



**Universidade de São Paulo**

**Biblioteca Digital da Produção Intelectual - BDPI**

---

Departamento de Física e Ciências Materiais - IFSC/FCM

Artigos e Materiais de Revistas Científicas - IFSC/FCM

---

2009

# Synthesis and characterization of copolymers of alkyl- and azo-thiophenes: chromic properties and photoinduced birefringence

---

Journal of Applied Polymer Science, Hoboken : John Wiley and Sons, v. 114, n. 2, p. 680-687, Oct. 2009

<http://www.producao.usp.br/handle/BDPI/49445>

*Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo*

# Synthesis and Characterization of Copolymers of Alkyl- and Azo-Thiophenes: Chromic Properties and Photoinduced Birefringence

Vanessa C. Gonçalves, Lígia M. M. Costa, Marcos R. Cardoso, Cleber R. Mendonca, Débora T. Balogh

Instituto de Física de São Carlos, USP, CP 369, São Carlos 13560-970, SP, Brazil

Received 2 December 2008; accepted 5 April 2009

DOI 10.1002/app.30575

Published online 8 June 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polyazothiophene is a type of polythiophene derivative that combines the electrical and luminescent properties of polythiophenes with the photoisomerization property of azopolymers. Extensive efforts have been made to improve the properties of polyazothiophenes, such as -solubility, optical, and chromic properties. We report the preparation of copolymers of an alkylthiophene (3-octylthiophene, 3-OT) and an azothiophene (2-[N-ethyl-N-[4-[(4-nitrophenyl)azo]phenyl]amino]ethyl 3-thienylacetate, 3-AzoT) in different ratios as an alternative route to improve these properties. The azosubstituted monomer contents in these copolymers were 6, 9, 12, and 51% (in mol), as evaluated by elemental analysis. Their chemical structures were confirmed by FTIR and  $^1\text{H-NMR}$ . HPSEC

and thermal analysis were used to characterize the polymers. The presence of thermochromic and solvatochromic properties was demonstrated by UV-Vis spectroscopy. Optically induced birefringence was detected only in polymers with 12 and 51 mol % of azo-units. The introduction of different ratios of the azothiophene in the copolymer alters the polymer solubility and emissive properties. The results indicate that the polyazothiophene copolymers presented are promising active layers for optical devices and sensors. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 680–687, 2009

**Key words:** polythiophene; azopolymers; conjugated polymers; chromism; photoinduced birefringence

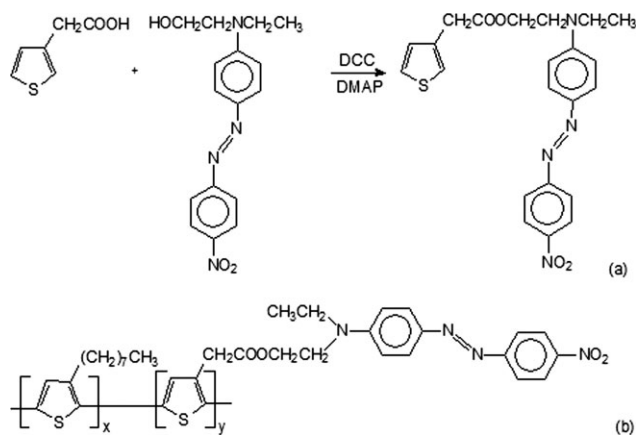
## INTRODUCTION

Polymers containing azobenzene moieties are promising materials for applications in optoelectronics and photonics, such as, optical switching, optical storage, surface relief gratings, holograms, and optical modulators.<sup>1</sup> The main property of these polymers is the reversible *trans-cis* photoisomerization of the azobenzene chromophore, which is influenced by the type of azobenzene ring substituent, the nature of polymer backbone, and presence of spacer groups.<sup>1–4</sup> Among the possible polymer backbones that can be used for preparing polymers containing azochromophores, conjugated ones seem to be an interesting option because of their conductivity on doping.<sup>5,6</sup> However, only a few papers on conjugated polymers containing azobenzene moieties have been reported. Matsui et al.<sup>7</sup> showed optical anisotropy of azobenzene side chains of poly(*p*-phenylenevinylene) and polyacetylene derivatives. Chen et al.<sup>8</sup> synthesized polypyrrole-based liquid crystalline polymer containing azobenzene groups. Huang

and Wan<sup>9</sup> reported the *trans-cis* photoisomerization, on irradiation with linearly polarized light, of an azobenzene side-chain of sulfonic-acid-doped PANI nanostructures. Polythiophene derivatives are the most studied class of conjugated polymers bearing azobenzene moieties<sup>10–12</sup> because of their good thermal and environmental stability and easier functionalization compared with other conjugated polymers.<sup>12,13</sup> Random polythiophene derivatives are synthesized by the introduction of different groups at the 3- and/or 4- positions of the thiophene rings, which are subsequently polymerized with a  $\text{FeCl}_3$ -based oxidative reaction.<sup>14</sup>

Polyazothiophenes have been used in thermochromic, solvatochromic, and photochromic studies.<sup>10,11,13,15–18</sup> The development of these chromic features has an important role for technological applications, mainly in the field of sensors.<sup>19–21</sup> The photoinduced birefringence of polyazothiophenes was first studied by Aubertin and Zhao<sup>22</sup> with a homopolymer of azothiophene. In that paper, a very small anisotropy was observed only when the sample was kept above the room temperature but below the glass transition temperature.<sup>22</sup> On the other hand, photoinduced birefringence was successfully achieved in a similar polyazothiophene homopolymer film at room temperature.<sup>23</sup>

Correspondence to: D. T. Balogh (balogh@if.sc.usp.br).



**Figure 1** (a) Synthetic scheme to Disperse red 1 functionalized thiophene monomer (3-AzT). (b) Poly[2-[N-ethyl-N-[4-[(4-(4-nitrophenyl)azo]phenyl)amino]ethyl] 3-thienylacetate-co-3-octylthiophene].

In general, the homopolymers of polyazothiophenes have limited solubility in common organic solvents and low molecular weights.<sup>23–27</sup> Several methods have been proposed to improve these properties, such as the copolymerization between azothiophene and alkylthiophene units<sup>26,27</sup> or post-polymerization functionalization reactions on soluble precursors.<sup>28</sup> In this work, we report on the preparation of copolymers of 3-octylthiophene and 3-azothiophene in different proportions to evaluate the influence of azosubstituted comonomers in the polythiophene properties, such as thermochromic and solvatochromic properties as well as photoinduced birefringence.

## EXPERIMENTAL

### Monomer synthesis

The 3-octylthiophene was purchased from Aldrich and used without purification. The (2-[N-ethyl-N-[4-[(4-(4-nitrophenyl)azo]phenyl)amino]ethyl] 3-thienyl)acetate was synthesized according to the procedure reported in Ref. 15. The monomer synthesis scheme is shown in Figure 1(a). Under nitrogen atmosphere, 3.58 g (17.4 mmol) of 1,3-dicyclohexylcarbodiimide, DCC, (Aldrich, 99%) in 100 mL of dichloromethane was added to a solution of 2.00 g (6.36 mmol) of Disperse Red 1 (Aldrich, 95%), 0.90 g (6.4 mmol) of 3-thiophenoacetic acid (Aldrich, 98%) and 0.080 g (0.64 mmol) of 4-(dimethylamino)pyridine, DMAP, (Aldrich, 99%). The mixture was stirred for 24 h at room temperature. Dicyclohexylurea was eliminated by washing with acetic acid solution (5%) followed by filtration. Product purification was accomplished by column chromatography on silica gel 60 (eluent, dichloromethane : hexane, 9 : 1).

### Polymer synthesis

The copolymers [Fig. 1(b)] were synthesized by chemical oxidation using anhydrous ferric trichloride ( $\text{FeCl}_3$ ) in a nitromethane/carbon tetrachloride mixture.<sup>23</sup> Under nitrogen atmosphere, 2.0 mmol of comonomers, in the ratios shown in Table I, was dissolved under magnetic stirring in 45 mL of  $\text{CH}_3\text{NO}_2$ . Solid  $\text{FeCl}_3$  was quickly added to the mixture by a powder addition funnel, and the reaction was stirred for 1 h. In the next step, 180 mL of  $\text{CCl}_4$  was added to the mixture, which was stirred for 3 h. The polymer was isolated and purified by precipitation into 1 L of methanol. The presence of unreacted monomer and residual ferric chloride in the final product was discarded by thin-layer chromatography and spot testing with potassium ferricyanide,<sup>29</sup> respectively.

### Polymer characterizations

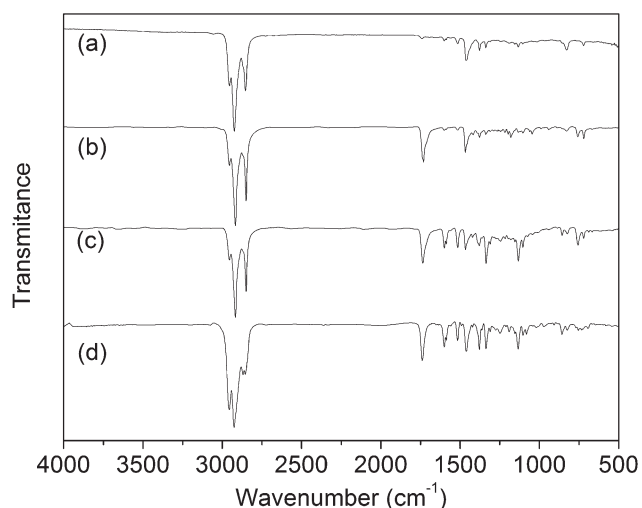
Polymer molecular weight distributions were determined by size exclusion chromatography (HPSEC) using tetrahydrofuran at 35°C (1.0 mL/min), two PL gel mixed columns, and polystyrene standards. FTIR spectra were registered from polymer thin film cast onto NaCl windows using a Nicolet Nexus 470 in transmittance mode.  $^1\text{H-NMR}$  spectra were recorded in a Bruker AC (200 MHz) using  $\text{CDCl}_3$  as solvent. Carbon, hydrogen, nitrogen, and sulphur contents were obtained by elemental analysis performed in a Carbo Erba elemental analyzer. DSC measurements were performed in a TA 2960 differential calorimeter from 25 to 250°C with a heating rate of 10°C/min, under nitrogen flow. Thermogravimetric curves were obtained in Netzsch TG-209 equipment, with a heating rate of 10°C/min and under nitrogen flow.

Chromic properties of polymer were analyzed by recording UV-vis spectra in a Hitachi U2001 spectrophotometer. Thermochromism was measured in toluene solutions, using a Neslab circulating water bath in the range of 20 to 70°C and in films in the range of 20 to 200°C using a resistance heater and an Ocean Optics 2000 fiber optic spectrometer. The

**TABLE I**  
Amount of 3-AzoT Comonomer Used in the Reactions of Copolymerization and Some Characteristics of Their Products

Reaction	Feed Ratio of 3-AzoT (mol %)	Total Yield (%)	3-AzoT Content <sup>a</sup> (mol %)	$M_n$ (g/mol)	PDI
CoAzoT6	25	40	6	4900	2.6
CoAzoT9	50	60	9	12400	1.8
CoAzoT12	75	32	12	8300	2.2
CoAzoT51	99	73	51	4700	2.0

<sup>a</sup> Calculated by elemental analysis.



**Figure 2** Transmission FTIR spectra of copolymers: (a) CoAzoT6, (b) CoAzoT9, (c) CoAzoT12, and (d) CoAzoT51. The copolymers are named according to Table I.

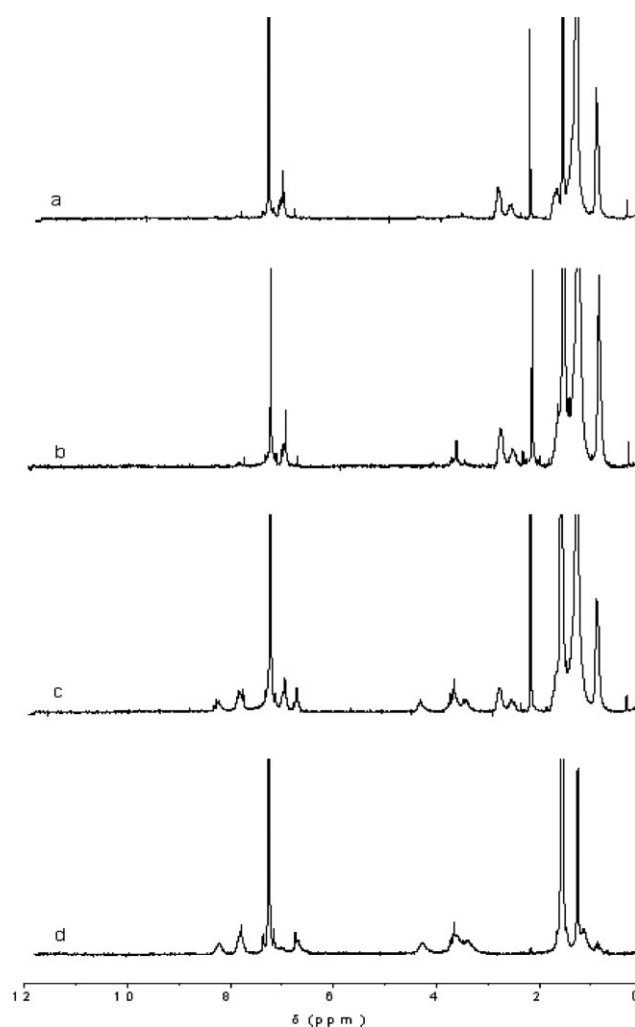
variations between sample in duplicates were within the system intrinsic error of  $\pm 0.004$  absorbance units and  $\pm 1$  nm in maximum wavelength. The solvatochromic behavior was studied in *n*-hexane, cyclohexane, toluene, dioxane, tetrahydrofuran, chloroform, and *N,N*-dimethylformamide. Photoluminescence measurements were performed with spin-coated films on B270 glass slides in a Shimadzu RF-5301PC spectrofluorometer. The optical birefringence in the copolymers films was induced using a linearly polarized Ar<sup>+</sup> continuous laser at 514 nm (writing beam), with a polarization angle of 45° with respect to the polarization orientation of the probe beam (reading beam). The power of the writing laser beam was varied up to 8 mW for a 2.9-mm spot. A low-power He-Ne laser at 633 nm, passing through crossed polarizers, was used as the probe beam (reading light) to measure the induced birefringence in the sample.

## RESULTS

The synthesized copolymers were named CoAzoT6, CoAzoT9, CoAzoT12, and CoAzoT51, according to the experimental azothiophene (3-AzoT) content presented in Table I. These values were calculated using the nitrogen/sulfur (N/S) content obtained by elemental analysis and they were lower than the feed ratio in all cases. This result was attributed to the lower reactivity of the azosubstituted thiophene ring, compared with the alkylated one, in the oxidative polymerization because of the electron-withdrawing effect and the steric hindrance exerted by the azobenzene group.<sup>25</sup> The low yield and poor solubility of polyazothiophenes has been reported by several authors.<sup>22,24</sup> The increase in 3-AzoT content

into the reaction mixture improves the total yields as described by Fraleoni-Morgera et al.,<sup>24</sup> except for sample with 12% of 3-AzoT. The number-average molecular weight ( $M_n$ ) values of copolymers (Table I) are consistent with the ones reported for other azothiophene and alkylthiophene copolymers.<sup>10,18,30</sup>

The transmission FTIR spectra of copolymers are shown in Figure 2. The characteristic peaks of 3-AzoT (1735  $\text{cm}^{-1}$  for C=O stretching of ester groups, 1599 and 1500  $\text{cm}^{-1}$  for C=C stretching in benzene rings, 1518  $\text{cm}^{-1}$  for NO<sub>2</sub> asymmetric stretching, 1336  $\text{cm}^{-1}$  for NO<sub>2</sub> symmetric stretching, 1242, 1252, and 1134  $\text{cm}^{-1}$  for asymmetric and symmetric C(=O)–O and O–C–C stretching vibrations of ester groups) can be observed in all copolymers spectra, with relative intensities increasing from CoAzoT6 to CoAzoT51. Other peaks at 2960 and 2850  $\text{cm}^{-1}$  for C–H stretching of 3-AzoT and 3-OT can be observed in all spectra. The occurrence of polymerization was confirmed by the absence of the band at 725  $\text{cm}^{-1}$  in all copolymers, which is



**Figure 3** <sup>1</sup>H-NMR (CH<sub>3</sub>Cl-*d*) spectra of copolymers: (a) CoAzoT6, (b) CoAzoT9, (c) CoAzoT12, and (d) CoAzoT51.

TABLE II  
Wavelengths of Maximum Absorption and Emission for Spin-Coated Film of the Copolymers and Thermal Properties of Copolymers

Sample	abs <sup>a</sup> $\lambda_{\max}$ (nm)	Emission $\lambda_{\max}$ (nm)	$T_g$ (°C)	$T_{id}$ (°C)	$T_{peak1}$ (°C)	$T_{peak2}$ (°C)
CoAzoT6	442	585	115	370	476	–
CoAzoT9	440	595	113	370	476	–
CoAzoT12	450	595	115	230	476	–
CoAzoT51	470	630	109	180	280	330

<sup>a</sup> At room temperature ( $\approx 25^\circ\text{C}$ ).

characteristic of the C–H<sub>α</sub> out-of-plane deformation in mono-substituted thiophene rings.<sup>30</sup>

Similar features can be observed in copolymers <sup>1</sup>H-NMR spectra shown in Figure 3. The hydrogen atoms of 3-AzoT can be observed with higher intensity for CoAzoT12 and CoAzoT51 than for CoAzoT6 and CoAzoT9. The characteristic signals of 3-AzT are observed in these copolymers at 3.4 (CH<sub>2</sub>–N–CH<sub>2</sub>–CH<sub>3</sub>), 3.6 (Th–CH<sub>2</sub>–COO), 4.3 (CH<sub>2</sub>–COO–CH<sub>2</sub>–CH<sub>2</sub>), 6.8 (Ar–H ortho to amine), 7.8 (Ar–H ortho to N=N) and 8.2 ppm (Ar–H ortho to NO<sub>2</sub>). The signals of 3-OT at 0.9 (Th–(CH<sub>2</sub>)<sub>7</sub>–CH<sub>3</sub>), 1.6 ppm (Th–CH<sub>2</sub>–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>5</sub>–CH<sub>3</sub>) are not clearly observed only in the CoAzoT51 spectrum. The two peaks at 2.5 and 2.8 ppm correspond to the α-CH<sub>2</sub> group of the 3-OT and have been attributed to head-to-head (HH) and head-to-tail coupling (HT),<sup>31</sup> respectively. These two peaks can be clearly visualized only in samples CoAzoT6, CoAzoT9, and CoAzoT12 and correspond to approximately 65% of HT and 35% of HH for all samples. Two peaks are present in all copolymers spectra: the first at 1.2 ppm corresponds to the proton (N–CH<sub>2</sub>–CH<sub>3</sub>) of 3-AzoT and (Th–CH<sub>2</sub>–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>5</sub>–CH<sub>3</sub>) of 3-OT, and the second at 7.0 ppm is the β-proton of thiophene ring of both comonomers.

The wavelengths of maximum absorption ( $\lambda_{\max}$  abs) and emission ( $\lambda_{\max}$  emission) of copolymers, obtained from the absorption and photoluminescence spectra of spin-coated films, are shown in Table II. As the 3-AzoT content increases, the absorption and emission maxima shift to longer wavelengths. It is worth noting that the emission intensity decreases with the increase of 3-AzoT content. The emissive component is the conjugated backbone, which emits light in wavelengths absorbed by the azo group. Therefore, if for a further application emissive properties are important, low contents of AzoT should be used.

Figure 4 illustrates the DSC second heating curve for the copolymers. The glass transition occurs in a large temperature range for all samples. The  $T_g$  values (Table II) were taken in the middle transition point. The  $T_g$  of the different copolymers decrease slightly only for the higher 3-AzoT content.

Thermogravimetric curves of copolymers, shown in Figure 5, exhibit a one-step weight loss process for CoAzoT6, CoAzoT9, and CoAzoT12. CoAzoT51 showed a two-step loss, more clearly seen in the derivative TG curves (inset of Fig. 4), which was also observed for the polyazothiophene homopolymer synthesized by Gonçalves et al.<sup>23</sup> The weight loss increases more rapidly for CoAzoT6, CoAzoT9, and CoAzoT12 than for CoAzoT51, and the residual weight at 975°C increases from 10 to 34% with the increase of 3-AzoT content. Temperatures of initial degradation ( $T_{id}$ ) and degradation peaks ( $T_{peak}$ ) decrease with the increase of 3-AzoT content (Table II), showing that the increase in the 3-AzoT content decreases the copolymers thermal stability.

Thermochromism in conjugated polymers have been attributed to a transition between a planar form (highly conjugated) and a nonplanar (less conjugated) conformational structure of the backbone.<sup>18</sup> Several driving forces have been proposed for this optic phenomenon (crystallization, aggregation, steric interactions, etc), but a concise structural analysis of the parameters involved was not yet described.<sup>30,31</sup> It is of general acceptance, however,

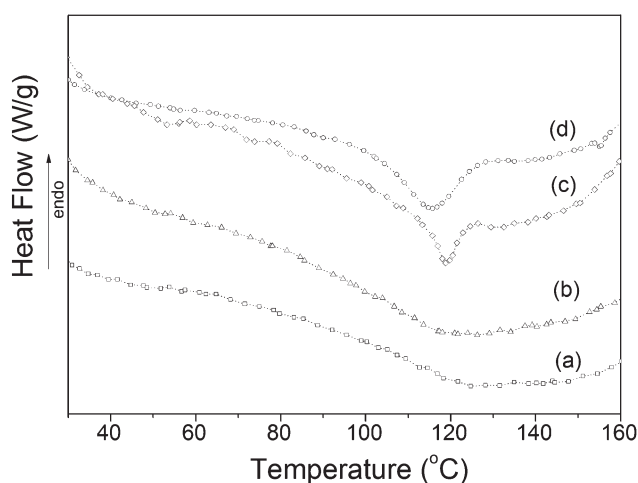
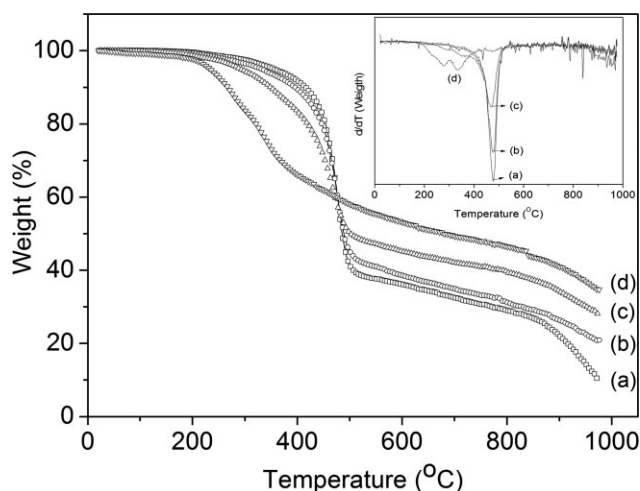
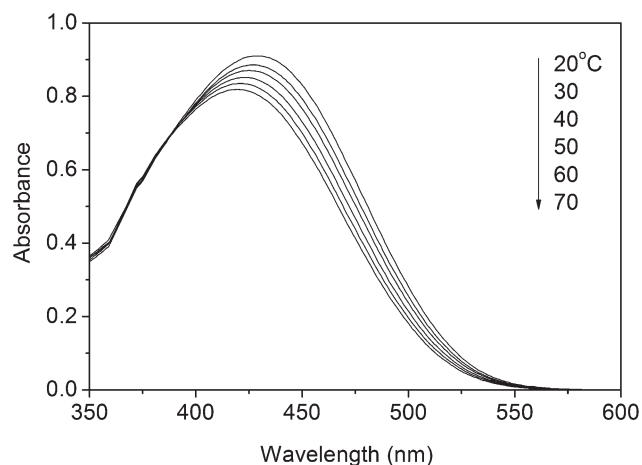


Figure 4 DSC curves of (a) CoAzoT6, (b) CoAzoT9, (c) CoAzoT12, and (d) CoAzoT51.



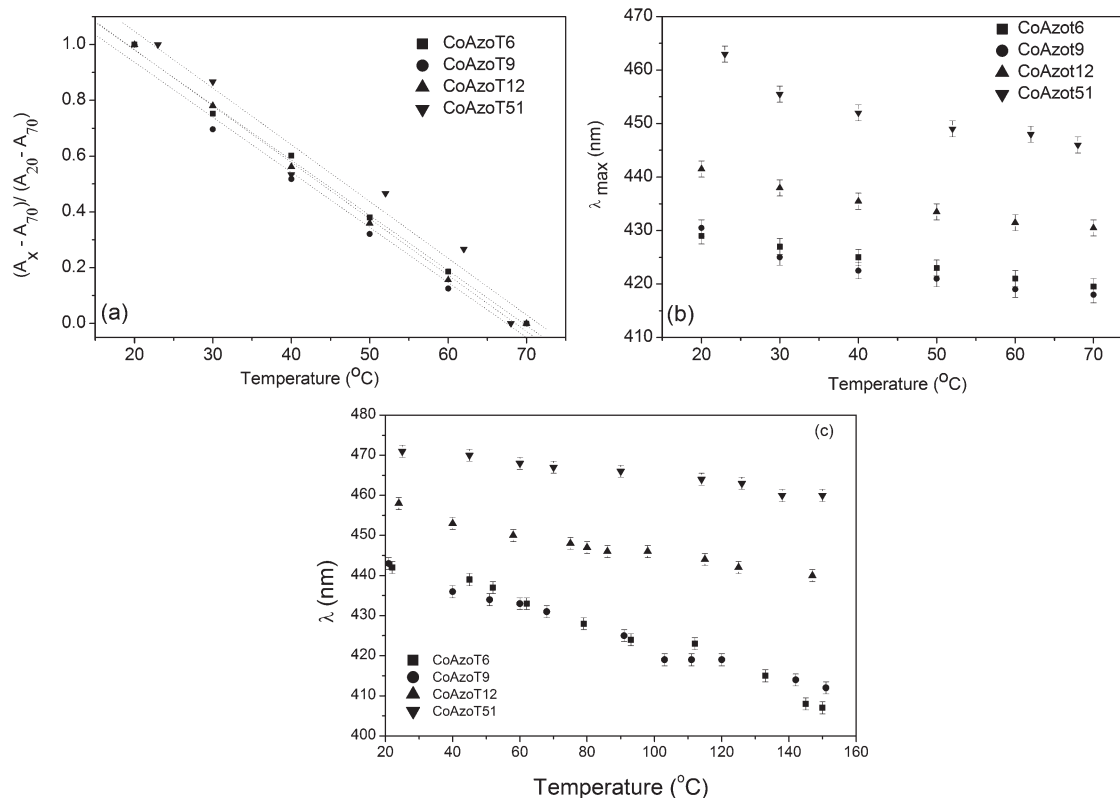
**Figure 5** Thermogravimetric (TG) curves of (a) CoAzoT6, (b) CoAzoT9, (c) CoAzoT12, and (d) CoAzoT51. The figure inset shows derivative TG curves of these copolymers.

that the steric interactions induced by the degree of regioregularity and greater size of side chains influence the thermochromic property. Thermochromic properties were explored for the polymers in toluene solution and in films. The temperature range, in the



**Figure 6** Temperature dependence of UV-vis absorption of CoAzoT6 in toluene solution.

case of solution, was limited to 70°C due to possible solvent evaporation. Figure 6 illustrates the temperature dependence of the UV-Vis absorption spectra for CoAzoT6 in toluene. On heating from 20° up to 70°C, the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) decreased about 10 nm (from 429 to 419 nm) and the maximum absorbance values decreased



**Figure 7** Temperature dependence for all copolymers: (a) absorbance in a specific wavelength, where  $A_x$  is absorbance at  $x$  temperature,  $A_{70}$  is absorbance at 70°C, and  $A_{20}$  is absorbance at 20°C for solutions in toluene; (b) wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) for solutions in toluene; and (c) wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) for spin-coated films on glass.

TABLE III  
Wavelength of Maximum Absorbance of Different Copolymers Solutions and Solvent Parameters: Polarity Index ( $k'$ ), Dielectric Constant ( $\epsilon$ ), and Hildebrand's Solubility Parameter,  $\delta$  (MPa<sup>1/2</sup>)

Solvent	$\lambda_{\max}$ (nm)				Solvent Parameters		
	CoAzoT6	CoAzoT9	CoAzoT12	CoAzoT51	$k'$	$\epsilon$	$\delta$
<i>n</i> -Hexane	414	414	420	Insol.	0.06	1.89	14.9
Cyclohexane	417	414	435	Insol.	0.04	2.02	16.8
Dioxane	414	420	440	459	4.8	2.22	20.5
Chloroform	426	425	441	465	4.3	4.81	16.8
THF	420	423	440	467	4.2	7.52	19.0
Toluene	426	430	438	458	2.4	2.38	24.3
DMF	Insol.	Insol.	Insol.	482	6.4	38.25	14.4

Insol., insoluble in this solvent.

from 0.91 to 0.82. The linear dependence of absorbance in a specific wavelength  $(A_x - A_{70})/(A_{20} - A_{70})$  with temperature for all copolymers in toluene solution is shown in Figure 7(a). The wavelengths used to build this plot were 429, 430, 441, and 463 nm, respectively, for CoAzoT6, CoAzoT9, CoAzoT12, and CoAzoT51. The linear coefficient is usually used to quantify the thermochromic response and the  $(A_x - A_{70})/(A_{20} - A_{70})$  approximation was used to eliminate any effect of solution concentration. For all copolymers, a linear coefficient of  $0.020^\circ\text{C}^{-1}$  is obtained, showing that different amounts of 3-AzoT units do not influence the thermochromic property in solution. No clear linear behavior was observed for the decrease of absorbance values of the films on heating. The variation of  $\lambda_{\max}$  was more significant than the variation of the absorbance with temperature for both solutions and solid films [Fig. 7(b,c)], and the decrease in  $\lambda_{\max}$  was more accentuated for the CoAzoT51.

Different  $\lambda_{\max}$  were obtained using copolymers in different solvents (Table III). This solvatochromic effect is positive, with a red shift of  $\lambda_{\max}$  with the increase of solvent polarity.<sup>32</sup> The red shift, in the case of polythiophenes, can be explained by changes in side-chain solvation and by the main-chain conformation in different solutions.<sup>18</sup> No direct correlation between  $\lambda_{\max}$  shifts and parameters related to the solvent polarity (Table III), such as polarity index, and with Hildebrand's solubility parameter or dielectric constant<sup>33</sup> could be noticed. Solutions prepared with *n*-hexane presented the lowest  $\lambda_{\max}$ , whereas the highest value was obtained in toluene for CoAzoT6, CoAzoT9, and CoAzoT12 and in DMF for CoAzoT51. Solutions of different copolymers in the same solvent, as shown in Figure 8 for toluene, present an increase of  $\lambda_{\max}$  with the 3-AzoT content in the copolymer up to 50 mol %. The values for the homopolymers of 3-AzoT and 3-OcT were obtained from the literature<sup>15,34</sup> and are included in Figure 8 for comparison.

Optically induced birefringence experiments were carried out using distinct writing beam powers on spin-coated films of similar thicknesses. We observed photoinduced birefringence only for CoAzoT12 and CoAzoT51, which were then determined by measuring the sample's transmitted signal through crossed polarizers. The optically induced birefringence curves obtained with a writing beam power of 5.5 mW are presented in Figure 9(a). On exposure to the linearly polarized light of the writing beam, *trans-cis-trans* photoisomerization cycles occur, leading to a reorientation process that ends when the dipole moment of the molecules is oriented perpendicularly to the polarization of the laser. At this point, several chromophores will be aligned and, consequently, optically induced birefringence takes place, which leads to an increase in the transmitted signal that is probed by the reading beam. The transmitted signal was higher for CoAzoT51 than for CoAzoT12, for all laser powers used,

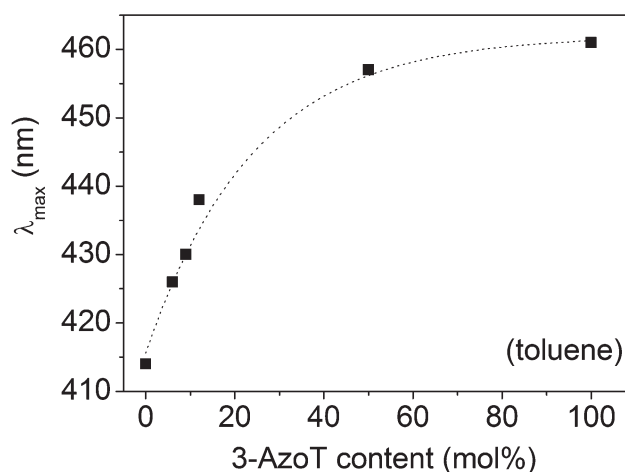
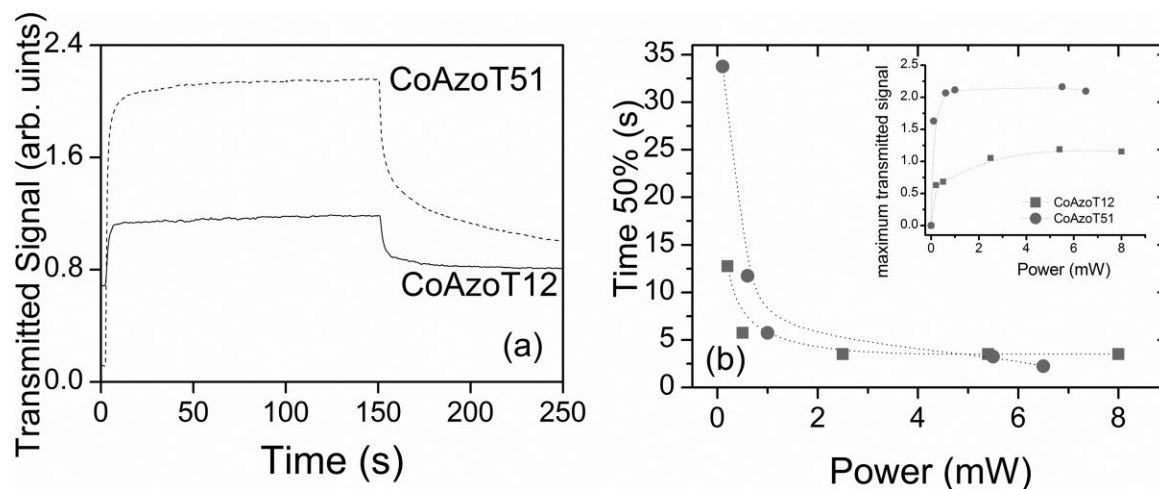


Figure 8 Wavelength of maximum absorbance of toluene solutions for different 3-AzoT contents in the copolymers. The values for 0 and 100% were taken from the literature.<sup>15,34</sup>



**Figure 9** Photoinduced birefringence on copolymers CoAzoT12 and CoAzoT51. (a) optical storage curves; (b) effect of laser power in the writing times and in the maximum transmitted signal (inset).

due to the higher content of azobenzene groups, which are responsible for the photoinduced birefringence. The residual signal (remaining birefringence after relaxation of the chromophores that occurs when the writing beam is switched off) observed was 67 and 50% for CoAzoT12 and CoAzoT51, respectively. The decrease in the residual value with the increase of azobenzene content was observed previously in methacrylic copolymers<sup>4</sup> and was attributed to cooperative effects. Also due to the cooperative effects, the saturation of the maximum signal was achieved at 0.5 mW for CoAzoT51 and at 2.5 mW for CoAzoT12 [Fig. 9(b)]. The amount of azosubstituted units does not change the writing time for laser powers above 0.7 mW, as shown in Figure 9(b). This value is in the range typical of azopolymers.<sup>1,4,23</sup> These results are promising, allowing the design of optical devices that ally optical induced birefringence and the properties of conjugated polymers.

## CONCLUSIONS

Copolymers of 3-octylthiophene and an azo-substituted thiophene (3-AzoT) were successfully prepared. The increase in the 3-AzoT units in the copolymer structure leads to significant changes in their solubility and in the decomposition behavior. The  $\lambda_{\text{max}}$  values of thin films and their emissive properties also presented significant changes with the introduction of different contents of 3-AzoT units. Thermochromic and solvatochromic properties were observed in all copolymers prepared. Photoinduced birefringence could be observed in films of copolymers with 12 and 51% of 3-AzoT units. The presence of these chromic properties turns the polyazothiophene copolymers presented here into prom-

ising candidates to active layers in optical devices and sensors.

## References

- Mendonça, C. R.; Dhanabalan, A.; Balogh, D. T.; Misoguti, L.; Santos, D. S., Jr.; Pereira-da-Silva, M. A.; Giacometti, J. A.; Zilio, S. C.; Oliveira, O. N., Jr. *Macromolecules* 1999, 32, 1493.
- Natansohn, A.; Rochon, R. *Chem Rev* 2002, 102, 4139.
- Kumar, G. S.; Neckers, N. C. *Chem Rev* 1989, 89, 1915.
- Dhanabalan, A.; Mendonça, C. R.; Balogh, D. T.; Misoguti, L.; Constantino, C. J. L.; Giacometti, J. A.; Zilio, S. C.; Oliveira, O. N., Jr. *Macromolecules* 1999, 32, 5277.
- Heeger, A. J. *Synth Met* 2002, 125, 23.
- Macdiarmid, A. G. *Synth Met* 2002, 125, 11.
- Matsui, T.; Nagata, T.; Ozaki, M.; Fujii, A. M.; Onoda, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth Met* 2001, 119, 599.
- Chen, Y.; Harrison, W. T. A.; Imrie, C. T.; Ryder, K. S. *J Mater Chem* 2002, 12, 579.
- Huang, K.; Wan, M. *Chem Mater* 2002, 14, 3486.
- Chittibabu, K. G.; Li, L.; Kamath, M.; Kumar, J.; Tripathy, S. K. *Chem Mater* 1994, 6, 475.
- Levésque, I.; Leclerc, M. *Macromolecules* 1997, 30, 4347.
- Zagórska, M.; Kulszewicz-Bajer, I.; Pron, A.; Sukiennik, J.; Raimond, P.; Kajzar, F.; Attias, A. J.; Lapkowski, M. *Macromolecules* 1998, 31, 9146.
- Della-Casa, C.; Fraleoni-Morgera, A.; Costa-Bizzarri, P.; Lanzi, M. *Synth Met* 2001, 124, 467.
- Roncali, J. *Chem Rev* 1992, 92, 711.
- Gonçalves, V. C.; Balogh, D. T. *Eur Polym J* 2006, 42, 3303.
- Mochizuki, H.; Nabeshima, Y.; Kitsunai, T.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Hiyama, T.; Maruyama, T.; Yamamoto, T.; Koide, N. *J Mater Chem* 1999, 9, 2215.
- Gan, L. H.; Xia, X.; Chan, C. Y.; Hu, X.; Zhao, X. *Polym Adv Technol* 2003, 14, 260.
- Zhao, X.; Niu, Y.; Hu, X. *J Polym Sci Part B: Polym Phys* 2005, 43, 1421.
- Leclerc, M. *Adv Mater* 1999, 11, 1491.
- Zagórska, M.; Kulszewicz-Bajer, I.; Pron, A.; Raimond, P.; Kajzar, F.; Attias, A. J. *Synth Met* 1999, 102, 1141.
- Dufresne, G.; Bouchard, J.; Belletete, M.; Durocher, G.; Leclerc, M. *Macromolecules* 2000, 33, 8252.



22. Aubertin, F.; Zhao, Y. *J Polym Sci Part A: Polym Chem* 2004, 42, 3445.
23. Gonçalves, V. C.; Ferreira, M.; Olivati, C. A.; Cardoso, M. R.; Balogh, D. T. *Colloid Polym Sci* 2008, 286, 1395.
24. Fraleoni-Morgera, A.; Della-Casa, C.; Lanzi, M.; Costa-Bizzarri, P. *Macromolecules* 2003, 36, 8617.
25. Fraleoni-Morgera, A.; Della-Casa, C.; Costa-Bizzarri, P.; Lanzi, M.; Missiroli, A. *Macromolecules* 2005, 38, 3170.
26. Lanzi, M.; Paganin, L.; Costa-Bizzarri, P. *Eur Polym J* 2004, 40, 2117.
27. Della-Casa, C.; Costa-Bizzarri, P.; Lanzi, M.; Paganin, L.; Bertinelli, F.; Pizzoferrato, R.; Sarcinelli, F.; Casalboni, M. *Synth Met* 2003, 138, 409.
28. Costa-Bizzarri, P.; Lanzi, M.; Paganin, L.; Della-Casa, C.; Bertinelli, F.; Mauro Casalboni, M.; Sarcinelli, F.; Quatela, A. *Macromol Chem Phys* 2003, 204, 1982.
29. Feigl, F.; Anger, V. *Spot Tests in Inorganic Analysis*; Elsevier Publishing Company: Amsterdam, 1972; p 275.
30. Zagórska, M.; Krische, B. *Polymer* 1990, 31, 1379.
31. Faid, K.; Frechette, M.; Ranger, M.; Mazerolle, L.; Lesvesque, I.; Leclerc, M. *Chem Mater* 1995, 7, 1390.
32. Reichardt, C. *Chem Rev* 1994, 94, 2319.
33. Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 85th ed.; CRC Press: Boca Raton, 2005.
34. Correa, D. S.; De Boni, L.; Gonçalves, V. C.; Balogh, D. T.; Mendonça, C. R. *Polymer* 2007, 48, 5303.