Investigation on Different Procedures in the Oxidative Copolymerization of a Dye-Functionalized Thiophene with 3-Hexylthiophene

Alessandro Fraleoni-Morgera,* Carlo Della-Casa, Massimiliano Lanzi, and Paolo Costa-Bizzarri

Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Viale del Risorgimento, 4 I-40136 Bologna, Italy

Received June 26, 2003; Revised Manuscript Received September 12, 2003

ABSTRACT: For the purpose of preparing materials for nonlinear optics applications, a 3-ethylthiophene bearing an NLO-active chromophoric group as a substituent at the end of the ethylic chain was copolymerized with 3-hexylthiophene. Different $FeCl_3$-based oxidative polymerization conditions in solvents such as CH_3NO_2 and CCl_4 and their effects on the copolymers characteristics and solubility in $CHCl_3$ (i.e., the copolymer's soluble fraction) were examined. This work allowed to achieve a satisfactory chloroform-soluble fraction of the copolymer, still containing a notable amount of NLO-active group, and to tune to some extent the main characteristics of the copolymer; moreover, the behavior of the monomers−solvent−oxidant system was investigated.

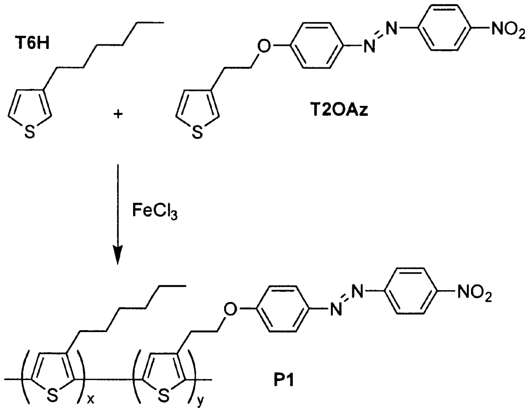
Introduction

In the past years the area on nonlinear optics (NLO) applications has drawn considerable attention from chemists because of the possibility to obtain both very high NLO responses and a molecular design tailored for the desired application from organic materials; in particular, polymeric systems of this nature are being widely investigated.[1,2] There are various methods for obtaining polymeric materials for NLO applications. Given the interesting electronic properties and the high thermal and chemical stability of the conjugated polythiophenes, our attention has focused on the grafting of a second-order NLO-active molecule as a side-chain pendant of a 3-alkylthiophene;[3−5] it cannot be ignored, however, that the intrinsic properties of the NLO-active molecules make it difficult to obtain satisfactory processable materials. In fact, the solubility of polythiophenes containing chromophoric groups is often very low.[6−11] The aim of the present study has hence been to overcome this problem so as to open the way for obtaining really application-suitable materials, through a systematic study aimed at optimizing the oxidative polymerization for achieving soluble products. In particular, our attention has focused on reagent and solvent addition modalities, as reaction results are deemed to be mainly affected by these parameters.

For this study the monomer 3-[2-(4-(4′-nitrophenylazo)phenoxy)]etylthiophene (T2OAz) was taken as the reference dye-functionalized compound and was copolymerized with 3-hexylthiophene (T6H) to yield the polymer P1 (Scheme 1).

More precisely, polymer P1 was prepared via $FeCl_3$ oxidative polymerization by different methods mostly based on a two-solvent approach (CH_3NO_2/CCl_4, where CH_3NO_2 is a solvent and CCl_4 a nonsolvent for $FeCl_3$), capable of giving better yields in terms of soluble polymer fraction than the usually employed $CHCl_3$-based one.[12] The key step of this procedure involved the use of a dissolved form of $FeCl_3$ which, upon contact with the nonsolvent CCl_4, probably precipitates in the form of microcrystals, thus providing a wider surface for polymerization to begin and leading to the formation of a more chloroform-soluble polymer.

Scheme 1. General Synthetic Route to Copolymers P1, Obtained Keeping the Molar Ratio between T6H and T2OAz in the Feed Constant to 1:1[a]



[a] With reference to the soluble fraction of the copolymers, x was found variable between 0.21 and 0.48 ($y = 1 - x$) depending on the reaction conditions used.

By varying reaction times, as well as solvent and reactant addition modalities, and keeping constant reaction temperature (room temperature) and comonomer feed ratio (1:1), a number of copolymers with different characteristics were obtained.

The presented results provide interesting information on the behavior of these systems, and the proposed synthetic methods permit to achieve acceptable yields in terms of soluble material.

Results and Discussion

The functionalized monomer T2OAz was made react with T6H in a 50:50 molar feed ratio under different reaction conditions. The operative parameters are shown in Table 1, where columns S1, S2, and S3 refer to the solvent placed in the reaction flask, the solvent used for delivering the reactants into the reactor, and the

---

* Corresponding author: e-mail fraleoni@ms.fci.unibo.it; Tel +39-051-2093672; Fax +39-051-2093673.

10.1021/ma0348730 CCC: $25.00

Table 1. Overview of the Main Operating Parameters

reaction	solvent S1[a]	solvent S2[b]	solvent S3[c]	reaction time T1[d] (min)	reaction time T2[e] (h)	reaction time T3[f] (h)
r1	CCl_4	CH_3NO_2		13		1
r2	CH_3NO_2	CH_3NO_2		20		157
r3	CH_3NO_2	CCl_4		<1		1
r4	CH_3NO_2	CCl_4		<1		3
r5	CH_3NO_2	CH_3NO_2	CCl_4	<1	21	3
r6	CH_3NO_2	CH_3NO_2	CCl_4	<1	21	9
r7	CH_3NO_2	CH_3NO_2	CCl_4	<1	1	3
r8	CH_3NO_2		CCl_4	$\ll$1	1	3

[a] Solvent placed in the reaction flask. [b] Solvent used for delivering the reactants into the reactor. [c] Solvent added after a first reaction step. [d] Time during which the oxidant was added to the comonomer mixture, or vice versa. [e] Time set for the first reaction step. [f] Time set for the reaction to proceed.

Table 2. Main Characteristics of the Obtained Copolymers

sample[a]	Y1[b] (%)	Y2[c] (%)	Y3[d] (%)	composition[e] (%)	M_n[f] (g/mol)	PDI[f]
1	61	4	7	30	6 100	2.75
2	34	24	72	28	24 800	2.50
3	28	11	39	35	5 700	2.80
4	60	18	30	48	8 300	2.10
5	36	33	92	32	5 500	2.50
6	40	31	78	33	17 300	2.50
7	37	26	70	26	13 700	2.40
8	41	25	61	21	27 300	2.00

[a] Numbered according to the reaction numbers reported in Table 1. [b] Overall yield. [c] Soluble copolymer yield. [d] Soluble copolymer yield with respect to overall yield. [e] Percentage of T2OAz in the main chain of the soluble fraction, as from ^{1}H NMR measurements. [f] Determined by means of GPC using polystyrene standards.

solvent added after a first reaction step, respectively. Reaction times T1, T2, and T3 refer to the addition time of the oxidant to the comonomer mixture or vice versa, the time set for the first reaction step, and the time set for the reaction to proceed, respectively. The main characteristics of the obtained copolymers are given in Table 2. The amount of dye-substituted monomer incorporated in the soluble fraction was determined by ^{1}H NMR through the weighted ratio between the signals coming from the protons in α to the oxygen atom of the chromophore (a multiplet centered at 4.32 ppm) and the ones belonging to the methylic group of the hexylic chain (singlet at 0.90 ppm).[3]

The results of reactions r1, r2, and r3 clearly show that the physical state of $FeCl_3$ (i.e., solid or dissolved) plays a very important role in the reaction behavior. In fact, as may be qualitatively inferred from the overall yields obtained (Table 2, Y1), reaction speed diminishes and copolymer soluble fraction significantly increases (Table 2, Y2 and Y3) when changing from a condition in which $FeCl_3$ is readily precipitated (r1) to one in which it is completely dissolved (r2).

In view of the foregoing, reaction r3 may be considered as an intermediate step between reactions r1 and r2. Under reaction r3 conditions, in fact, reactant addition modalities are such as to cause $FeCl_3$ to precipitate gradually from the reaction mixture, so that the comonomers remain in contact with the solvated oxidant for a longer time than in reaction r1. While leading to a lower overall yield Y1 as compared to that of reaction r1, this method permits to achieve a noteworthy increase (almost 3-fold) of the soluble fraction (Y2).

On the basis of these findings, it would appear that $FeCl_3$ is less active in the dissolved form than in the solid one, requiring a longer time for generating concurrently less polymer and a higher soluble fraction. This assumption is borne out by the comparison between the modalities of polymerization and the respective soluble fractions relative to the overall yields (Table 2, Y3) recovered from reactions r1, r2, and r3, the extent of which may be ordered as r1 < r3 < r2. Moreover, the findings reported by Niemi et al., according to whom no polymer formation is detected within 20′ from the starting of the reaction in solvents where $FeCl_3$ is soluble,[13] are further confirmation that the reaction rate is definitely slow when that oxidant is kept in its solvated form.

Compared to the results of reaction r3**,** those of reaction r4 show that the longer reaction time T3 of the latter (Table 1) greatly enhances the overall yield Y1 and adversely affects the soluble fraction of the polymer obtained. In fact, the overall yield in soluble fraction (Y2) is higher for reaction r4 than for r3, but considering that value relative to the total copolymer obtained (Table 2, Y3), it is clear that a lowering of the soluble fraction of the copolymer has indeed occurred in reaction r4. Since during the reaction time T3 the oxidant is in its precipitated form, this result sounds as a further confirmation of the already exposed hypothesis about the lower activity of $FeCl_3$ in its solvated form.

Another interesting point is that the functionalized unit content of the copolymers, as determined from ^{1}H NMR spectra, is considerably higher in reaction r4 than in r3. This finding, clearly ascribable to the longer T3 set for reaction r4 compared to r3, points to a different reactivity of the dye-functionalized unit toward T6H in the reaction (a topic that will be addressed by the authors in a forthcoming study) and suggests the possibility of tuning to some extent the T2OAz content of the copolymer by appropriately choosing the reaction conditions.

In view of the observed influence of the state of $FeCl_3$ on the reaction results, attempts were made to find a method for accelerating reaction r2, that is, the reaction that proved to yield the highest soluble fraction of the copolymer. Polymerizations were hence started in pure CH_3NO_2, and only after a given period of time (Table 2, T2) CCl_4 was introduced in the system, so as to cause $FeCl_3$ to precipitate, after which the reaction mixture was allowed to react for an additional reaction time T3.

The results of this latter method confirmed our first observations. In fact, as can be seen in reactions r5 and r6**,** the addition of CCl_4 clearly boosts the reaction, giving a yield Y3 comparable to the one of reaction r2 but in a considerably shorter time (Table 2). Moreover, these findings furtherly confirm that the longer $FeCl_3$ is kept in a precipitated form, the less is the amount of soluble fraction recovered from the reaction (Table 2, samples 5 and 6).

To investigate the impact of the T2 time on both the yield and characteristics of the polymer recovered from the system another reaction, r7, was performed. As can be seen in Table 2 (sample 7), a good amount of soluble fraction was obtained without any need for long T1 reaction times. This finding suggests that the initial chain segment generation is fast enough to allow subsequent chain growth and that reactions of this kind may be performed over a reasonable time by following this "step-by-step" solvent addition method.

Aiming to check other possible reaction conditions, another polymerization method, in which the oxidant was added all at once in its solid form to the comonomers solution in CH_3NO_2 (reaction r8), was investigated. This latter procedure led to the formation of a copolymer with a slightly lower dye-substituted monomer content than the previous ones, but with the same yields in terms of soluble fraction which, most interestingly, was found to have fairly high molecular weights (Table 2, sample 8). This result is probably ascribable to the peculiarity of the method, in which $FeCl_3$ is made to enter the reaction environment in its reactive solid form; upon the quick mixing with CH_3NO_2, however, the oxidant is promptly solvated, thus lowering its activity and leading to soluble material with interesting molecular weights.

Conclusions

To summarize, in this work the $FeCl_3$-based oxidative polymerization of the 3-alkylthiophenic copolymer P1 was investigated.

Reaction speed and copolymer characteristics are greatly affected by the synthetic method employed, and the precipitation of $FeCl_3$ from a solvated form boosts the reaction speed, suggesting that the physical state of the oxidant would play a major role in determining the reaction behavior. Moreover, it has been seen that this kind of polymerization takes place, albeit at a very slow rate, even when $FeCl_3$ is present in a dissolved form.

Taking into account these results, different methods of synthesis that proved to be efficient, in terms of both chloroform soluble fractions and reaction times, were developed for a very interesting class of chromophore-functionalized thiophenic copolymers; the main characteristics of these copolymers (molecular weights, percentage of dye-substituted monomer in the soluble fraction, chloroform soluble fraction) may be to some extent tuned by adopting appropriate reaction conditions. In particular, for obtaining the highest possible soluble fraction the best procedure is the one depicted in reaction 5, while for achieving the highest molecular weights the method used for reaction 8 is more appropriate. If one would want to obtain the maximum possible amount of dye-functionalized comonomer in the soluble fraction, the method used for reaction 4 is the more favored.

Finally, the obtained results permitted to shed some light on the basic mechanism of oxidative polymerization; nonetheless, a much higher level of comprehension of this reaction is needed in order to refine the preparation of the examined materials.

Experimental Section

^{1}H NMR spectra were run on a Varian Gemini 300 FT-NMR spectrometer operating at 300 MHz, using TMS as a reference. IR spectra of the polymers (dispersion powder in a KBr pellet) were recorded using a Perkin-Elmer 1750 FT-IR spectrophotometer. UV−vis spectra ($CHCl_3$ solutions of the polymers) were carried out using a Perkin-Elmer Lambda 19 spectrophotometer. Molecular weights were determined by means of gel permeation chromatography (GPC) on a HPLC Lab Flow 2000 apparatus equipped with a Phenogel MXM column and a linear UVIS-200 UV−vis detector, using polystyrenic standards as reference, with THF as eluent at a flow rate of 1.0 mL/min.

All the solvents and reagents used for the synthesis were purchased from Aldrich Chemical Co. The monomer T2OAz was prepared as described elsewhere,[14] while T6H was purchased from Sigma-Aldrich and used without further purification.

All reactions were carried out under a dry nitrogen atmosphere and with anhydrous solvents, employing 1.0 mmol of each comonomer (i.e., 1.0 mmol of T2OAz, 0.353 g, plus 1.0 mmol of T6H, 0.168 g), with the feed ratio being kept constant at 1:1. The molar ratio between $FeCl_3$ (anhydrous) and the comonomers was always kept at 4:1 (i.e., 8 mol of $FeCl_3$ for 1 mol of T2OAz plus 1 mol of T6H).

When CH_3NO_2 was used to dissolve the comonomers, it was sometimes required to slightly warm the solution and then to let it cool to obtain a clear solution.

The reactions were carried out by the procedures described below.

Reaction r1. The comonomers were placed in a three-necked round flask and dissolved in 27 mL of CCl_4 (Table 1, S1), with the mixture being kept under stirring. A solution of an appropriate amount of $FeCl_3$ in 9 mL of CH_3NO_2 (Table 1, S2) was added drop by drop in 13 min (Table 1, T1).

The resulting mixture was allowed to react for 1 h (Table 1, T3) and then quenched with a CH_3OH/HCl (5% in HCl) solution with a 1:10 v/v ratio.

The solid copolymer was then filtered off and washed with CH_3OH until no iron(III) was detectable by means of the NH_4SCN test. It was then extracted with CH_3OH in a Soxhlet apparatus until the solvent was colorless, to eliminate unreacted monomers and oligomers, and finally dried under vacuum on P_2O_5 to give 0.318 g of raw copolymer (Table 2, overall yield Y1: 61%).

The raw material was then extracted with $CHCl_3$ in a Soxhlet apparatus until the solvent was colorless; the insoluble fraction was separated, while the recovered $CHCl_3$ solution was concentrated, dried, and weighed to give 0.021 g of soluble copolymer (Table 2, soluble fraction yield Y2: 4%).

Reaction r2. The comonomers were placed in a three-necked round flask and dissolved in 38 mL of CH_3NO_2 (S1), with the mixture being kept under stirring. The solution of $FeCl_3$ in 9 mL of CH_3NO_2 (S2) was added drop by drop to the first one in 20 min (T1), and the resulting mixture was allowed to react under stirring for 157 h (T3).

The reaction mixture was then quenched and worked up as for reaction r1, giving 0.177 g of raw copolymer (Y1 = 34%), from which 0.125 g of soluble copolymer (Y2 = 24%) was recovered.

Reactions r3 and r4. A solution of $FeCl_3$ in 9 mL of CH_3NO_2 (S1) was placed in a three-necked round flask and kept under stirring. The comonomers were then dissolved in 27 mL of CCl_4 (S2) and added to the $FeCl_3$ solution in less than 1 min (T1), and the resulting mixture was allowed to react under stirring for 1 h (T3) in the case of reaction r3 and for 3 h (T3) in the case of reaction r4.

In both cases the resulting reaction mixture was then quenched and worked up as for reaction r1**.** In reaction r3 0.146 g of raw copolymer (Y1 = 28%) was obtained, from which 0.057 g of soluble copolymer (Y2 = 11%) was recovered, while in reaction r4 0.313 g of raw copolymer (Y1 = 60%) was obtained, of which 0.094 g (Y2 = 18%) was found to be soluble.

Reactions r5, r6, and r7. The comonomers were placed in a three-necked round flask and dissolved in 38 mL of CH_3NO_2 (S1), with the mixture being kept under stirring. The solution of $FeCl_3$ in 9 mL of CH_3NO_2 (S2) was added to the first one in less than 1 min (T1), and the resulting mixture was allowed to react under stirring for 21 h (T2), 21 h (T2), and 1 h (T2) for reactions r5, r6, and r7, respectively. CCl_4 (180 mL, S3) was then added to the mixture, which was kept under stirring for an additional 3 h (T3), 9 h (T3), and 3 h (T3) for reactions r5, r6, and r7, respectively.

The resulting reaction mixture was then quenched and worked up as for reaction r1.

For reaction r5 0.188 g of raw copolymer (Y1 = 36%) was recovered, from which 0.172 g of soluble copolymer (Y2 = 33%) was extracted; for reaction r6 0.208 g of raw copolymer (Y1 = 40%) was recovered, from which 0.162 g of soluble copolymer (Y2 = 31%) was extracted; for reaction r7 0.193 g of raw copolymer (Y1 = 37%) was recovered, from which 0.135 g of soluble copolymer (Y2 = 26%) was extracted.

Reaction r8. The comonomers were placed in a three-necked round flask and dissolved in 45 mL of CH_3NO_2 (S1), with the mixture being kept under stirring. Solid $FeCl_3$ was added to the system all at once (T1) by mean of a navel. So as to prevent air from entering the reaction flask, the operation was carried out under a sustained dry N_2 flow. The reaction mixture was allowed to react under stirring for 1 h (T2). CCl_4 (180 mL, S3) was then added to the system, and the mixture was kept under stirring for an additional 3 h (T3).

The reaction mixture was then quenched and worked up as for reaction r1, giving 0.214 g of raw copolymer (Y1 = 41%), from which 0.130 g of soluble copolymer (Y2 = 25%) was recovered.

Molecular weights are reported in Table 2.

Since the same kind of copolymer was obtained from all the reactions, only one set of characterization results is reported here. The only appreciable differences between the various samples, apart of the molecular weights, were found in the relative intensities of the peaks in the ^{1}H NMR, UV−vis, and FT-IR spectra owing to the different dye content of each copolymer batch.

^{1}H NMR ($CDCl_3$): $\delta = 8.32$ (s), 7.84 (s), 7.18−7.08 (m), 7.06−6.98 (m), 4.42−4.22 (m), 3.37 (s), 3.15 (s), 2.80 (s), 2.60 (s), 1.74−1.52 (m), 1.48−1.24 (m), 0.90 (s) ppm.

UV−vis ($CHCl_3$): λ_{max} 385 nm (shoulder: 450 nm).

IR (KBr): 2952, 2924, 2854, 1598, 1521, 1499, 1455, 1341, 1249, 1137, 1106, 859, 835 cm^{-1}.

Acknowledgment. Dr. Matteo Zandri is gratefully acknowledged for his assistance in copolymer synthesis. This work was supported by the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), and by the Università di Bologna, Italy (funds for selected research topics).

References and Notes

(1) Nalwa, H. S. In *Handbook of Organic Conductive Molecules and Polymers*, 1st ed.; Nalwa, H. S., Ed.; J. Wiley & Sons: Chichester, 1997; Vol. 4, p VI, p 261 ff.
(2) Samyn, C.; Verbiest, T.; Persoons, A. *Macromol. Rapid Commun.* **2000**, *21*, 1.
(3) Della Casa, C.; Fraleoni, A.; Costa Bizzarri, P.; Lanzi, M. *Synth. Met.* **2001**, *124*, 467.
(4) Della Casa, C.; Fraleoni, A.; Costa Bizzarri, P.; Lanzi, M.; Paganin, L. *Macromol. Symp.* **2002**, *180*, 217.
(5) Lanzi, M.; Paganin, L.; Costa-Bizzarri, P.; Della-Casa, C.; Fraleoni, A. *Macromol. Rapid Commun.* **2002**, *23*, 630.
(6) Chen, S.-A.; Liao, C.-S. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 69.
(7) Chittibabu, K. G.; Li, L.; Kamath, M.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1994**, *6*, 475.
(8) Lévesque, I.; Leclerc, M. *Macromolecules* **1997**, *30*, 4347.
(9) Zagórska, M.; Kulszewicz-Bajer, I.; Proń, A.; Sukiennik, J.; Raimond, P.; Kajzar, F.; Attias, A.-J.; Łapkowski, M. *Macromolecules* **1998**, *31*, 9146.
(10) 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.
(11) Zhao, X.; Hu, X.; Yue, C. Y.; Xia, X.; Gan, L. H. *Thin Solid Films* **2002**, *417*, 95.
(12) Costa Bizzarri, P.; Andreani, F.; Della Casa, C.; Lanzi, M.; Salatelli, E. *Synth. Met.* **1995**, *75*, 141.
(13) Niemi, V. M.; Knuuttila, P.; Österholm, J.-E.; Korvola, J. *Polymer* **1992**, *33*, 1559.
(14) Della Casa, C.; Costa Bizzarri, P.; Lanzi, M.; Paganin, L.; Bertinelli, F.; Pizzoferrato, R.; Sarcinelli, F.; Casalboni, M. *Synth. Met.* **2003**, *138*, 409.

MA0348730