Regioregular Improvement on the Oxidative Polymerization of Poly-3-octylthiophenes by Slow Addition of Oxidant at Low Temperature

B. B. M. Torres, D. T. Balogh

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

ABSTRACT: Many pathways can be used to synthesize polythiophenes derivatives. The polycondensation reactions performed with organometallics are preferred since they lead to regioregular polymers (with high content of heat-to-tail coupling) which have enhanced conductivity and luminescence. However, these pathways have several steps; the reactants are highly moisture sensitive and expensive. On the other hand, the oxidative polymerization using $FeCl_3$ is a one-pot reaction that requires less moisture sensitive reactants with lower cost, although the most common reaction conditions lead to polymers with low regioregularity. Here, we report that by changing the reaction conditions, such as $FeCl_3$ addition rate and reaction temperature, poly-3-octylthiophenes with different the regioregularities can be obtained, reaching about 80% of heat-to-tail coupling. Different molar mass distributions and polydispersivities were obtained. The preliminary results suggest that the oxidative polymerization process could be improved to yield polythiophenes with higher regioregularity degree and narrower molar mass distributions by just setting some reaction conditions. We also verified that it is possible to solvent extract part of the lower regioregular fraction of the polymer further improving the regioregularity degree. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3222–3228, 2012

Key words: poly-3-alkylthiophenes; conductive polymers; conjugated polymers; synthesis; oxidative polymerization

INTRODUCTION

Polythiophenes are a very important class of materials today and has been subject of intensive research for the development of several devices, such as, organic light emitting diodes,[1,2] field effect transistors,[3] photo-voltaic cells,[3] solid state sensors[4,5] (e.g., e-noses) and anticorrosive coatings.[6] When compared to other conjugated polymers, polythiophenes derivatives exhibit better chemical and environmental stability. As example, they do not easily suffer ring opening reactions like polyfurans and polypyrrols[7] and the photo-oxidation is less pronounced when compared to PPVs and polyacetylenes.[8] Furthermore, it is relatively easy to synthesize new thiophene derivatives by attaching pendant groups.[9,10] This strategy has been extensively used to design new polymers and to get more efficient devices.

The polythiophenes can be synthesized by, at least, four methods: acid catalysis,[11–14] electropolymerization,[8,15] oxidative polymerization[16,17] and polycondensation using organometallic reactants.[18–20] Acid catalysis was the first attempt to obtain unsubstituted polythiophenes but the reactions led to sulfur deficient oligomers and, since then, there is no report in the literature on this method. The electropolymerization is a well-developed methodology and is generally used to obtain thin films *in situ* by a clean way, but these materials have low molar mass and many regioregular defects. The McCullough and Rieke methods use Grignard-like thiophene monomers and some organometallic catalysts to perform the polymerization reaction. These methodologies are the only that invariably leads to polymers with high regioregularity degree (which is the content of heat-to-tail (HT) coupling of thiophene ring in the polymer main chain) greater than 95% even for low regioselective monomers like 3-alkylthiophenes. Hence, they are the most used to synthesize materials for applications which requires high regioregularity degree, but the reactants and catalysts are highly moisture sensitive and methods demand many reactions steps that difficult their handling, besides being of high cost. The oxidative polymerization is a good alternative to the organometallic methods because it is a one-pot reaction and the reactants have low cost and are easier to handle, but the commonly used conditions (i.e., direct addition of oxidant, room temperature) usually leads

TABLE I
Reaction Conditions, Regioregularity Degree, Values of λ_{max}, Iron Content, Solubility in $CHCl_3$, Molar Mass Averages (M_n, M_w) and Polydispersivities (PDI)

T (°C)	Oxidant addition	Yield	HT (%)	λ_{max} (nm)	Iron content (%)	Solubility in $CHCl_3$ (%)	M_n (g/mol)	M_w (g/mol)	PDI
25	Inst.	86%	69.6	432	<0.01	87	21,000	41,600	2.0
25	dp* 15 min	99%	75.1	438	0.29	92	37,100	11,2000	3.0
25	dp 60 min	92%	75.6	438	0.24	98	29,000	79,700	2.7
25	dp 180 min	81%	75.9	438	0.04	98	32,600	103,300	3.2
−18	dp 60 min	78%	79.0	442	0.02	93	48,000	86,700	1.8

* dp, dropwise.

to polymers with low regioregularity degree (about 65%). However, the use of symmetrical monomers[21,22] or voluminous substituents[23,24] on the thiophene rings can lead to polymers with high regioregularity. Only few studies have focused on optimizing the oxidative polymerization of unsymmetrical monomers and understanding its mechanism, even that some reports suggest that it is possible to improve the regioregularity by just changing the oxidant/monomer ratio or lowering the temperature.[25]

In this article, we explored different reaction conditions, e.g., method and rate of oxidant addition and reaction temperature, of poly-3-octylthiophene synthesis. The preliminary results show that the reaction can be better controlled yielding polymers with improved regioregularities and narrower molecular weight distributions simply by changing the reaction conditions.

EXPERIMENTAL

Materials

3-Octylthiophene was purchased from Aldrich and used without further purification. Chloroform and nitromethane (J. T. Baker) were dried with molecular sieve 4 Å. Poly-3-octylthiophene regiorandom (50% HT) and regioregular (>98.5% HT) were purchased from Aldrich and used for comparison in some of the experiments.

Synthesis

The polymerization reactions were carried out under dried N_2 atmosphere as it follows: 3 mmol of 3-octylthiophene were dissolved in 31 mL of $CHCl_3$ (0.1 M). After, 12 mmol of anhydrous $FeCl_3$ previously dispersed in 4.6 mL of CH_3NO_2 were added dropwise or instantaneously to the monomer solution. The dropwise addition rate was set to last 15, 60, and 180 minutes. The reaction temperature was controlled by a thermostatic bath and set to 25 or −18°C. Each polymerization was carried out for 4 hours and the polymers were precipitated in methanol (1 L). After, they were collected in a Büchner

funnel and washed with methanol until the characteristic color of $FeCl_3$ was vanished. All polymers were dried and stored under vacuum before use. Table I summarizes the conditions of all reactions performed.

Characterization

The regioregularity degree of the polymers was evaluated by H^1-NMR. The chemical shifts were recorded using TMS as reference in a 400 MHz Bruker NMR spectrometer with $CDCl_3$ as solvent. The soluble fraction in $CHCl_3$ was evaluated gravimetrically by evaporating a solution, filtered on paper and glass wool, with a nominal concentration of 8 mg mL^{-1}.

The residual iron was determined colorimetrically by using 1,10-phenantroline method. FTIR spectra were recorded from KBr pellets in a ThermoNicolet Nexus 470 spectrometer. UV-vis (Hitachi U-2001) and fluorescence (RF-5301PC Shimadzu Spectrofluorimeter) spectra were obtained from 0.03 and 0.008 mg mL^{-1} $CHCl_3$ solutions, respectively. The excitation wavelength was set to 436 nm. Molar mass distribution was determined by size exclusion chromatography (SEC) using polystyrene standards and THF as solvent at 1 mL/min flow rate in an Agilent 1100 Liquid chromatography system equipped with Plgel Mixed-B and Mixed-C columns and refraction index detector.

RESULTS AND DISCUSSION

All reaction conditions resulted in materials with good solubility in $CHCl_3$ and high yields (Table I). The regioregularity degree was calculated based on the ratio of the areas of methylene signals at 2.79 and 2.56 ppm, attributed to the α-methylene in the HT and head-to-head (HH) or tail-to-tail (TT) dyads, respectively, as illustrated in Figure 1. The regioregularity degree increases ca. 4% with the temperature decrease from 25 to −18°C. It increases, also by changing the addition mode from instantaneous to dropwise, about 6% (Fig. 1 and Table I). It is
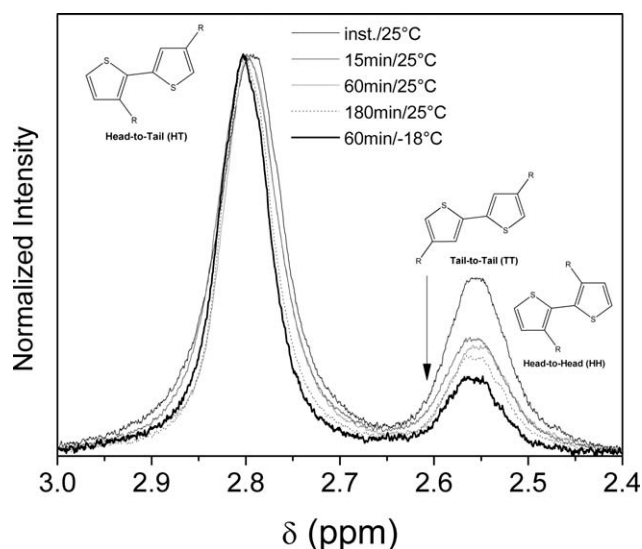
Figure 1 Methylene signals of H^1-NMR spectra of the polyoctylthiophenes samples in deutered chloroform.

a remarkable preliminary result, since with simple changes in the reaction conditions an increase of 10% in the regioregularity degree can be reached compared to the instantaneous addition at room temperature. Similar improvements on the regioregularity were reported[24] at low temperatures (-15, $-45°C$) but with much longer reaction times (24 hours or more) and lower yields.

UV-vis spectra (Fig. 2) of the polymers in chloroform solutions show a small red shift as the regioregularity degree increases, as expected, because the conjugation length increases with the regioregularity. The polymer with higher regioregular degree obtained here (79%) exhibits a maximum absorption at 442 nm while the regioregular poly-3-octylthiophene (Aldrich) exhibits at 449 nm and the regiorandom at
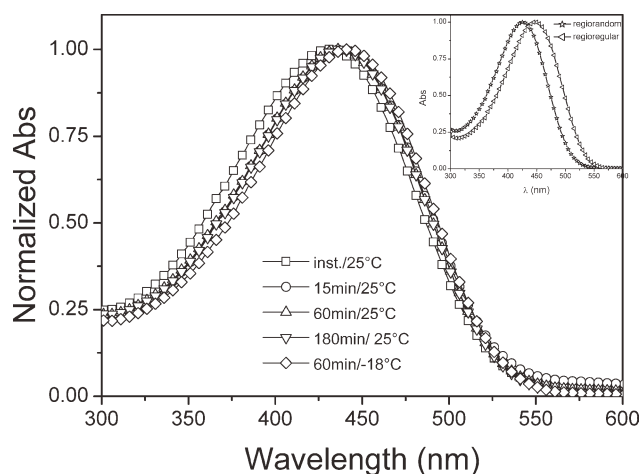

Figure 2 UV-vis spectra of the polyoctylthiophenes samples in $CHCl_3$ solutions. The inset shows the spectra of the regiorandom and regioregular commercial polyoctylthiophenes.
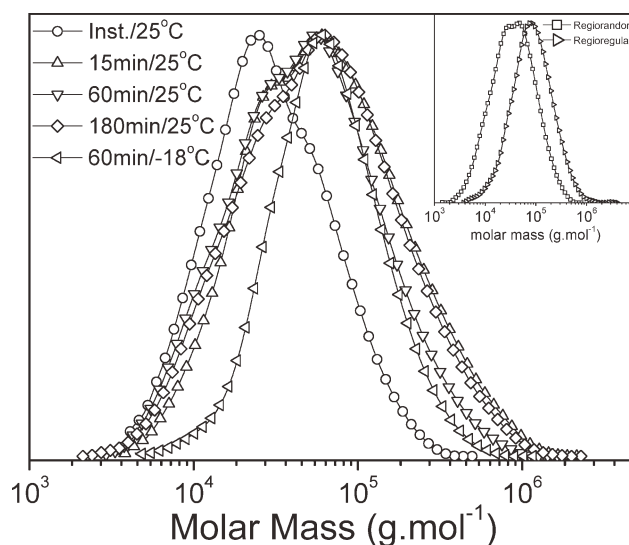

Figure 3 Molar mass distributions of the polyoctylthiophenes samples. The inset shows the molar mass distributions of the regiorandom and regioregular commercial polyoctylthiophenes.

427 nm. Although, these spectra suggest an insignificant doping level of the polymers prepared in this work as evaluated by the absence of any electronic transition at wavelengths greater than 700 nm (not shown), some FTIR spectra exhibit a quite broad signal at about 1340 cm^{-1} which points out that some polymers are still doped by the oxidant, even that the doping level is very low. To evaluate the residual iron content (dopant), a colorimetric method was used. Table I summarizes the iron content for each sample and shows that there is no correlation between it and the reaction conditions. Despite the residual iron presence that could quench the fluorescence, all polymers exhibit a similar fluorescence at 570 nm without any significant intensity difference.

SEC results showed in Figure 3 suggest that the reaction mechanism changes within different reaction conditions. It seems that the distribution is a convolution of two main components that change their relative importance according to the oxidant addition method. These two main components may be typical chain lengths of two different populations, and hence, from two different propagation mechanisms, or be due to different elution behavior of the chains with low and high contents of HT coupling. The elution profiles of the regiorandom and regioregular commercial polymers show a clear presence of two components in molar mass distribution of the regiorandom poly(3-octylthiophene) while only one component can be seen in regioregular sample, indicating that the regioregularity degree can influence on the elution profile, reflected in the format of the molar mass distributions. Regarding to our samples, when the instantaneous addition is changed to any
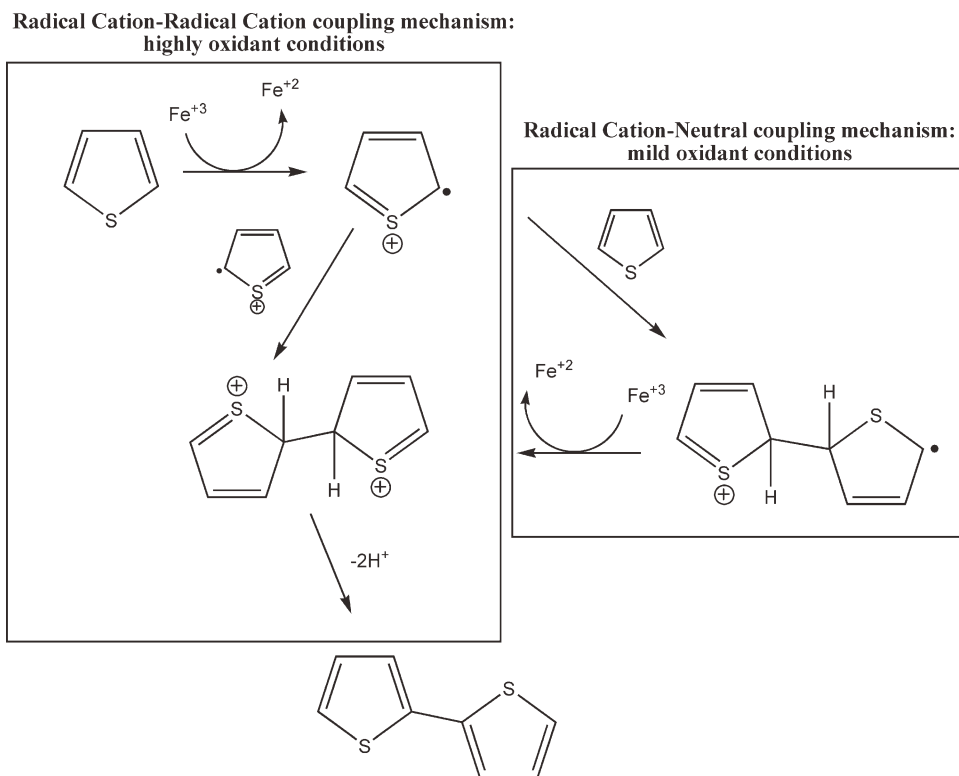
Figure 4 Reaction mechanism—initiation step—coupling between radical-cation species with other radical-cations or neutral molecules.

controlled one, the molar mass distribution exhibits a significant change in the profile. The peak maximum that appears at ca. 25,000 g mol^{-1} in the instantaneous addition sample changes towards higher values of molar mass (around 60,000 g mol^{-1}). The shoulder that appears at around 50,000 g mol^{-1} in the instantaneous addition sample appears at lower molar mass for the other samples (around 25,000 g mol^{-1}). However, the rate of dropwise oxidant addition did not seem to have a direct correlation with molar mass distribution profile. Furthermore, the reaction at lower temperature results in a narrower molar mass distribution which also suggests a more controlled reaction. The average molar mass values and dispersity indexes are shown in Table I. The values obtained for the commercial regiorandom polymer were: M_n 22,000 and M_w 57,000 g mol^{-1} and for the commercial regioregular, M_n 54,000 and M_w 128,000 g mol^{-1}.

The generally accepted mechanism (Fig. 4) for the oxidative polymerization describes that the monomer is oxidized to a cation-radical and that the coupling between two cation-radicals is responsible for the chain growth.[16] Indeed, this mechanism have described very well the polymerization of thiophene derivatives, such as 3-phenylthiophene and 3-alkysulfanylthiophene whose cation-radicals exhibit a quite asymmetric chemical activation of the carbons 2 and 5,[26,27] leading to a higher degree of HT coupling.

In the case of the 3-alkythiophenes, their spin density distribution is only slightly asymmetric, as evaluated by DFT methods,[27] and thus the probability of HT, TT or HH coupling is quite similar. However, in this case, the steric hindrance of the alkyl pendant chain should be significant and because of that, it seems reasonable to assume that the TT would be the most favorable coupling, followed by HT and HH.

For the instantaneous addition of oxidant, all monomers are oxidized at once, and hence, we have several cation-radicals that would promptly couple leading preferentially to TT and HT dimers. Due to the strong oxidative conditions, monomer concentration depletes very fast and the coupling between dimers and monomers are less probable than between two dimers. Further reactions between these TT and HT dimers essentially leads to regiodefective oligomers, and hence, if the chain propagation continues mainly by coupling between dimers, tetramers and so on, the result is a lesser regioregular polymer due to the defects introduced in the earlier steps of the polymerization.

However, this propagation mechanism does not comprise changes in the oxidant addition rate. When the oxidant concentration is kept low, the propagation mechanism should include reactions between cation-radicals and neutral molecules (Fig. 5), similar to the traditional radicalar chain-growth mechanism. The regioregularity improvement observed by the
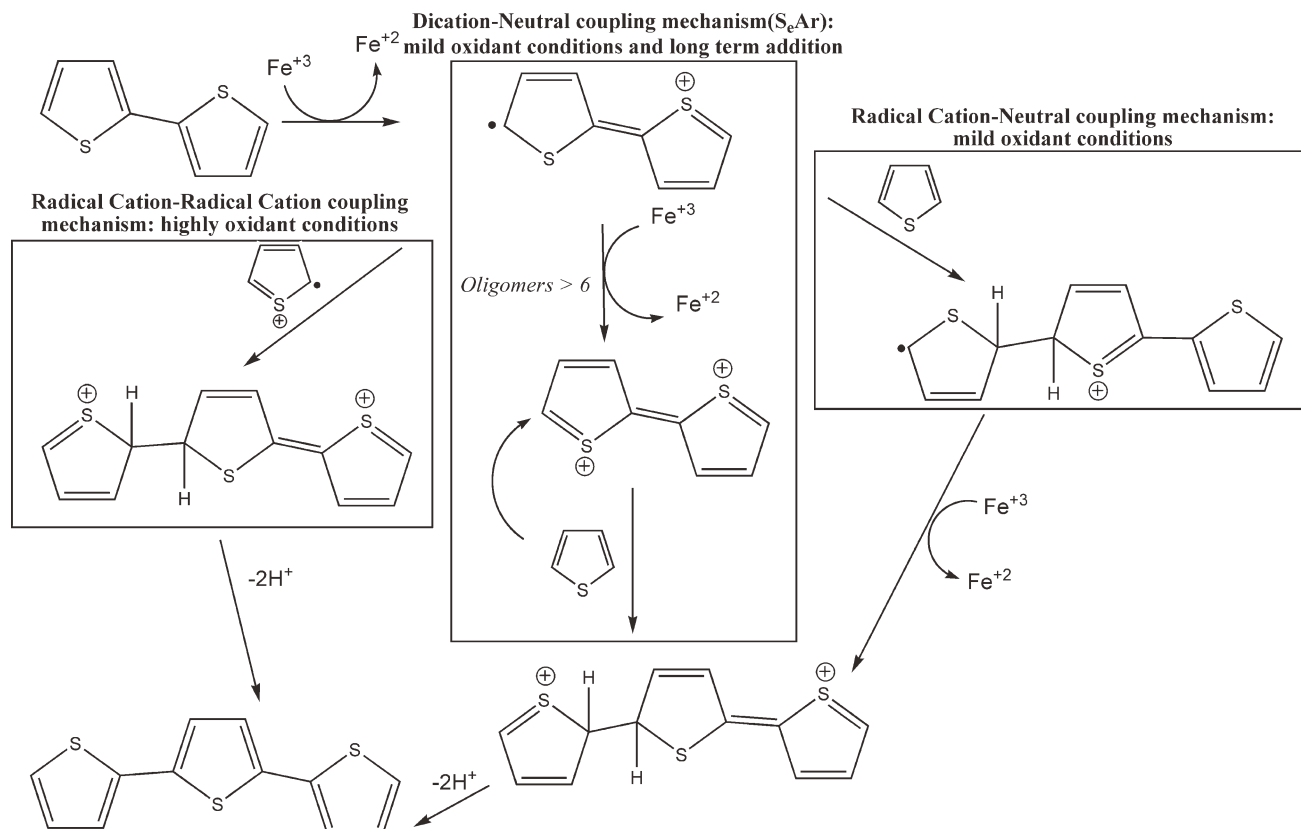
Figure 5 Reaction mechanism—possible chain propagations and their relation with different reaction conditions.

slow oxidant addition might be understood considering that lower oxidant addition rate favors the coupling between neutral species with radical-cations and cations rather than the coupling between two cation-radicals.[17] Moreover, since the oligomers are more easily oxidized than monomers, when the oxidant addition rate is lowered, it could favor the coupling between oligomers and monomers rather than the coupling between oligomers, and consequently, increasing the probability of HT coupling. The effect of temperature on the regioregularity can be due only to kinetic effects, since the diffusion

rates and thermal activation will be greatly affected by changing the reaction temperature. As slower the reaction, more selective the couplings can be and slightly differences in chemical activation of the ring atoms can become more important.

TABLE II
Effect of n-Hexane Extraction – Regioregularity Degrees, Yields, Molar Mass Averages (M_n, M_w) and Poydispersivities (PDI) of Crude Polymer, Soluble and Insoluble Fraction in n-Hexane

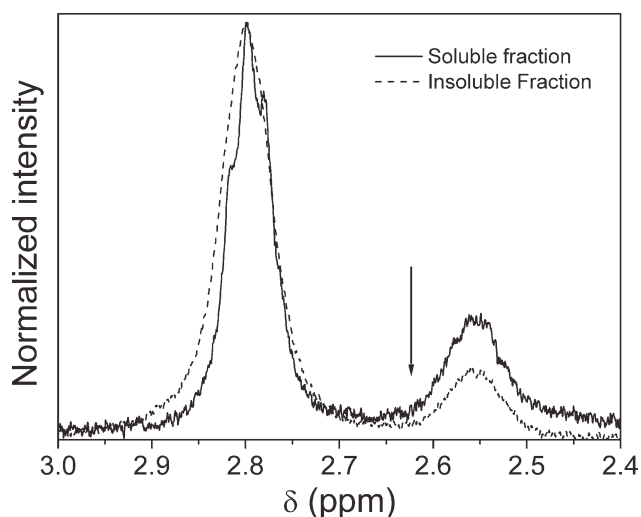| Reaction conditions	%HT	M_n	M_w	PDI
25°/Instantaneous				
Crude	69.6%	21,000	41,600	2.0
Insoluble Fraction	69.3%	17,400	33,200	1.9
Soluble Fraction	66.4%	10,800	14,600	1.3
−18°/60 min				
Crude	79.0%	48,000	86,700	1.8
Insoluble fraction	81.4%	74,500	145,800	1.9
Soluble fraction	67.6%	15,900	19,900	1.2

Figure 6 Effect of hexane extraction for the condition −18°C/1 hour of addition on the methylene signals of H^1-NMR spectra of the polyoctylthiophenes samples in deutered chloroform.
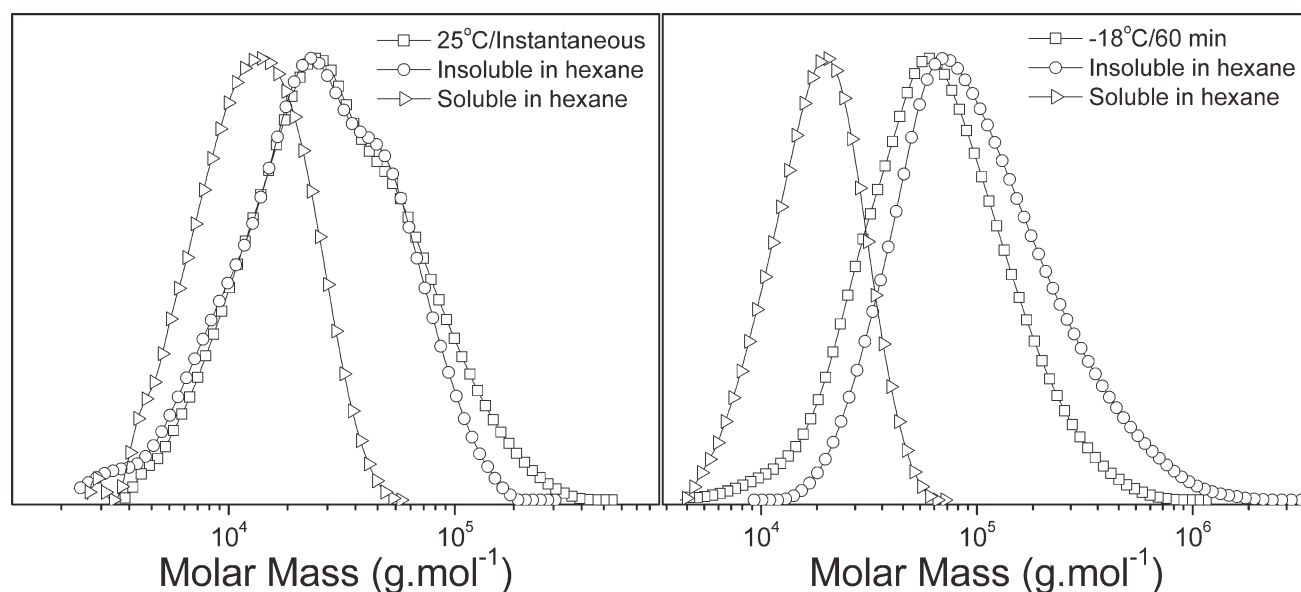
Figure 7 Molar mass distributions for the products of 25°C/instantaneous and −18°C/60 min reactions, before (crude polymer) and after extraction (soluble and insoluble fraction) with n-hexane.

It is well known that regioregular poly-3-alkythiophenes has higher crystallinity and poorer solubility compared to random ones.[25] Thus, it seems feasible to extract the lesser regioregular fractions with a poor solvent for the regioregular fraction. We carried out the extraction of two polymers (25°C/instantaneous addition of oxidant and −18°C/60 min) with n-hexane in a Soxhlet apparatus for 24 hours. For the synthesis at 25°C with instantaneous addition, no improvement on the regioregularity degree was observed for the insoluble fraction. On the other hand, we observed an increase of 3% for the −18°C/1 hour condition (Table II and Fig. 6), indicating that the proper solvent choice can lead to a significant improvement in the content of the more regioregular fraction. For the reaction 25°C/Instantaneous, SEC results show that there is no significant difference between the molar mass distributions of the crude polymer and the insoluble fraction in n-hexane (Fig. 7), both samples presenting a peak at ca. 25,000 g mol^{-1} and a shoulder ca 50,000 g mol^{-1}. On the other hand, for the reaction −18°C/60 min, the insoluble fraction has slightly greater molar mass averages than the crude polymer (peaks at ca. 70,000 g mol^{-1} and 60,000 g mol^{-1}, respectively), while for both reactions the soluble fraction shows smaller ones, with peaks at 13,000 g mol^{-1} and 20,000 g mol^{-1} for instantaneous addition and −18°C/60 min samples respectively. These results suggest that exists a possible direct correlation between the molar mass distribution obtained by SEC and the regioregularity (Table II). Further experiments on optimizing the extraction and on the relation between regioregularity degree and the size exclusion chromatographic profiles are being carried out.

CONCLUSIONS

We showed that is possible to easily synthesize poly-3-alkylthiophenes with improved regioregularity degree through oxidative polymerization by simply lowering the reaction temperature and changing the oxidant addition method. Moreover, it is possible to further improve the regioregularity by extracting the lesser regioregular fraction with poor solvents. However, these strategies still result in materials with lesser regioregularity than those obtained by using organomettalics. Therefore, other modifications, such using different solvents and longer addition times at lower reaction temperatures are being investigated to verify if it is possible to increase even more the regioregularity degree of the materials obtained by the oxidative polymerization. Furthermore, experiments aiming to improve the separation of low regioregular components and on the relation between regioregularity degree and the size exclusion chromatographic profiles are being carried out.

References

1. Pei, J.; Yu, W. L.; Huang, W.; Heeger, A. J. Macromolecules 2000, 33, 2462.
2. Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. Adv Mater 2005, 17, 2281.
3. Zou, Y. P.; Sang, G. Y.; Wu, W. P.; Liu, Y. Q.; Li, Y. F. Synth Met 2009, 159, 182.
4. Wang, F.; Gu, H. W.; Swager, T. M. J Am Chem Soc 2008, 130, 5392.
5. Pandey, P.; Arya, S. K.; Matharu, Z.; Singh, S. P.; Datta, M.; Malhotra, B. D. J Appl Polym Sci 2008, 110, 988.
6. Ocampo, C.; Armelin, E.; Liesa, F.; Aleman, C.; Ramis, X.; Iribarren, J. I. Prog Org Coat 2005, 53, 217.

7. Benvenuti, F.; Galletti, A. M. R.; Carlini, C.; Sbrana, G.; Nannini, A.; Bruschi, P. Polymer 1997, 38, 4973.
8. Roncali, J. Chem Rev 1992, 92, 711.
9. Della-Casa, C.; Fraleoni-Morgera, A.; Lanzi, M.; Costa-Bizzarri, P.; Paganin, L.; Bertinelli, F.; Schenetti, L.; Mucci, A.; Casalboni, M.; Sarcinelli, F.; Quatela, A. Eur Polym J 2005, 41, 2360.
10. Li, Y. W.; Xue, L. L.; Xia, H. J.; Xu, B.; Wen, S. P.; Tian, W. J. J Polym Sci Part A: Polym Chem 2008, 46, 3970.
11. Meisel, S. L.; Johnson, G. C.; Hartough, H. D. J Am Chem Soc 1950, 72, 1910.
12. Ramsey, J. S.; Kovacic, P. J Polym Sci Part A: Polym Chem 1969, 7, 127.
13. Kovacic, P.; McFarland, K. N. J Polym Sci Part A: Polym Chem 1979, 17, 1963.
14. Armour, M.; Davies, A. G.; Upadhyay, J.; Wasserma, A. J Polym Sci Part A: Polym Chem 1967, 5, 1527.
15. Leclerc, M.; Diaz, F. M.; Wegner, G. Macromol Chem Phys 1989, 190, 3105.
16. Niemi, V. M.; Knuuttila, P.; Osterholm, J. E.; Korvola, J. Polymer 1992, 33, 1559.
17. Andersson, M. R.; Selse, D.; Berggren, M.; Jarvinen, H.; Hjertberg, T.; Inganas, O.; Wennerstrom, O.; Osterholm, J. E. Macromolecules 1994, 27, 6503.
18. Chen, T. A.; Wu, X. M.; Rieke, R. D. J Am Chem Soc 1997, 117, 233.
19. Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. Adv Mater 1999, 11, 250.
20. McCullough, R. D. Adv Mater 1998, 10, 93.
21. Wu, Y.; Liu, P.; Gardner, S.; Ong, B. S. Chem Mater 2005, 17, 221.
22. Mcculloch, I.; Heeney,M.; Bailey,C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; Mcgehee, M. D.; Toney, M. F. Nat Mater 2006, 5, 328.
23. Miyasaka, M.; Yamazaki, T.; Tsuchida, E.; Nishide, H. Macromolecules 2000, 33, 8211.
24. Andersson, M. R.; Selse, D.; Berggre, M.; Järvinen, H.; Hjertberg, T.; Inganäs, O.; Wennerström, O.; Österholm, J. E.; Macromolecules 1994, 27, 6503.
25. Amou, S.; Haba, O.; Shirato, K.; Hayakawa, T.; Ueda, M.; Takeuchi, K.; Asai, M. J Polym Sci Part A: Polym Chem 1999, 37, 1943.
26. Barbarella, G.; Zambianchi, M.; DiToro, R.; Colonna, M.; Iarossi, D.; Goldoni, F.; Bongini, A. J Org Chem 1996, 61, 8285.
27. Ando, S.; Ueda, M. Synth Met 2002, 129, 207.