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# Acid-Catalyzed Polycondensation of 2-Hydroxymethylthiophene and Some of Its Homologues

**Paola Stagnaro,**[†] **Giovanna Costa,**[†] **and Alessandro Gandini***[,‡]

*Istituto di Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali (IMAG)-CNR, Via De Marini 6-16149 Genova, Italy, and Matériaux Polymères, Ecole Française de Papeterie et des Industries Graphiques (INPG), BP 65, 38402 Saint Martin d'Hères, France*

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ABSTRACT: 2-Hydroxymethylthiophene and its acetate were placed in acidic organic media of various natures and strengths and at different temperatures. Polycondensations involving the alcohol or acetate function and a thiophene proton only occurred if the solutions were heated and the acid concentration was relatively high. The thorough assessment of the structure of the ensuing polymers, including those arising from differently methylated derivatives of the parent structures, indicated that the electrophilic substitutions had taken place at all free thiophene sites and that conjugated sequences had also formed. The kinetic and mechanistic features of these systems are examined and discussed in comparison with those displayed by furfuryl alcohol.

## Introduction

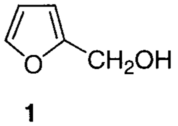
Furfuryl alcohol (**1**) has been extensively studied in the context of its acid-catalyzed or heat-induced polycondensations which give rise to resins that find useful applications in the foundry and chemical industries.[1] The intricate mechanistic features which characterize these processes have puzzled polymer chemists for decades, and only recently a good understanding of most of them has been attained.[2] The basic step in the first phase of this complex process is a condensation reaction involving the OH group and the hydrogen atom at the C5 position of the heterocycle. The ease with which this specific site undergoes electrophilic substitution has been widely exploited in furan chemistry for a variety of synthetic purposes related to both fine chemicals[3] and polymers with controlled architecture.[4] The products of the polycondensation of **1** have the peculiarity of being black and cross-linked, because major side reactions accompany the linear chain growth, namely a series of $H^-$ and $H^+$ transfer mechanisms leading to conjugated sequences and cross-linking reactions induced by the resulting unsaturated segments of the polymer.[2]

Benzyl alcohol (**2**) is known to undergo condensation reactions similar to those encountered with **1**, but to a much more modest extent because the rates are considerably lower.[5] An interesting counterpart to this reduced reactivity is the fact that the acid-catalyzed polycondensation of **2** is less sensitive to side reactions which mar the corresponding systems with **1**. However, these systems have received little attention, and the corresponding products have not been the object of studies related to their possible interest as novel materials.

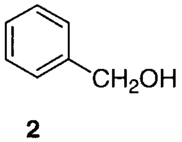
To the best of our knowledge, the behavior of the thiophene homologue of **1** and **2**, viz. 2-hydroxymethylthiophene (**3**), has only been briefly described in a recent note,[6] which reported that a soluble poly(thienylene methylene) was obtained by the acid-catalyzed self-condensation of **3**. However, the mechanism of the reaction(s), the detailed structure of the product, and the optimization of the process were not tackled in this work.

The thiophene heterocycle (Th) is known to possess a higher aromatic character than that of its furan (Fu) counterpart and a correspondingly lower dienic character. In other words, its electronic structure results in chemical features which lie usually between those of furan and benzene. Given the difference in reactivity between **1** and **2**, it seemed interesting to examine **3**, for which an intermediate behavior was therefore expected.

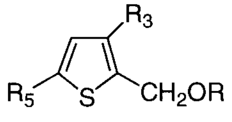
The present investigation describes a study that was initially based only on the use of **3**. However, to clarify both the reaction mechanism and the structure of the products, it was later extended, on one hand, by introducing methyl substituents at different ring positions (monomers **5** and **7**) and, on the other hand, by calling upon the corresponding acetates (monomers **4**, **6**, and **8**) in order to avoid the accumulation of water in the reaction medium. The latter expedient had been found useful in the mechanistic study of the polycondensation of **1**,[2] where its acetate had proved a more suitable monomer, since it released acetic acid, instead of water, upon self-condensation. In the present work, furthermore, a few experiments were also carried out with **1** and **2** in order to compare their behavior with that of **3** in similar experimental conditions.



**1**



**2**



**3**: $R=R_3=R_5=H$;
**4**: $R=COCH_3$; $R_3=R_5=H$;
**5**: $R=R_3=H$; $R_5=CH_3$;
**6**: $R=COCH_3$; $R_3=H$; $R_5=CH_3$;
**7**: $R=R_5=H$; $R_3=CH_3$;
**8**: $R=COCH_3$; $R_3=CH_3$; $R_5=H$.

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[†] Istituto di Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali (IMAG)-CNR.

[‡] Ecole Française de Papeterie et des Industries Graphiques (INPG).

* Corresponding author. E-mail Alessandro.Gandini@efpg.inpg.fr.

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## Experimental Section

**Monomers.** Commercial samples of furfuryl alcohol (**1**) (Aldrich, 99%) and of benzyl alcohol (**2**) (Fluka, 99.8%) were used as received. Commercial samples of 2-hydroxymethylthiophene (**3**) (Aldrich, 98%) were purified by fractional vacuum distillation.

2-Hydroxymethyl-5-methylthiophene (**5**) and 2-hydroxymethyl-3-methylthiophene (**7**) were obtained by the reduction of the corresponding commercial aldehydes with lithium aluminum hydride in diethyl ether and purified by vacuum distillation (80−85% yields).

2-Acetoxymethylthiophene (**4**), 2-acetoxymethyl-5-methylthiophene (**6**), and 2-acetoxymethyl-3-methylthiophene (**8**) were prepared by esterification of the corresponding alcohols **3**, **5**, and **7** with acetyl chloride in anhydrous pyridine and purified by vacuum distillation (85−90% yields).

All the monomers were characterized by FTIR, $^1$H NMR, and $^{13}$C NMR spectroscopy as shown in Table 1.

**Other Reagents and Solvents.** 3-Methyl-2-thiophenecarboxaldehyde (Aldrich, tech 90%) was distilled before use. 5-Methyl-2-thiophenecarboxaldehyde (Acros, 98%) and all high-purity solvents, acids, and other reagents were used as received.

**General Polymerization Procedure.** Polymerization reactions were carried out under nitrogen by dissolving the monomer in the solvent (methylene chloride or 1,4-dioxane) to give 1.5 M solutions and by adding slowly, and under vigorous stirring, the catalyst solution. (Various Lewis and Brønsted acids were used in a preliminary approach, before choosing $TiCl_4$ and $H_2SO_4$, respectively, for a more detailed investigation.) During the addition, the temperature was controlled by a cooling bath. The reaction vessel was then dipped in a bath kept at the desired constant temperature. Reactions were ended, generally after 5 h, by neutralizing the medium with a slight excess of triethylamine. *Workup A*: the organic phase was then extracted with methylene chloride, washed with water, and dried over sodium sulfate. The resulting products were isolated by vacuum removal of the volatile components. *Workup B:* the reaction mixture was poured into an excess of stirred methanol, and the resulting precipitate was filtered, washed with methanol, and vacuum-dried to constant weight. The specific experimental conditions related to the polycondensations of monomers **3**−**8** are given in Table 2.

**Polymer Characterization.** Polymers were characterized by FTIR, NMR, and UV spectroscopy, elemental analysis, vapor pressure osmometry (VPO), GPC, TGA, and DSC.

## Results and Discussion

Since in the only published note about the polycondensation of **3** a single reaction system was reported with scanty details and without any attempt to optimize the system,[6] it was decided to undertake a systematic study on the role of various parameters capable of affecting the course of the polymerization. Thus, several experiments were carried out varying the type and strength of the acidic catalyst, the temperature, the solvent, and the monomer-to-catalyst molar ratio.

A preliminary investigation showed that **3**, dissolved in methylene chloride and treated *at room temperature* with modest to quite high concentrations ($10^{-2}$ to $1.5 \times 10^{-1}$ M) of various Lewis or Brønsted acids, gave only traces (if any) of oligomeric products, even with long reaction times (1−10 days). In these conditions, of which an example is given in expt 0 of Table 2, the reaction media only acquired a slightly yellow coloration. After neutralization with triethylamine, high-vacuum fractionation left, besides large amounts of unreacted **3**, very small (if any) quantities of a residue that readily crystallized on standing. This residue was characterized by standard spectroscopic techniques complemented by elemental analysis and DSC. Its FTIR spectrum (KBr pellet) showed a band at 1065 $cm^{-1}$ assigned to the C−O stretching vibration of an ether bridge and, besides other typical features relative to the 2-Th−$CH_2$ moiety, two peaks at 830 and 700 $cm^{-1}$ corresponding to =C−H out-of-plane vibrations in 2-substituted thiophenes. Its $^1$H NMR spectrum in $CD_2Cl_2$ exhibited three peaks at 4.68, 6.99, and 7.31 with 2:2:1 relative intensities, assigned respectively to protons belonging to a methylene moiety of an ether bridge, to the H3 and H4 protons of the heterocycle, and to the corresponding H5 protons. From all this evidence, the residue was identified as the product arising from the head-to-head condensation reaction between two OH groups of **3**, namely bis(2-methylthiophene) ether (**9**), according to Scheme 1. The mechanism responsible for the formation of dimer **9** will be discussed below.

It is important to emphasize that these features related to **3** are very different from those displayed by **1**, pointing to a much higher reactivity of the latter at room temperature. Indeed, when **1** is polymerized under the same conditions, the systems develop an intense color and produce gelled materials which, after neutralization and drying, are brown-blackish insoluble powders.[2] Only working under even milder conditions and short reaction times is it possible to isolate oligomers of **1** with DPs of up to 5, which are essentially made up of linear structures containing methylene moieties joining C2−C5 furan rings[2,7] formed from head-to-tail condensations between an OH group and a hydrogen atom at the C5 position of the heterocycle (Scheme 2).[2] More sporadically, the condensation takes place by a head-to-head reaction, followed by loss of formaldehyde, but of course this type of interaction is excluded when 2-furfuryl acetate is used as monomer.[2]

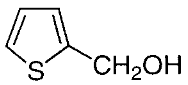
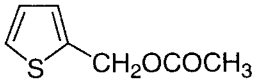
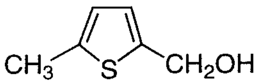
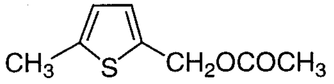
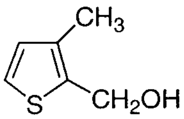
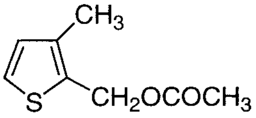
With **3**, the temperature plays a very important role in terms of promoting its actual polycondensation. In fact, carrying out the reaction at low temperatures (Table 2, expt 0 and 3), even in the presence of a high concentration of acid (expt 3), only traces of oligomeric products were obtained. Instead, in the same general conditions, but with *refluxing* either methylene chloride or 1,4-dioxane at *90−100* °C, **3** gave rise to methanol-insoluble products in reasonable yields.

The other two decisive parameters for the successful polycondensation of **3** were the acidity of the reaction medium and the reaction time, as shown by the poor results of experiments carried out at high temperature but with a high monomer-to-catalyst molar ratio (expt 4) or for a short time (expt 6).

It was therefore decided to fix the reaction conditions as follows—monomer concentration 1.5 M, monomer-to-catalyst molar ratio 10, reaction temperature ca. 40 °C (refluxing methylene chloride) or 90−100 °C (1,4-dioxane)—and to vary the type and strength of the acidic catalyst. Normally, the workup procedure A was adopted for the reactions carried out in methylene chloride and procedure B for those conducted in 1,4-dioxane.

When $H_2SO_4$ was employed in 1,4-dioxane (expt 1, Table 2) to reproduce the conditions reported by Uehara et al.,[6] a brown solid product was obtained. Sulfuric acid was then replaced by a Lewis acid, namely $TiCl_4$, as shown in Table 2 (expt 2 and 5). Yields were similar, but less reproducible, because of experimental difficulties in recovering the polymer associated with the precipitation of a titanium hydroxide gel in the reaction medium (hydrolysis of $TiCl_4$ with the water formed in

**Table 1. Spectroscopic Characterization of Monomers 3−8; FTIR Spectra from Liquid Films; NMR Spectra (200 MHz) from CDCl$_3$ Solutions**

| | |
|---|---|
| <br>**3**<br>FTIR (cm$^{-1}$): 3382 (O-H stretch); 3107 (=C-H stretch); 2933, 2873 (C-H stretch); 1010 (C-O stretch); 702 (=C-H out-of-plane wag in 2-substituted thiophene).<br>$^1$H-NMR (δ): 4.83 (s, 2H, **CH$_2$**); 6.95-7.04 (m, 2H, H3 and H4); 7.28 (dd, 1H, J 5.1 and 1.5 Hz, H5).<br>$^{13}$C-NMR (δ): 60.04 (**C**H$_2$); 125.50 (C3); 125.65 (C4); 126.89 (C5); 143.96 (C2). | <br>**4**<br>FTIR (cm$^{-1}$): 3108, 3076 (=C-H stretch); 2954, 2885 (CH stretch); 1742 (C=O stretch); 1235 (C-O stretch); 709 (=C-H out-of-plane wag in 2-substituted thiophene).<br>$^1$H-NMR (δ): 2.06 (s, 3H, **CH$_3$**CO); 5.23 (s, 2H, **CH$_2$**); 6.96 (m, 1H, H3); 7.07 (m, 1H, H4); 7.29 (m, 1H, H5).<br>$^{13}$C-NMR (δ): 20.98 (**C**H$_3$CO); 60.50 (**C**H$_2$); 126.85 (C3 and C4); 128.22 (C5); 137.94 (C2); 170.73 (**C**O). |
| <br>**5**<br>FTIR (cm$^{-1}$): 3330 (O-H stretch); 3066 (=C-H stretch); 2919, 2869 (C-H stretch); 1007 (C-O stretch); 799 (=C-H out-of-plane wag in 2,5-disubstituted thiophene).<br>$^1$H-NMR (δ): 2.46 (s, 3H, **CH$_3$**); 4.71 (s, 2H, **CH$_2$**); 6.61 (m, 1H, H3); 6.78 (d, 1H, J 3.4 Hz, H4).<br>$^{13}$C-NMR (δ): 15.43 (**C**H$_3$); 60.22 (**C**H$_2$); 124.86 (C3); 125.66 (C4); 140.50 (C5); 141.59 (C2). | <br>**6**<br>FTIR (cm$^{-1}$): 3068 (=C-H stretch); 2953, 2922, 2864 (C-H stretch); 1741 (C=O stretch); 1231 (C-O stretch); 802 (=C-H out-of-plane wag in 2,5-disubstituted thiophene).<br>$^1$H-NMR (δ): 2.07 (s, 3H, **CH$_3$**CO); 2.46 (s, 3H, ThC**H$_3$**); 5.16 (s, 2H, **CH$_2$**); 6.62 (m, 1H, H3); 6.87 (m, 1H, H4).<br>$^{13}$C-NMR (δ): 15.36 (**C**H$_3$); 21.02 (**C**H$_3$CO); 60.82 (**C**H$_2$); 124.92 (C4); 128.43 (C3); 135.49 (C2); 141.75 (C5); 170.78 (**C**O). |
| <br>**7**<br>FTIR (cm$^{-1}$): 3329 (OH stretch); 3103, 3065 (=C-H stretch); 2922, 2871 (CH stretch); 999 (C-O stretch); 705 (=C-H out-of-plane wag in 2,5-disubstituted thiophene).<br>$^1$H-NMR (δ): 2.24 (s, 3H, **CH$_3$**); 4.74 (s, 2H, **CH$_2$**); 6.83 (d, 1H, J 5.1 Hz, H4); 7.16 (d, 1H, J 5.1 Hz, H5).<br>$^{13}$C-NMR (δ): 13.49 (**C**H$_3$); 57.82 (**C**H$_2$); 123.73 (C5); 130.30 (C4); 134.98 (C3); 136.58 (C2). | <br>**8**<br>FTIR (cm$^{-1}$): 3104, 3065 (=C-H stretch); 2954, 2929, 2869 (CH stretch); 1740 (C=O stretch); 1226 (C-O stretch); 715 (=C-H out-of-plane wag in 2,5-disubstituted thiophene).<br>$^1$H-NMR (δ): 2.08 (s, 3H, **CH$_3$**CO); 2.26 (s, 3H, ThC**H$_3$**); 5.20 (s, 2H, **CH$_2$**); 6.84 (d, 1H, J 5.1 Hz, H4); 7.22 (d, 1H, J 5.1 Hz, H5).<br>$^{13}$C-NMR (δ): 13.61 (**C**H$_3$); 20.94 (**C**H$_3$CO); 58.63 (**C**H$_2$); 125.06 (C5); 130.04 (C4); 130.97 (C2); 137.23 (C3); 170.83 (**C**O). |

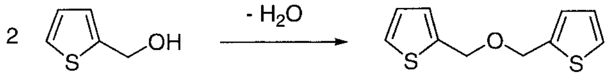
the condensation reactions). To avoid, or at least limit, this technical problem, acetate **4** was used instead of **3**: yields improved (expt 7 and 8), but not to the expected extent, because during the workup, titanium-based gels formed which made it difficult to isolate the polycondensation products quantitatively. For these reasons,

**Table 2. Experimental Conditions Applied to the Various Polycondensations**

| expt | Mon[a] | catalyst | $[Mon]_0/[Cat]_0$ | solvent | temp (°C) | time (h) | yield[b] (mol %) |
|---|---|---|---|---|---|---|---|
| 0 | **3**[c] | $TiCl_4$ | 100 | $CH_2Cl_2$ | r.t. | 24 | traces[d] |
| 1 | **3** | $H_2SO_4$ | 5 | dioxane | 90–100 | 5 | ~45 |
| 2 | **3** | $TiCl_4$ | 5 | dioxane | 90–100 | 5 | ~44 |
| 3 | **3** | $TiCl_4$ | 5 | dioxane | r.t. | 5 | traces[d] |
| 4 | **3** | $TiCl_4$ | 50 | dioxane | 90–100 | 5 | traces[d] |
| 5 | **3** | $TiCl_4$ | 10 | dioxane | 90–100 | 5 | ~56 |
| 6 | **3** | $TiCl_4$ | 10 | dioxane | 90–100 | 5 min | traces[d] |
| 7 | **4** | $TiCl_4$ | 10 | dioxane | 90–100 | 5 | ~61 |
| 8 | **4** | $TiCl_4$ | 10 | $CH_2Cl_2$ | 40 | 5 | ~72 |
| 9 | **4** | $CH_3SO_3H$ | 10 | dioxane | 90–100 | 5 | 33 |
| 10 | **4** | $BF_3{\cdot}Et_2O$ | 10 | $CH_2Cl_2$ | 40 | 5 | 90 |
| 11 | **4** | $TiCl_4$ | 10 | $CH_2Cl_2$ | 40 | 10 | n.d. |
| 12 | **4** | $CH_3SO_3H$ | 10 | dioxane | 90–100 | 11 | 95 |
| 13 | **4** | $CF_3SO_3H$ | 10 | dioxane | 90–100 | 5 | 95 |
| 14 | **4** | $BF_3{\cdot}Et_2O$ | 10 | dioxane | 90–100 | 5 | 97 |
| 15 | **4** | $CH_3SO_3H$ | 10 | $CH_2Cl_2$ | 40 | 5 | n.d.[e] |
| 16 | **5** | $BF_3{\cdot}Et_2O$ | 10 | $CH_2Cl_2$ | 40 | 5 | 96 |
| 17 | **6** | $BF_3{\cdot}Et_2O$ | 10 | $CH_2Cl_2$ | 40 | 5 | 90 |
| 18 | **8** | $BF_3{\cdot}Et_2O$ | 10 | $CH_2Cl_2$ | 40 | 5 | n.d.[e] |
| 19 | **8** | $CH_3SO_3H$ | 10 | dioxane | 90–100 | 5 | 88 |
| 20 | **1** | $BF_3{\cdot}Et_2O$ | 10 | $CH_2Cl_2$ | 40 | 5 | 85[f] |
| 21 | **2** | $BF_3{\cdot}Et_2O$ | 10 | $CH_2Cl_2$ | 40 | 5 | 0[g] |
| 22 | **2** | $CH_3SO_3H$ | 10 | dioxane | 90–100 | 5 | 0[g] |

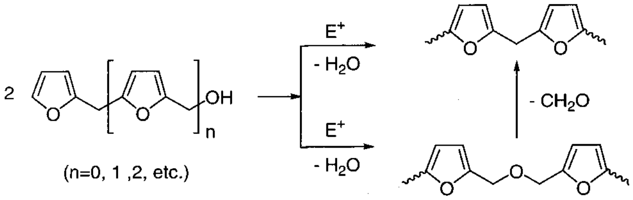
[a] $[Mon]_0 = 1.5$ M. [b] Yield related to the isolated and purified product. [c] $[Mon]_0 = 2.0$ M. [d] Unreacted **3** was recovered. [e] Not determined. [f] 70% fraction insoluble in $CH_2Cl_2$, 15% fraction soluble in $CH_2Cl_2$. [g] Unreacted **2** was recovered.

**Scheme 1**



**3** **9**

**Scheme 2**



and similar ones related to the handling of $H_2SO_4$, most of the remaining experiments were conducted with $CH_3SO_3H$ or $BF_3{\cdot}Et_2O$ as Brønsted and Lewis acid, respectively. To eliminate the possibility of head-to-head reactions, avoid the accumulation of water in the reaction medium, and simplify the workup at the end of the reactions, the acetates **4**, **6,** and **8** were preferred to the corresponding alcohols. Clearly defined products were thus obtained in high yields, although the behavior of these systems was on the whole entirely similar to that of polycondensations with the alcohol precursors **3** and **5**, which indicated that the elimination of acetic acid, instead of water, did not alter the basic chain-growth mechanism.

The *qualitative* features of systems in which solvent, catalyst, temperature, and reaction time were varied widely (expt 7–15) remained very similar. All the products obtained were solids insoluble in methanol but soluble in common solvents like methylene chloride, chloroform, and THF. Their color ranged from creamy to dark brown passing through orange, red, and light brown, depending upon the reaction system and the workup procedure. Their thermal stability (TGA) under nitrogen was good, extending to about 380 °C.

The results from the elemental analysis and molecular weight of some of these polymers are given in Table 3. The agreement between the molecular weights obtained from VPO and GPC was reasonable and showed that these polycondensations can reach $DP_n$ values of about 50 with products that remain entirely soluble. This is in stark contrast with the features of the corresponding reactions involving **1** or its acetate, which, as already mentioned, give either oligomers or cross-linked polymers.[2] The mechanistic origin of this qualitative difference is discussed below. The elemental analyses data in Table 3 are compared with that calculated for the corresponding linear polymer of infinite length (**P**∞) arising from successive bimolecular eliminations of water or acetic acid. Thus, the residual oxygen content should reflect the concentration of the terminal groups bearing the alcohol or acetate function and thereby give an additional way to calculate the $DP_n$ of each product. However, whereas the carbon, hydrogen, and sulfur contents were very close to the expected figures, the oxygen counterparts were more erratic and gave consistently $DP_n$ values that were lower than those obtained from direct measurements by VPO and GPC. This small anomaly is attributed to some slight and variable oxidation of the polymers through their unsaturated sequences (see below). We believe therefore that

**Table 3. Molecular Characteristics of Some Polymers**

|  | EA |  |  |  | VPO | GPC |
|---|---|---|---|---|---|---|
| polymer[a] | C (%) | H (%) | O (%) | S (%) | ($M_n$) | ($M_{peak}$) |
| **P1** | 61.57 | 4.09 | 2.47 | 32.08 |  | 2520 |
| **P7** | 61.73 | 4.08 | 1.44 | 32.67 |  | 3560 |
| **P7**[b] | 61.86 | 4.22 | 1.54 | 33.17 |  | 3390 |
| **P8** | 61.82 | 3.93 | 1.13 | 32.98 | 4790 | 4080 |
| **P9** | 61.83 | 4.01 | 1.94 | 32.58 | 1650 | 1770 |
| **P10** | 61.97 | 4.15 | 1.59 | 32.94 | 2710 | 3560 |
| **P12**[c] | 61.75 | 4.23 | 1.37 | 32.88 |  | 3550 |
| **P12**[d] | 62.22 | 4.43 | 0.74 | 33.58 |  | 3140 |
| **P13** | 62.64 | 4.01 | 1.03 | 32.54 |  |  |
| **P**∞[e] | 62.46 | 4.19 |  | 33.35 |  |  |
| **P17** | 65.14 | 5.20 | 1.07 | 28.53 |  |  |
| **P**∞[f] | 65.41 | 5.49 |  | 29.10 |  |  |

[a] Correspond to experiment number in Table 2. [b] Polymer purified by flash chromatography. [c] Reaction time: 3 h. [d] Reaction time: 11 h. [e] Calculated composition for a poly(**3**) or poly(**4**) of infinite length. [f] Calculated composition for a poly(**5**) or poly(**6**) of infinite length.

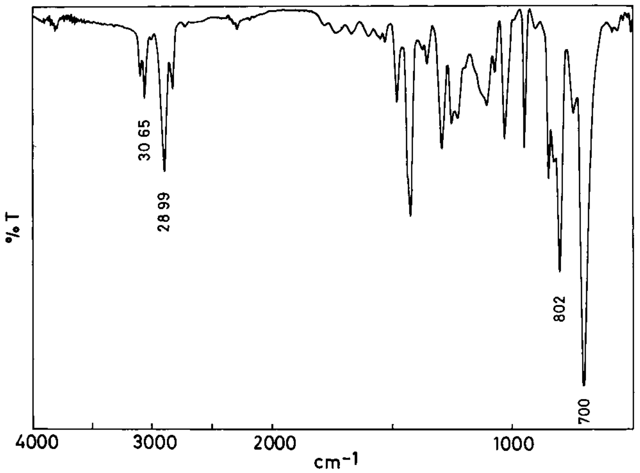


**Figure 1.** Typical FTIR spectrum of a poly(**4**) (film of **P10**).

the chain lengths are indeed close to those gathered from the two agreeing experimental techniques.

Calorimetric analysis, carried out by DSC (repeated cycles), consistently showed only the occurrence of a glass transition, generally ranging from 25 to 45 °C, indicating that all the polymers were amorphous.

The FTIR spectra of the various poly(**3**) and poly(**4**), of which an example is given in Figure 1, were very similar. They showed (i) all the typical features expected for a $-Th-CH_2-$ unit, (ii) the absence of bands relative to C$-$O$-$C moieties, (iii) the virtual absence of bands due to terminal functions, such as OH, C$=$O, thus corroborating the relatively high DP values determined by VPO and GPC, and (iv) the presence of differently disubstituted thiophene rings as indicated by the appearance of a band at about 800 $cm^{-1}$, corresponding to $=$C$-$H out-of-plane vibrations in 2,5-disubstituted thiophenes, and a band at about 700 $cm^{-1}$, relative to the same vibration in 2,3-disubstituted counterparts. It was more difficult to detect unambiguously the peaks related to the presence of 2,4-disubstituted rings. The spectra of the products obtained from the methylated monomers **5**, **6,** and **8** were characterized by the same peaks of the basic repeat unit with additional typical bands arising from the presence of $CH_3$ moieties and of trisubstituted thiophenes.

All the $^1$H NMR spectra of poly(**3**) and poly(**4**) showed (i) the presence of thiophenic H3, H4, and H5 protons in modestly variable relative abundance, (ii) the absence of signals around 5 ppm, where $ThC\mathbf{H}_2O-$ protons would resonate, (iii) the presence of methylene protons bridging two thiophene rings, and (iv) the presence of a small peak at 2.2 ppm, attributed to a methyl group attached to the heterocycle. The integration ratio $\mathbf{H}_{Th}/\mathbf{H}_{methylene}$ was consistently close to unity, as expected for a $(-Th-CH_2-)_n$ structure. Figure 2 shows two such spectra related to polymers **P10** and **P12** obtained respectively with a Lewis and a Brønsted acid. The integration ratio $\mathbf{H}_{Th}/\mathbf{H}_{methylene}$ was very close to unity for **P10**, while for **P12** this value was around 1.2; the relative abundance of thiophenic H5, H4, and H3 protons was 1:1.7:3 for **P10** and 1:1.4:1.9 for **P12**, indicating that in both instances the C5 position had been the most reactive of the three possible sites for electrophilic attack. The corresponding spectra of the products prepared with the methylated monomers **5**$-$**8** differed from those in Figure 2 only in terms of a strong $Th-C\mathbf{H}_3$ resonance at 2.2 ppm and Th protons in the aromatic region corresponding to a $\mathbf{H}_{Th}/\mathbf{H}_{methylene}$ ratio of 0.5 (moreover, $\mathbf{H}_{methyl}/\mathbf{H}_{Th}$ was close to 3, as expected). Figure 3 shows one such spectrum, namely that of polymer **P17,** obtained from monomer **6**.

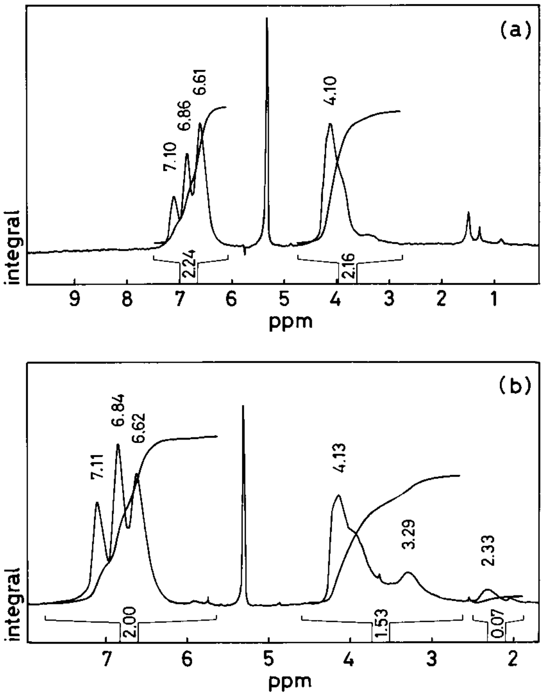


**Figure 2.** $^1$H NMR spectra (200 MHz, $CD_2Cl_2$) of polymers **P10** (a) and **P12** (b) obtained from **4** with $BF_3 \cdot Et_2O$ and $CH_3SO_3H$, respectively.

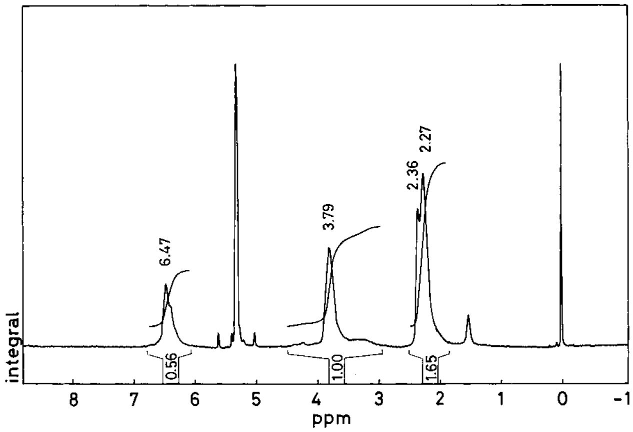


**Figure 3.** $^1$H NMR spectrum (200 MHz, $CD_2Cl_2$) of polymer **P17**.

The $^{13}$C NMR spectra of poly(**4**), of which an example is given in Figure 4, showed (i) various signals around 30 ppm due to $-Th-\mathbf{C}H_2-Th-$ moieties, (ii) the presence of signals between 122 and 130 ppm due to the thiophenic carbon bearing a hydrogen atom, and (iii) the presence of signals between 135 and 145 ppm, attributed to fully substituted thiophenic carbons. The corresponding spectra of the polymers obtained from the methylated monomers **6** and **8** differed only in terms of the additional appearance of $-Th-\mathbf{C}H_3$ signals at 12$-$16 ppm. Thus, the $^{13}$C NMR spectroscopy confirmed the presence of differently substituted thiophenic rings in all the polymers obtained in this study.

The electronic spectra of all these polymers, of which an example is provided in Figure 5, showed a first absorption around 220 nm and a second broad peak

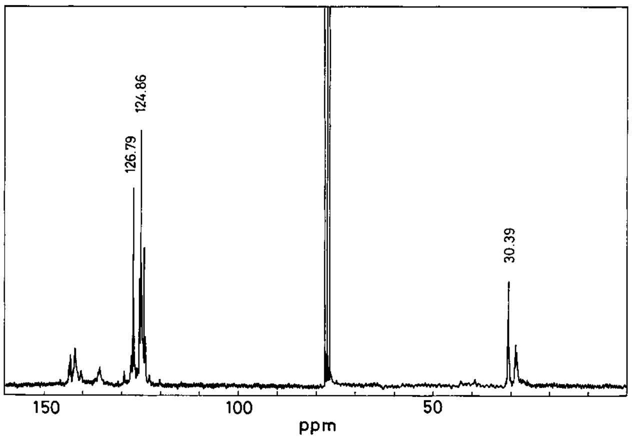


**Figure 4.** $^{13}C$ NMR spectrum (200 MHz, $CDCl_3$) of polymer **P13**.

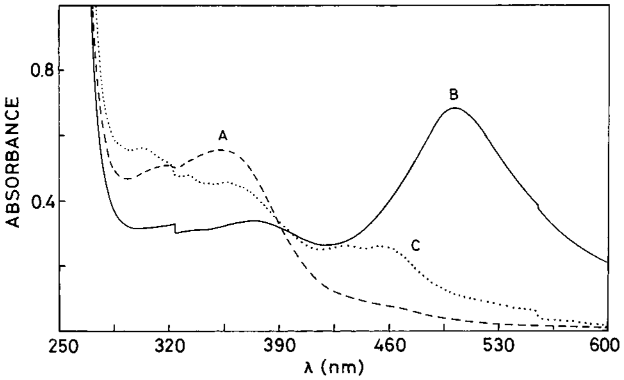


**Figure 5.** UV–vis spectra ($CH_2Cl_2$) of (A) polymer **P9**, (B) A + an equal volume of 1 M $CH_3SO_3H$ solution in $CH_2Cl_2$; (C) B, after neutralization with triethylamine.

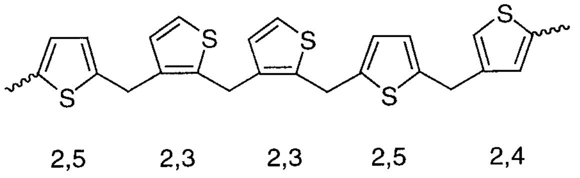
centered between 320 and 360 nm and tailing into the visible. Since alkyl-substituted thiophenes absorb only around 220 nm, the high-wavelength maximum strongly suggested the presence of conjugated sequences along the chains. This was confirmed by the fact that protonation of the polymers with methanesulfonic acid produced systematically a strong bathochromic shift of the second peak to maxima at 510–520 nm. The consecutive neutralization of these acidic media with triethylamine did not restore completely the original structure, since if on one hand the maximum at about 520 nm disappeared and the peak around 350 nm was restored, on the other hand, a new shoulder appeared at 450–470 nm. This overall behavior is entirely similar to that observed previously with the oligomers of **1**[2] and corroborates a close structural resemblance between the conjugated segments along the chains, as discussed below.

All the evidence, acquired through the molecular and spectroscopic characterization described above, points to the following structural features for the thiophenic polycondensates:

(i) The only chain growth mechanism related to **3** and **4** involves a terminal OH (or acetate) function and a thiophene hydrogen atom. The major difference between this behavior and that of **1** is the lack of regiospecificity in the former, since the furan heterocycle was shown to direct the condensation *exclusively* at C5,[2] whereas its sulfur homologue does not impose a very strong preference among the available reactive sites. This difference must be attributed to the enhanced aromatic character of the thiophene ring, compared to the higher dienic features of the furan structure. A further and unequivocal confirmation of the reactivity of the C3 *and/or* C4 positions comes from the fact that monomers **5** and **6**, which bear a methyl group at C5, gave polymers when treated in the same reaction conditions used for **3** and **4**. As for monomer **8**, the presence of two peaks related to the H4 and H5 protons in the NMR spectra of its polymers confirmed the availability of both positions for the condensation reaction.

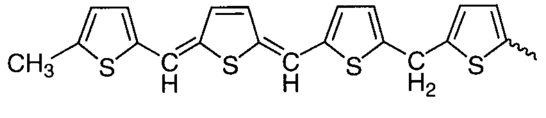
(ii) Branching is therefore likely to occur in all these systems, since any condensation reaction of the alcohol (or acetate) moiety can take place either through a head-to-tail mode or with any unsubstituted positions on the thiophene rings along the chains. The extent of branching could not be readily assessed, however, because neither FTIR nor NMR spectroscopy was of any help in this context. In fact, the relative importance of different growth reactions would not affect either the overall distribution of the various $-Th-CH_2-$ units or the unity ratio between methylene and ring protons. Given the solubility of all products, even with DPs of about 50, it seems likely that the extent of branching was however not particularly high, probably because of steric hindrance, which limited chain growth mostly to head-to-tail enchainments. Indeed, preponderant branching would have resulted in some cross-linking, given the 4-fold functionality of monomers **3** and **4**.

(iii) The *main* structural units in the polymers derived from **3** and **4** can be summarized as follows, arbitrarily placed in a linear fashion:



(iv) The structures of the polymers formed from monomers **5**–**8** are likely to be entirely analogous, except for the presence of the appropriate methyl substituents in different positions on the heterocycle and hence with less frequent branches because of enhanced steric problems associated with this type of chain growth and the lower potential functionality (3 instead of 4) of these monomers.

(v) As for the unsaturated sequences, the mechanism of their formation must be the same as that found in the analogous systems involving **1** and its homologues,[2] viz. the abstraction of a hydride ion from a methylene bridge by a terminal cationic species (e.g., $-Th-CH_2^+$) with formation of a delocalized $-Th-CH^+-Th-$ carbenium ion, which loses a proton upon neutralization to give exo-unsaturated dihydrothiophene moieties linked by a methyne bridge. The first reaction gives rise to a terminal methyl group, so that a typical sequence in polymers from **3** or **4** (neglecting C3 and C4 enchainments and branchings) would therefore be



(vi) Monomers **5**–**8** are also open to this mechanism, as suggested by the same type of electronic spectra obtained from their polymers. It follows that similar conjugated moieties must have formed in these polycondensations.

(vii) Of course, this cycle of hydride ion−proton loss can continue in principle and give rise to longer conjugated sequences.[2] However, in the present conditions, this pursuit does not seem to have occurred to any appreciable extent, given the features of the UV−vis spectra of the thiophenic polymers, which did not display the other strong bathochromic absorptions beyond 350 nm displayed by their furanic counterparts.[2] This must again be related to the less pronounced dienic character of the former heterocycle which would result in a lower driving force for the formation of the intermediate $-\mathrm{Th}-\mathrm{CH}^{+}-\mathrm{Th}-$ carbenium ions.

A comparison of the mechanistic behavior of **1** and its derivatives with respect to **3**−**8** shows strong similarities in (i) the nature of the growth condensation reaction leading to methylene bridges between heterocycles and (ii) the subsequent formation of conjugated sequences arising from those moieties. These qualitative similarities are however accompanied by quantitative kinetic discrepancies in favor of the furanic structures for both mechanisms. Conversely, the comparison shows strong differences in (i) the regiospecificity of the reactive positions on the heterocycle, going from extremely selective with furan to moderately selective with thiophene, and, for the first phase of the chain growth, leading to linear oligomers with **1** and branched counterparts with **3**−**8**, and (ii) the second phase of the process which leads to cross-linked materials with **1**, formed from Diels−Alder coupling reactions among oligomers,[2] which do not take place with **3**−**8**.

The latter difference, ascribed to the fact that the limited dienic character of the thiophene heterocycle makes it entirely unsuitable for the Diels−Alder reaction, constitutes a very important asset for the use of thiophenic monomers, because the ensuing products retain their solubility and thus the possibility of being processed.

The head-to-head dimerization of **3** to give **9** did not seem to proceed via an electrophilic reaction, because in the systems in which very high polymer yields were obtained, no such dimer was detected, and the small amounts of **9** isolated at the end of room-temperature reactions, which gave no polymer, appear to have formed during the workup procedure, rather than during the process itself. Blank experiments, simulating various isolation protocols in the presence of **3**, showed that **9** was indeed formed, particularly when the mixtures were heated in vacuo to remove the volatile components. This thermal dimerization reaction was confirmed by a DSC experiment in which **3** was heated under nitrogen: at about 160 °C an exotherm was registered. After cooling to room temperature, the product in the capsule was analyzed by FTIR and NMR spectroscopy and shown to be dimer **9**. It seems therefore clear that, contrary to **1**, the head-to-head coupling of **3** does not compete with its acid-catalyzed polycondensation in solution and only occurs when concentrated solutions or bulk samples of **3** are heated.

Finally, one run with monomer **1** (expt 20) and two with monomer **2** (expt 21 and 22, Table 2) were carried out to test their behavior in the typical conditions used for monomers **3**−**8**. The first confirmed the higher reactivity of the furanic monomer already discussed above. As for the benzenic monomer, in both cases, i.e., with Lewis or Brønsted acid catalysis, unreacted **2** was recovered quantitatively. Thus, the relative reactivity of primary alcohols **1**, **2,** and **3**, in terms of their kinetics of polycondensation in an acidic medium, showed the expected order related to the decreasing dienic character and, conversely, increasing aromatic features, viz. **1** > **3** > **2**.

## Conclusion

This investigation constitutes a first thorough inspection of the polycondensation of 2-hydroxymethylthiophene and its acetate and of the structure of the ensuing polymers. The possibility of exploiting them as precursors to highly conjugated macromolecular architectures and obtain materials with special properties and applications seems now a viable working hypothesis. Work is in progress toward that goal through the use of powerful hydride ion abstractors.

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