer backbones or oriented films.

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Experimental Section

3-Bromothiophene, bromobenzene, *o*-, *m*-, and *p*-bromoanisole, iodotrimethylsilane, 1-iodooctane, and 3,4-dibromothiophene were obtained from Aldrich Chemical Co. and were used without further purification.

3-Phenylthiophene was obtained by a cross-coupling reaction between phenylmagnesium bromide and 3-bromothiophene in anhydrous ether in the presence of a nickel catalyst, according to the procedure described by Kumada et al.[51] The monomer was sublimed under reduced pressure [mp 88.5–89.5 °C (lit.[52] 92 °C)], yield 60%.

IR (cm^{-1}) 3150, 1585, 1455, 1205, 860, 790, 745, 685. ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 142.23, 135.72, 128.67, 126.99, 126.32, 126.21, 126.07, 120.14.

3-(4′-Methoxyphenyl)thiophene was obtained by a cross-coupling reaction between *p*-methoxyphenylmagnesium bromide and 3-bromothiophene following the same procedure that was used for the synthesis of 3-phenylthiophene. The residue was sublimed under reduced pressure [mp 115–118 °C (lit.[53] 130–131 °C)], yield 63%.

IR (cm^{-1}) 3100, 2950, 1605, 1500, 1240, 860, 825, 770. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 7.54 (2H, dt, J = 8.8 Hz and 2.2 Hz), 7.36 (3H, m), 6.94 (2H, dt, J = 8.8 Hz and 2.1 Hz), 3.85 (3H, s). ^{13}C NMR (75.4 MHz, CD$_2$Cl$_2$, ppm) 159.33, 150.46, 142.25, 128.84, 127.77, 126.46, 119.19, 114.46, 55.61.

3-(3′-Methoxyphenyl)thiophene was synthesized following the procedure used for the synthesis of the para derivative. The residue was first distilled [bp 120 °C/1.4 mmHg] and then chromatographed on a silica gel column using a mixture of chloroform/hexanes (7:3) as eluent [mp 37–39 °C], yield 57%.

IR (cm^{-1}) 3100, 2950, 1600, 1475, 1215, 865, 835, 760, 680. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.80–7.50 (7H, m), 3.86 (3H, s). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 159.85, 142.12, 137.15, 129.67, 126.29, 126.02, 120.39, 118.93, 112.34, 112.21, 55.15.

3-(2′-Methoxyphenyl)thiophene was obtained following the same experimental procedure as above. 3-(2′-(Methoxy)phenyl)thiophene was purified by distillation under reduced pressure [bp 120–122 °C/0.5 mmHg], yield 71%.

IR (cm^{-1}) 3100, 2950, 1600, 1475, 1240, 860, 780, 740. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.95–7.60 (7H, m), 3.86 (3H, s). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 156.24, 138.09, 129.49, 128.30, 128.07, 124.86, 124.14, 122.88, 120.59, 111.17, 55.17.

3-(4′-Hydroxyphenyl)thiophene:[54] To a solution of 3-(methoxyphenyl)thiophene (5.705 g, 0.030 mol) in chloroform (15 mL), iodotrimethylsilane (8.998 g, 0.045 mol) was added via a dry syringue. The reaction mixture was refluxed for 14 h under an atmosphere of argon. The mixture was then poured into methanol. Volatile solvents were evaporated. The residue was taken up in ether, washed with aqueous sodium bisulfite, aqueous sodium bicarbonate, and water, dried over magnesium sulfate, and concentrated. The residue was sublimed under reduced pressure [mp 186.5–187.5 °C], yield 77%.

^{1}H NMR (300 MHz, CDCl$_3$, ppm) 7.49 (2H, dt, J = 8.4 Hz and 1.7 Hz), 7.34 (3H, m), 6.87 (2H, dt, J = 8.3 and 1.6 Hz), 4.74 (1H, s).

3-(3′-Hydroxyphenyl)thiophene was synthesized following the same experimental procedure that was used in the synthesis of 3-(4′-hydroxyphenyl)thiophene. The residue was purified by chromatography on a silica gel column (eluent: chloroform/ethyl acetate, 9:1) [mp 91–93 °C], yield 48%.

^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.75–7.50 (7H, m), 4.78 (1H, s).

3-(2′-Hydroxyphenyl)thiophene was obtained following the same procedure that was used in the synthesis of the para and meta derivatives. The residue was distilled under reduced pressure [bp 168 °C/15 mmHg] and finally chromatographed on silica gel using chloroform as eluent, yield 40%.

^{1}H NMR (300 MHz, CDCl$_3$, ppm) 6.94–7.50 (7H, m), 5.29 (1H, s).

3-(4′-(Octyloxy)phenyl)thiophene was synthesized following a procedure described by Birosel.[55] A mixture consisting of 0.989 g (0.0056 mol) of 3-(4′-hydroxyphenyl)thiophene, 2.315 g (0.0096 mol) of 1-iodooctane, 1.047 g (0.0076 mol) of potassium bicarbonate and 2.5 mL of acetone was refluxed for 7 h. After being cooled to room temperature, the mixture was poured into water. The aqueous layer was extracted with ether. The combined organic layers were washed with dilute sodium hydroxide and then with distilled water. The ether solution is dried over sodium carbonate, and the solvent is evaporated. The solid was recrystallized in methanol [mp 91–92 °C], yield 59%.

IR (cm^{-1}) 3100, 2920, 1605, 1500, 860, 830, 765. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, ppm) 7.53 (2H, dt, J = 8.8 Hz and 2.2 Hz), 7.37 (3H, m), 6.92 (2H, dt, J = 8.9 Hz and 2.2 Hz), 3.97 (2H, t, J = 6.6 Hz), 1.78 (2H, m), 1.48–1.20 (10H, m), 0.89 (3H, t, J = 6.8 Hz). ^{13}C NMR (100.6 MHz, CDCl$_3$, ppm) 158.43, 142.05, 128.49, 127.42, 126.16, 125.86, 118.71, 114.75, 68.07, 31.72, 29.27, 29.22, 29.13, 25.97, 22.55, 13.96.

3-(3′-(Octyloxy)phenyl)thiophene was obtained following the same procedure that was used in the synthesis of 3-(4′-(octyloxy)phenyl)thiophene. The residue was distilled under reduced pressure (bp 162–166 °C/0.3 mmHg), yielding 51% of a white solid with a melting temperature at 28–30 °C.

IR (cm^{-1}) 3100, 2950, 1590, 1470, 1215, 860, 840, 760, 680. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 7.43–6.80 (7H, m), 3.98 (2H, t, J = 6.6 Hz), 1.79 (2H, m), 1.5–1.3 (10H, m), 0.89 (3H, t, J = 6.8 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$, ppm) 159.41, 142.19, 137.07, 129.60, 126.28, 125.93, 120.28, 118.70, 112.89, 112.83, 67.91, 31.71, 29.27, 29.22, 29.14, 25.97, 22.55, 13.98.

3-(2′-(Octyloxy)phenyl)thiophene was synthesized following the same experimental procedure that was used in the synthesis of the para and meta derivatives. The residue was distilled under reduced pressure (bp 150 °C/0.3 mmHg), yielding 50% of a white solid with a melting temperature at 36–39 °C.

IR (cm^{-1}) 3100, 2920, 1595, 1460, 1240, 860, 780, 740. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) 7.64–6.94 (7H, m), 4.01 (2H, t, J = 6.6 Hz), 1.81 (2H, m), 1.52–1.26 (10H, m), 0.89 (3H, t, J = 6.8 Hz). ^{13}C NMR (100.6 MHz, CDCl$_3$, ppm) 156.15, 138.51, 129.72, 128.63, 128.25, 125.31, 124.12, 123.06, 120.73, 112.60, 68.62, 31.86, 29.3 (3 carbon atoms), 26.24, 22.71, 14.15.

Chemical Polymerization. Polymers were prepared by chemical oxidation of the monomers using iron trichloride according to a procedure similar to that of Sugimoto et al.[56] In a 100-mL three-neck flask, 10 mmol of iron trichloride was dissolved in 25 mL of chloroform under argon and 2.5 mmol of the monomer in 20 mL of chloroform was added dropwise. The mixture was stirred for 24 h at room temperature. Then the solution was precipitated into methanol (1 L). The precipitate was collected on a Büchner funnel and washed with methanol. The polymer was then washed by Soxhlet extraction using methanol and dried under reduced pressure at room temperature.

Electrochemical Polymerization. The polymers were electropolymerized following a procedure similar to that of Sato et al.[28] The films were prepared in a propylene carbonate solution containing monomer (0.1 M) and tetrabutylammonium hexafluorophosphate (0.02 M) as an electrolyte. The oxygen in the solution was swept out with argon prior to the electrolysis. The polymerization was performed at 5 °C by applying a constant current density of 1 mA/cm^2 on platinum electrodes. Polymerization time varied from 5 min to 1 h, and the polymer was obtained as a film covering the anode of the electrolysis cell. The neutral polymer was obtained by reversing the polarity of the electrodes.

Characterization. NMR spectra were obtained in deuterated chloroform or methylene chloride solutions on a 300-MHz Varian instrument. The ^{13}C NMR spectra of polymers (and their corresponding monomers) were performed on a 400-MHz Bruker pulsed Fourier transform instrument. UV–visible spectra (except for thin films used for third harmonic generation measurements; see below) were recorded on a Hewlett-Packard diode array

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spectrophotometer (Model 8452A). A temperature control unit was installed to allow measurements over the range from 25–200 °C. The sample temperature was measured by a thermocouple with a maximum error of ± 2.0 °C. UV–visible absorption measurements were taken from neutral polymers dissolved in chloroform, from neutral polymer films cast on quartz plates or from neutral polymers electropolymerized on ITO (indium tin oxide) coated glass electrode. Melting temperatures are measured using a Gallenkamp melting point apparatus. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC-4 apparatus calibrated with an ultrapure indium (T_m = 156.6 °C and ΔH_m = 28.4 J/g) sample. Cyclic voltammetry was carried out in an one-compartment cell using an EG&G PAR (Model 273) potensiostat/galvanostat. These measurements were performed in dry acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The oxidation potential were determined at a scan rate of 100 mV/s versus a saturated calomel electrode (SCE).

Third Harmonic Generation Measurements. Thin films were deposited by spinning chloroform solutions of each polymer onto glass microscope slides. Surfaces were prepared by spinning on a thin film of commercial photoresist adhesion promoter (hexamethyldisilane). Concentrations of polymer solutions were typically 20–25 mg/mL. The solutions were filtered through a 0.5-μm Millex-FH_{13} filter, deposited onto substrates from a syringe and spun at 3000 rpm for 15 s. The resulting films had thickness in the range 160–180 nm. Absorption spectra of films were recorded immediately after production using a Cary 3 UV–visible spectrophotometer. Films were subsequently stored protected from daylight.

Film thickness and refractive indexes at 365 nm were estimated using a Rudolph 436 spectroscopic ellipsometer. The order of the film thickness was confirmed using a Michelson interferometer attachment to an optical microscope. We were unable to make accurate ellipsometric measurements at 1053 nm. A Kramers–Kronig analysis was used to determine refractive indexes at this wavelength (the method of analysis has been described in detail previously[13]) and also to make the short extrapolation from values at 365–351 nm. Uncertainties in indexes from ellipsometric measurements are estimated to be ±0.005. Uncertainties in the Kramers–Kronig analysis are dependent on the quality of the fit and on the absence of significant absorpion bands outside the observed wavelength region. In all cases we were able to generate fits with close agreement to the absorption data and estimate the uncertainty in the dispersion to be ±0.01.

Third harmonic generation measurements were carried out using a Quantronix mode-locked Q-switched Nd:YLF laser operating at 1.053 μm. Individual 60-ps pulses were extracted from the mode-locked train by a Pockels cell. The repetition rate was 40 Hz and the extracted pulse energy was approximately 150 μJ. A sample holder to align the film vertically and facing the detector was mounted on a rotation stage housed within an evacuated chamber. The beam was focused with a 30-cm focal length lens onto the sample. This arrangement gave power densities of ≈100 MW cm^{-2} at the film. All the films supported these power densities with no signs of damage. Third harmonic generation at 351 nm from the sample was collected with short (5 cm) focal length lens and detected by a Hamamatsu R943-02 photomultiplier with a series of filters mounted in front to cut out the incident radiation at 1.053 μm (2 Corning 7-54 glass filters, 2 Hoya U340 glass filters and an Omega 351-nm bandpass filter). Maker fringes were generated by rotating the sample through −30° to +30° from normal. The polarization of the laser beam was maintained parallel to the rotation axis by a half-wave plate. Signals from the photomultiplier were collected using an EG&G PARC 162 boxcar averager and an IOTech ADC488 A/D converter. Rotation of the sample stage and data collection were controlled by a personal computer.

Third harmonic generation measurements were carried out on thin films of each polymer. Reference data from glass substrates were obtained by washing a portion of the film off each sample. We used $\chi^{(3)}(-3\omega; \omega,\omega,\omega) = 4.67 \times 10^{-14}$ esu at 1053 nm for the glass as a reference value.[57] Maker fringes (oscillation in intensity) are observed in the detected third harmonic signal as the sample is rotated. The method of analysis to obtain the magnitude and the phase of $\chi^{(3)}(-3\omega; \omega,\omega,\omega)$ has been described in detail elsewhere.[13,58] The absorbance of the films at the third harmonic frequency and hence the complex refractive index of the film were accounted for. Contributions to the fringe pattern from air were not considered as the measurements were carried out under vacuum.

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