Acid-Catalyzed Polycondensation of 2-Acetoxymethyl-3,4-dimethylthiophene. Access to a Novel Poly(thienylene methine) with Alternating Aromatic- and Quinoid-like Structures[†]

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ABSTRACT: This paper reports the synthesis of a novel soluble poly(thienylene methylene) by a straightforward process based on the methanesulfonic acid-catalyzed self-condensation of 2-acetoxymethyl-3,4-dimethylthiophene. These macromolecules were found to generate in situ conjugated sequences consisting of thiophene and exo-unsaturated 2,5-dihydrothiophene moieties. The kinetics of these polycondensations, in which both the temperature and the monomer-to-catalyst molar ratio were varied, were followed by HPLC, as regards the rate of monomer consumption, and by GPC, as regards the evolution of the molecular weight of the growing chains. The ensuing polymers were characterized by FTIR, ^{1}H NMR, UV−vis spectroscopy, DSC, and TGA.

Introduction

Conjugated polymers have attracted increasing interest because of the wide range of their possible applications, thanks to their unique optical, electrical, and mechanical properties, which include, among others, organic light-emitting diodes, field effect transistors, and photovoltaic cells.[1] In this field, polythiophenes, and in general thiophene-based functional polymers, have been extensively investigated and, in particular, their synthetic aspects have been focused on novel low-bandgap and regioregular materials.[2,3] The reduction of the energy bandgap can facilitate doping, giving the possibility of achieving intrinsic metallic conductivity. An important prerequisite for low-bandgap materials is the contribution of quinoid-like structures to the electronic ground state of the polymer backbone. In this respect, some poly(thienylene methine)s with alternating aromatic and quinoid moieties in the main polymer chain have been prepared[4] following a two-step process involving the formation of nonconjugated polymer precursors, by the reaction between thiophene derivatives and aromatic aldehydes, and their subsequent conversion to the corresponding conjugated homologues via oxidative elimination of bridge hydrogen atoms.

We reported novel soluble poly(thienylene methylene)s with alternating conjugated aromatic- and quinoid-like moieties along their backbone through a very simple acid-catalyzed self-condensation of 2-hydroxymethylthiophene (HMT) and several of its derivatives.[5,6] The acid-catalyzed or heat-induced polycondensation of the furan counterpart of HMT, viz. furfuryl alcohol, had previously been extensively studied[7] and shown to give rise, irrespective of the specific experimental conditions, to black and cross-linked materials because major side reactions, arising in part from the dienic character of the furan ring, accompany the linear chain growth.[8] Given the lower dienic and higher aromatic character of the thiophene heterocycle, compared with those of the furan counterpart,[7] we started a systematic investigation of the polycondensation of HMT, its ester 2-acetoxymethylthiophene, and other derivatives, induced by various Lewis and Brønsted acids,[5] in which the emphasis was placed on the optimization of the processes and the elucidation of the structure of the ensuing polymers.

The main differences encountered with respect to the furan-based systems[8] were (i) the fact that the 3- and 4-positions of the thiophene ring are as reactive toward electrophilic substitution as the 5-position (the only reactive site for the furfuryl structures) and (ii) the lack of cross-linking reactions among polymer chains, due to the very poor dienic character of the thiophene heterocycle, since the cross-linking mechanism of the furfuryl homologues was shown to take place through intermolecular Diels−Alder couplings.[8] Conversely, the most relevant common features between these systems[5,8] were the formation of (i) sequences of thienylene−methylene ($-$Th$-$CH$_2-$) units and (ii) conjugated quinoid-like moieties containing exo-unsaturated 2,5-thiophene structures formed through sequences of hydride ion and proton losses.

The possibility of exploiting these systems as precursors to highly conjugated macromolecular architectures prompted us to pursue this investigation with the aim of acquiring the necessary insight into their kinetics and mechanisms[6] as a precondition to a study of the actual materials. The monomers chosen were 2-acetoxymethylthiophene and its C3 and C5 methylated homologues. The acetates were preferred to the corresponding alcohols in order to avoid moisture accumulation in the reaction medium. The methyl substitutions were introduced in order to examine the alternative modes of condensation on the thiophene ring and their possible electronic and steric influence on the kinetics of this reaction. The presence of a methyl substituent at the 3- or 5-position did not affect the qualitative features of the polymerizations, whereas their rates were enhanced owing to the donor character of the appended substituent. All reactions followed a first-order behavior with respect to the monomer, and the activation energies were systematically around 50 kJ mol^{-1}. The DP of the polymer products grew as a function of the reaction time to reach values of about 40 at complete monomer consumption, and thereafter further chain growth could be reactivated by subsequent monomer additions. Initiation in the presence of added polymer led to its grafting, with a substantial increase in molecular weight. The evidence gathered suggested that these polycondensations bear a living character.

To avoid the irregular enchainment of the monomer units, while maintaining the possibility of forming conjugated se-

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[†] This contribution is dedicated to the fond memory of our dear friend and colleague Giovanna Costa, who died while this investigation was in progress.

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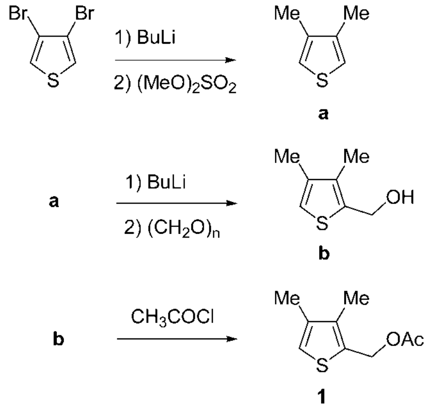
Scheme 1. Synthetic Route Followed to Prepare Monomer 1



quences, the initial study was now extended to a new monomer, namely 2-acetoxymethyl-3,4-dimethylthiophene (**1**). This double methyl substitution at the 3- and 4-positions of the thiophene ring relegates the possibility of the electrophilic attack exclusively to the 5-position, thus leading to a regular enchainment of methylene-bridged C2−C5 thiophene rings, hopefully favoring the formation of longer conjugated sequences. The present study describes the behavior of **1** in terms of the kinetics and mechanism of its straightforward acid-catalyzed polycondensation, together with the structure and properties of its ensuing polymers.

Experimental Section

Reagents and Solvents. 3,4-Dibromothiophene (Aldrich, 99%), *n*-butyllithium (BuLi, Aldrich, 10 and 1.6 M in hexanes), dimethyl sulfate (Aldrich, 99+%), paraformaldehyde (Aldrich, 95%), acetyl chloride (Fluka, ≥99%), commercial anhydrous diethyl ether, tetrahydrofuran (THF), and pyridine, as well as other chemicals, were used as received for the monomer synthesis. Methanesulfonic acid ($MeSO_3H$, Fluka, ≥99%), triethylamine (TEA, Fluka, 99.5%), and the two high-purity solvents, 1,4-dioxane (dioxane) and 1,1,2,2-tetrachloroethane (TCE), were used as received for the polycondensations. Pure commercial methanol was used as the polymer precipitation medium. 2-Phenyl-4,5-dimethyldioxolenium hexafluoroarsenate (PDDFA), used as a hydride ion abstractor, was a generous gift of Professor Zedlinski of the Polish Academy of Sciences in Zabrze.

Characterization Techniques. The ^{1}H NMR spectra of monomer and intermediates were recorded using a Varian Gemini 300 spectrometer ($CDCl_3$ as solvent and TMS as internal standard). ^{1}H NMR spectra of the polymers were recorded in TCE-d_2 on a Bruker Avance-400 spectrometer (internal standard hexamethyldisiloxane). The FTIR spectra were taken with a Bruker IFS-28 spectrometer using KBr pellets for solid samples and neat film between two NaCl windows for liquid samples. HPLC analyses were performed with a Beckman System Gold 126 chromatograph (Beckman 167 UV detector, gradient elution water/methanol, SUPELCOSIL-LG18-DB column). GPC analyses were carried out with a Perkin-Elmer chromatograph (diode array detector 235C, eluent THF, flow rate 1 mL/min, μ-styragel column set: 10^5, 10^4, 10^3, 500 Å), whose calibration curve was obtained with monodispersed polystyrene standards. UV−vis spectra (CH_2Cl_2 solutions) were recorded with a Varian Cary 400 BIO spectrophotometer. A computer-interfaced Mettler DSC 821^e was used for the calorimetric analysis (scanning rate 10 °C/min, under N_2). Thermal stabilities (TGA) were assessed with a Perkin-Elmer TGA7 analyzer (heating rate 20 °C/min, under N_2).

Monomer Synthesis. 2-Acetoxymethyl-3,4-dimethylthiophene (**1**) was synthesized following the route sketched in Scheme 1. 3,4-Dimethylthiophene (**a**) was prepared slightly modifying a procedure described in the literature.[9] Under a dry argon atmosphere, a solution of 3,4-dibromothiophene in anhydrous ether (100 mL per 0.05 mol) was cooled to −70 °C. 130 mL of 1 M BuLi (obtained by diluting commercial 10 M BuLi in hexanes with anhydrous ether) was added dropwise into the vessel, and the reaction mixture stirred thereafter at −70 °C for 30 min. A solution of dimethyl sulfate in ether (42 mL per 0.3 mol) was then *slowly* added in order to keep the temperature below −30 °C. The mixture was stirred for a further 45 min, the cooling bath removed, and the flow of argon stopped. A 4 N aqueous solution of sodium hydroxide (1.2 equiv based on dimethyl sulfate) was added, and the mixture was stirred overnight. The ether layer was then separated, the aqueous phase was extracted twice with ether, and the combined extracts were washed three times with water and dried over sodium sulfate. The solvent was then removed under reduced pressure, and the residue was purified by vacuum distillation to yield 80% of **a** (bp 40 °C/30 mmHg; lit.[9] 144 °C/760 mmHg). ^{1}H NMR (δ, ppm): 2.19 (s, 6H, CH_3); 6.91 (s, 2H, *H*2 and *H*5) (lit.[9] 2.15 and 6.84). FTIR (ν, cm^{-1}): 3090 (=C−H stretch); 2971, 2939, 2917, 2862 (−C−H stretch); 1444 (ν thiophene ring breathing); 861 and 781 (=C−H out-of-plane wag in 3,4-disubstituted thiophenes[10]).

2-Hydroxymethyl-3,4-dimethylthiophene (**b**) was prepared by the modification of a literature procedure[11] used for the homologous HMT. 37.5 mL (0.06 mol) of 1.6 M BuLi in hexanes was slowly added, under an argon atmosphere, to a stirred solution of **a** in anhydrous THF (50 mL per 0.05 mol) kept at 0 °C. After 45 min, the mixture was brought to room temperature, and a suspension of paraformaldehyde in THF (0.09 mol in 10 mL) was transferred with a cannula into the reaction vessel. The mixture was then stirred for 3 h at room temperature before removing the solvent by flushing argon into the vessel. The ensuing slurry was poured into water, the pH was adjusted to ~6 with concentrated HCl, and the mixture was extracted three times with ether. The combined extracts were washed three times with water and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude alcohol **b**, obtained in 90% yield, was directly used in the following step. ^{1}H NMR (δ, ppm): 2.13 (s, 3H, CH_3 at C3); 2.15 (d, 3H, J 1.0 Hz, CH_3 at C4); 4.73 (s, 2H, CH_2OH); 6.84 (d, 1H, J 1.0 Hz, *H*5). FTIR (ν, cm^{-1}): 3333 (OH stretch); 3095 (=C−H stretch); 2919, 2869 (−C−H stretch); 1443 (thiophene ring breathing); 992 (C−O stretch); 861, 735 (=C−H out-of-plane wag in 2,3,4-trisubstituted thiophenes[10]).

2-Acetoxymethyl-3,4-dimethylthiophene (**1**). 4.27 mL (0.06 mol) of acetyl chloride was slowly added, under an argon atmosphere, to a stirred solution of **b** in anhydrous pyridine (40 mL per 0.05 mol) kept at 0 °C. After 15 min, the cooling bath was removed, and the mixture was stirred at room temperature for 2 h. It was then poured into acidic water, in order to obtain a pH of about 6, and the ensuing mixture was extracted with ether. The combined extracts were washed with water and dried over sodium sulfate before removing the solvent under reduced pressure and purifying the residue by vacuum distillation to yield 70% of monomer **1** (bp 50 °C/10 mmHg). ^{1}H NMR (δ, ppm): 2.07 (s, 3H, CH_3CO); 2.14 (s, 3H, CH_3 at C3); 2.15 (d, 3H, J 1.0 Hz, CH_3 at C4); 5.18 (s, 2H, CH_2O); 6.89 (q, 1H, J 1.0 Hz, *H*5). FTIR (ν, cm^{-1}): 3093 (=C−H stretch); 2923, 2863 (−C−H stretch); 1739 (C=O stretch); 1443 (thiophene ring breathing); 1228 (C−O stretch); 862, 747 (=C−H out-of-plane wag in 2,3,4-trisubstituted thiophenes[10]).

General Polymerization Procedure. Polymerization reactions were carried out under nitrogen by dissolving the monomer in the solvent (TCE or dioxane) and by adding thereafter under vigorous stirring the catalyst solution (1 M $MeSO_3H$ in TCE or dioxane) to give 1.5 M solutions with respect to the monomer. In a typical polymerization run, with $[Mon]_0/[Cat] = 20$, 1.00 g (0.86 mL, 5.4 mmol) of monomer **1** was dissolved in 2.49 mL of solvent before adding 0.27 mL (2.7 mmol) of a 1 M solution of acid catalyst. During both the addition and the polymerization, the reaction mixture was maintained at the desired constant temperature by keeping the vessel in a thermostated oil bath. Reactions were followed by HPLC, as regards the rate of monomer consumption and by GPC as regards the evolution of the molecular weight of the polymer being formed. During each experiment, samples of the reaction mixture were regularly withdrawn, quenched with a

Table 1. Experimental Conditions Applied to the Various Polycondensations of 1[a]

run	[Mon]$_0$/[Cat][b]	solvent	temp (°C)	time[c] (h)	M_{p1}[d]	M_{p2}[d]
1	20	TCE	r.t.	30	4610	240 500
2	20	TCE	0	96	3680	600 000[e]
3	100	TCE	r.t.	120	4180	803 600[e]
4	20	TCE	−15	120	1700	
5	40	TCE	r.t.	24	5100	shoulder
6	20	dioxane	20	118	2420	shoulder
7	20	dioxane	40	70	3990	
8	20	dioxane	60	23	4130	shoulder
9	20	dioxane	40	25	2130	
10	20	dioxane	60	24	3600[f]	
11	20	dioxane	60	7	2690	687 000
12	20	dioxane	60	24	2400	662 000
13	40	dioxane	60	20	2100	600 600[e]
14	40 (80)[g]	dioxane	60	20 (42)[g]	2190	1 680 000
15	40	dioxane	60	20	2700	129 500[e]
16	40	dioxane	60	20	2700	580 000[e]
17	40	dioxane	60	116	1850	shoulder[h]
18	100	dioxane	60	76	2400	>1 000 000[h]

[a] Italic numbers indicate reactions which were followed by a kinetic treatment. The same number are used for runs and their corresponding polymer products. [b] [Mon]$_0$ = 1.5 M; catalyst: $MeSO_3H$ 1 M in TCE or dioxane. [c] At which the run was stopped. [d] Determined by GPC at the stop time. [e] Weak peak. [f] Purified polymer. [g] Second monomer addition of 50% of the initial monomer aliquot, performed 20 h after the beginning of the polymerization. [h] A fraction of the polymer was insoluble.

slight excess of TEA, and poured into a large excess of methanol. The resulting precipitate was separated by centrifugation, washed with methanol, and vacuum-dried to constant weight. The monomer conversion was measured by HPLC on the basis of a calibration curve relating monomer peak area to monomer concentration. The progressive decrease in monomer concentration during each experiment was then determined by injecting a known volume of the various methanol solutions corresponding to the sample withdrawals. The specific experimental conditions related to the various polycondensations are given in Table 1.

Polymer Characterization. Polymers were characterized by FTIR, ^{1}H and ^{13}C NMR, UV−vis spectroscopy, GPC, TGA, and DSC.

Results and Discussion

The experimental conditions applied to the various polycondensations are summarized in Table 1. The polycondensation of **1** was performed using methanesulfonic acid as catalyst; reaction parameters, such as temperature and monomer-to-catalyst molar ratio, [Mon]$_0$/[Cat] = R, were varied. As specified above, the kinetics of these polymerizations were followed by HPLC, as regards the rate of monomer consumption, and by GPC, as regards the evolution of the molecular weight being formed.

Figure 1a,b shows the conversion vs time plots for runs carried out in TCE and in dioxane, respectively (***1***, ***2***, ***4*** and ***6***−***9***; Table 1), keeping R constant and varying the reaction temperature. The corresponding first-order plots are given in Figure 2a,b. The good linearity of these plots indicates that the polycondensation of monomer **1** followed a first-order behavior with respect to the monomer.

Figure 3 shows the Arrhenius plots obtained for the two solvent media. Table 2 gives the relevant kinetic data for all these systems. The values of the first-order rate constant k were much higher in TCE than in dioxane, namely a factor of over 100 at 20 °C. The values of the activation energy increased from about 40 to about 70 kJ mol^{-1}, going from TCE to dioxane. These features are consistent with both the lower dielectric constant and the higher nucleophilic character of dioxane, with respect to TCE, which strongly reduced the reactivity and made the formation of the active species (polar or ionic) more difficult.

The external order in acid was determined in two sets of experiments involving the two solvent media (runs ***1***, ***3***, ***5*** and ***8***, ***17***, ***18***; Table 1). Figure 4 shows the dependence of the first-order rate constant on the acid concentration, which were 1.1 in dioxane and 1.5 in TCE.

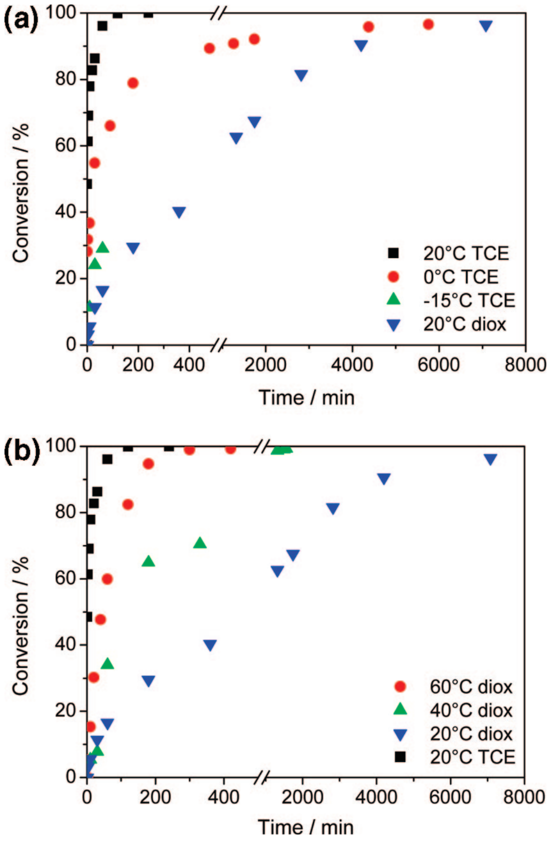


Figure 1. Conversion vs time plots for the polycondensation of **1** at various temperatures (a) in TCE, plus data of the run carried out in dioxane at 20 °C, and (b) in dioxane, plus data of the run carried out in TCE at 20 °C, for comparison purposes.

The polycondensation of monomer **1** displayed kinetic features qualitatively similar to those observed for the homologous monomers with no, or one, methyl substituent, previously studied[6] in terms of their first-order behavior with respect to the monomer. However, the actual rate of monomer consumption was considerably higher because of the electron donor effect of the two methyl substituents on the thiophene ring. As for the external order in acid, the present systems displayed

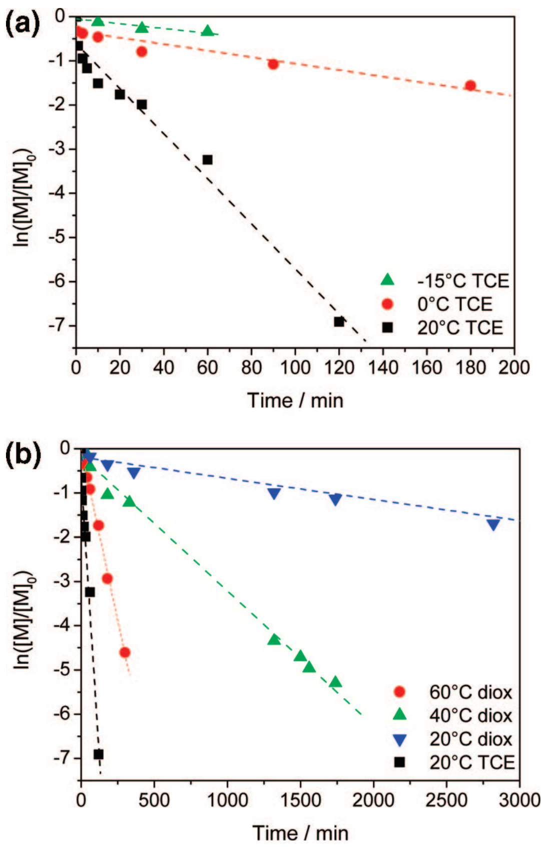


Figure 2. Typical first-order plots for the polycondensations of **1** at various temperatures (a) in TCE and (b) in dioxane, plus data of the run carried out in TCE at 20 °C, for comparison purposes.

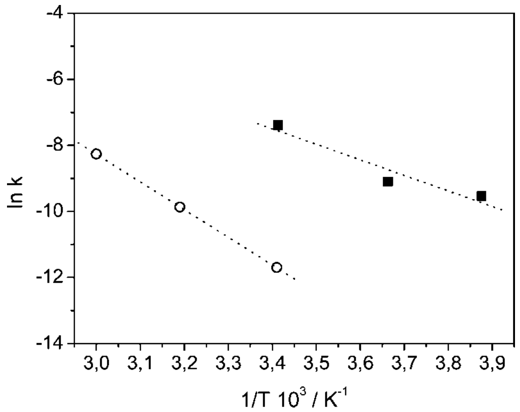


Figure 3. Arrhenius plots for the polycondensations of monomer **1** in TCE (■) and dioxane (○).

Table 2. Kinetic Data for the Polycondensation of 1[a]

solvent	temperature (°C)	k (10^5 s^{-1})	E_a (kJ mol^{-1})
TCE	−15	9.2	40.7
	0	12.2	
	20	85	
dioxane	20	0.83	69.7
	40	5.2	
	60	25.8	

[a] $[\mathrm{Mon}]_0$ = 1.5 M; catalyst: MeSO$_3$H, 1 M in TCE or dioxane.

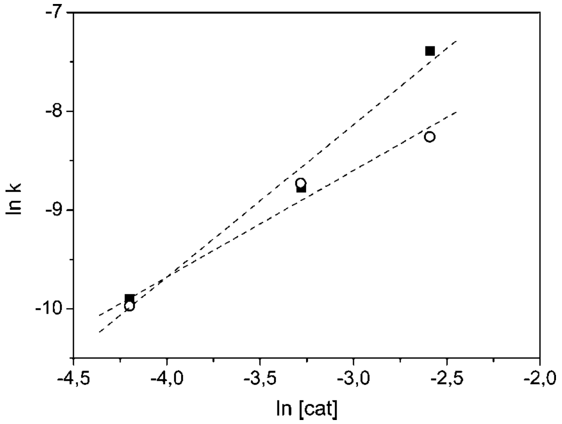


Figure 4. Dependence of the first-order rate constant on the CH_3SO_3H concentration for the polycondensations of **1** in TCE at r.t. (■) and diox at 60 °C (○).

significantly lower values than those found with the unmethylated counterpart, viz. close to 2.[6] The latter value had been rationalized by calling upon the need of a second molecule of acid in order to form the protonated acetate moiety, i.e., the active species. It seems reasonable to explain this difference now by considering that the presence of the two methyl groups in **1**, because of their electron donor effect, reduced the need of acid molecules to just over one, in order to generate the corresponding active species. After a fast initiation step, propagation takes place by successive condensation reactions between an active species and a monomer molecule, as shown in Scheme 2.

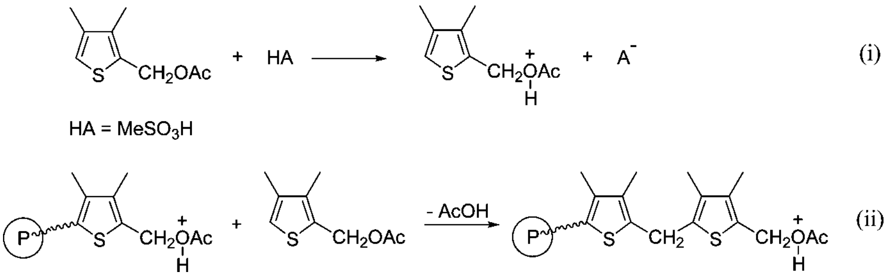
The GPC analysis showed that the DP of the polymers grew as a function of the reaction time, to reach values of about 40 at complete monomer consumption. Generally the products obtained were soluble, even when the polymers were kept for days in the reaction medium after complete monomer conversion. At high monomer conversion, the formation of a very high molecular weight polymer fraction was always observed, as shown in the example of Figure 5. This phenomenon was however more pronounced when the polymerizations were carried out in TCE, where the reaction rates were higher than those in dioxane. The M_{p1} and M_{p2} values reported in Table 1 refer to the GPC peak values of the low and the high molecular weight fractions, respectively, obtained at the time at which the run was stopped, that in some instances was much longer than that at which the monomer consumption had reached completion. In one case (run ***17***) the system developed very high molecular weights to such an extent that a fraction of the polymer become insoluble, and as already observed for the unsubstituted homologue,[6] the soluble fraction has a lower molecular weight. The fact that the molecular weight continued to increase, even after the complete consumption of the monomer, suggested the possibility of an alkylation reaction of a polymer chain by a macromolecular active species, as sketched in Scheme 3.

This grafting-onto reaction cannot lead to the formation of a polymer network and only contributes to a progressive increase in branching and, correspondingly, in the polymer DP, without affecting its solubility.

It is also worth noting that this kind of polycondensations exhibit the typical features of a living character, as previously evidenced for the less substituted homologues of monomer **1**. Indeed, either by adding fresh monomer toward the end of a given polymerization or by starting a polymerization in the presence of a polymer recovered from another run resulted in a significant increase of the molecular weight.[6] The former experiment was conducted here in run **14** and gave a fraction with a very high molecular weight.

All the products obtained were solid and insoluble in methanol, but soluble in common organic solvents such as dichloromethane, chloroform, and THF. Their color ranged from yellow to brown, depending on the reaction system. Their thermal stability under nitrogen was good, since the onset of

Scheme 2. Mechanism of Polycondensation of Monomer 1: (i) Initiation Step; (ii) Chain Propagation



decomposition temperature was around 350 °C, with 20% of carbonaceous residue at 700 °C, and remained high even under oxygen, with an onset at around 280 °C, although of course the polymers left no residue at ~600 °C. Further TGA experiments under oxygen were carried out in an isothermal mode that showed that the oxygen uptake was very slow (less than 0.2% of weight increase after 2 h at 200 °C). This was attributed to the presence of the two methyl substituents, which protect the polymer backbone from thermo-oxidative degradation.

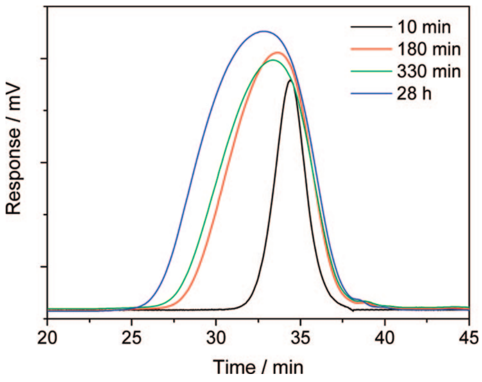


Figure 5. GPC traces of the polymers being formed at different times during run ***17***.

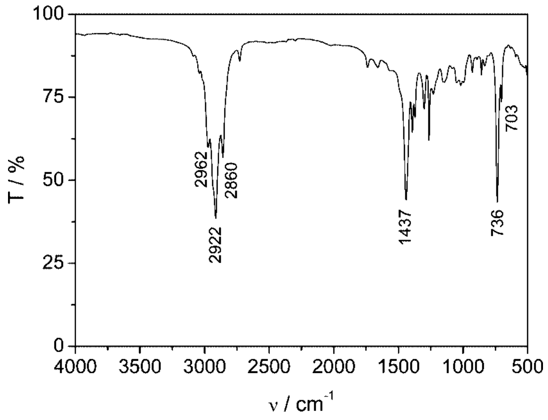


Figure 6. FTIR spectrum of polymer **13**.

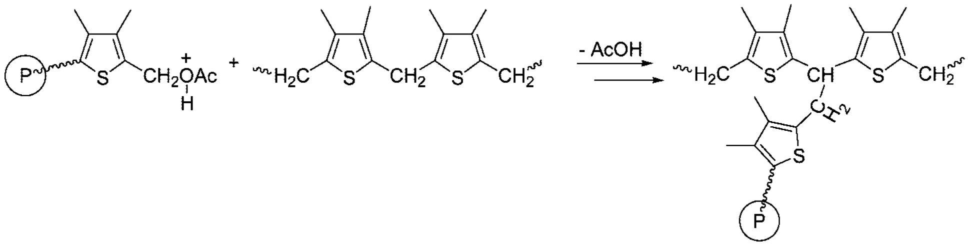
The DSC thermograms evidenced only the presence of a glass transition at about 100 °C. Even after annealing at temperatures above T_g, the products maintained an amorphous character.

The structural evidence provided by both FTIR (Figure 6) and ^{1}H NMR (Figure 7) spectra gave evidence of the disappearance of the carbonyl group (lack of peak at 1740 cm^{-1}) and of the proton 5 (lack of peak around 7 ppm) and the presence of inter-ring methylene bridges, which confirmed that the polycondensation mechanism was based on the electrophilic attack of the active species onto the free 5-position of the heterocycle, with elimination of a molecule of acetic acid. The other spectroscopic features were consistent with the presence of regular thienylene methylene sequences **A** sketched in Figure 8.

The formation of conjugated sequences, arising from reorganization reactions associated with some of the units, similarly to the furan-based systems,[8] was evidenced by both the ^{1}H NMR (Figure 7) and UV−vis spectra (Figure 9). The relevant features here were, on the one hand, resonances around 6.7 ppm and the multiplicity of the methyl signal and, on the other hand, a broad absorption centered at ~370 nm, tailing off into the visible, apart from the strong peak at ~245 nm arising from the unconjugated thiophene heterocycles. These features were a clear indication of the presence, beside the main structure **A**, of conjugated sequences made up of alternating aromatic- and quinoid-type rings (structure **B**, Figure 8). The other "anomalous" resonances in the ^{1}H NMR were attributed to branching sites arising from competitive condensations on the bridging carbons. A detailed study of these microstructural features will be described elsewhere.

More conclusive evidence for the presence of the conjugated sequences was obtained by UV−vis spectroscopy, as previously done in the case of both furfuryl-type polymers[8] and those obtained from homologues of **1**.[5] Figure 10 shows a typical example of electronic spectra of one of these polymers recorded in different conditions. Trace **a** shows, as already mentioned (Figure 9), that a certain degree of conjugation was already present in the pristine polymer, as suggested by the weak absorptions in the near-UV and visible regions. The addition of a hydride abstractor, e.g. a dioxolenium salt, gave rise to a bathochromic shift with various absorption maxima, whose intensity increased with time, ascribed to positively charged conjugated sequences of different length (traces **b**). The

Scheme 3. Alkylation of a Polymer Chain by a Macromolecular Active Species



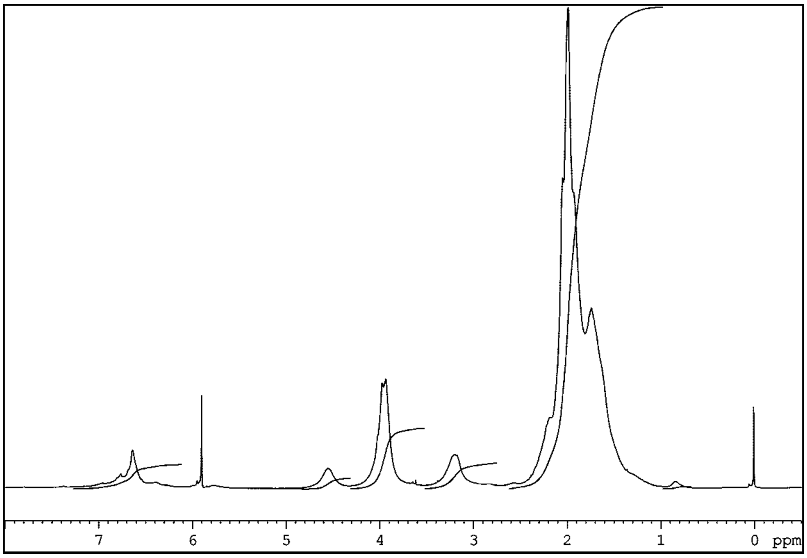


Figure 7. ^{1}H NMR spectrum of polymer **12**.

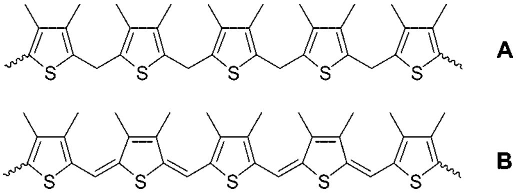


Figure 8. Regular sequence of thienylene methylene units (**A**) and a conjugated sequence of alternating aromatic- and quinoid-like rings (**B**).

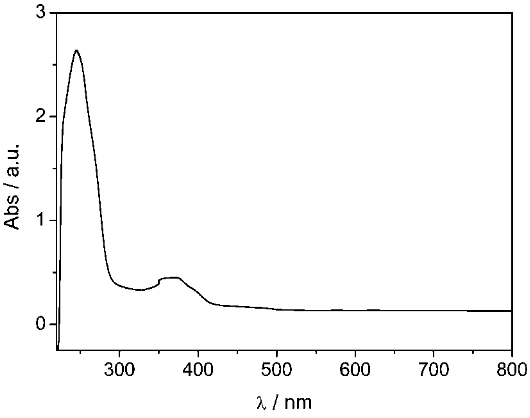


Figure 9. UV−vis spectrum of polymer **13**.

neutralization with triethylamine restored, albeit not completely, the original structure, as shown by trace **c**. Finally, the neutralized materials could be reversed to their partially conjugated structure by repeating the treatment with the hydride abstractor (traces **d**). This cyclic phenomenology could also be activated using a strong Brønsted acid, iodine, or other hydride abstractors, like trityl salts. The fine points of this structural study based on electronic spectra will be discussed separately, together with the detailed analysis of the ^{1}H and ^{13}C NMR spectra of the corresponding polymers.

The materials obtained from the polycondensation of **1** displayed a good film-forming aptitude. Different doping treatments of the cast films revealed the same UV−vis phenomenology as with the corresponding polymer solutions discussed above. In particular, a simple dipping into an HCl solution, or indeed the film exposure to HCl vapor, brought about its rapid coloration associated with the formation of protonated conjugated sequences. This behavior suggests a possible exploitation of these materials as sensors for acidic environments.

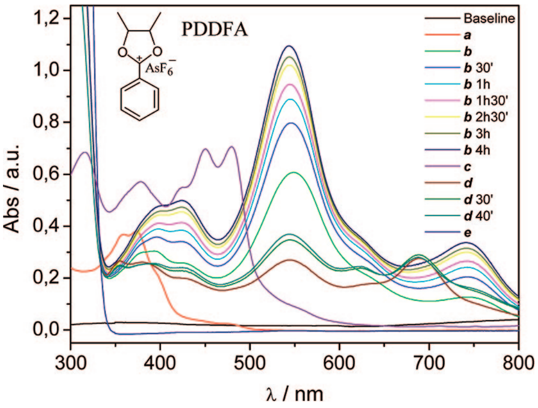


Figure 10. UV−vis spectra of polymer ***9***: **a** = polymer in CH_2Cl_2; **b** = **a** + PDDFA; **c** = **b** + TEA; **d** = **c** + PDDFA; **e** = PDDFA.

Conclusions

This study constitutes a basic inspection of the kinetics and mechanism of the polycondensation of 2-acetoxymethyl-3,4-dimethylthiophene in acidic media. The system behaves as a *polycondensation* in terms of the chemical nature of each step growth (a molecule of acetic acid is eliminated at each step) but as a *chain polymerization* in terms of both its kinetic features and the chain growth mechanism for which the only occurring reaction is that involving the growing active species and a *monomer* molecule, as in classical polyaddition systems. The presence of the two methyl substituents on the thiophene ring enhanced the rate of monomer consumption compared with that of homologous monomers with no, or one, methyl substituent. Moreover, this C3 and C4 double substitution led to a regular monomer enchainment, based on 2,5-disubstituted thiophene moieties, thus favoring the subsequent formation of more extended conjugated sequences along the polymer backbone through cyclic hydride ion/proton losses. These sequences are constituted by alternating aromatic- and quinoid-like thiophene rings, as confirmed by NMR and UV−vis spectroscopy. These basic results paved the way to promising exploitation of novel conjugated macromolecular architectures in areas like sensors and low-bandgap materials for electronic and optoelectronic devices.

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