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Novel poly(3,3″- and 3′,4′-dialkyl-2,2′:5′,2″-terthiophene)s by chemical oxidative synthesis: evidence for a new step towards the optimization of this process

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The synthesis of poly(3,3″- and 3′,4′-dialkyl-2,2′:5′,2″-terthiophene)s possessing a full ordered regiochemistry of bonding and substitution, as well as a conjugated chain with the minimum possible amount of steric interactions between the substituents, is described. The synthesis was achieved through the simplest chemical method, namely the oxidative polymerization reaction based on $FeCl_3$ as oxidant. The structural regularities of the polymers have been confirmed by Fourier transform infra-red (*FT* i.r.) and ^1H nuclear magnetic resonance (n.m.r.) spectroscopy. Experimental conditions of special interest for improving the yields and molecular weights of the neutral soluble polymers are discussed.

(Keywords: conducting polymers; poly(alkylthiophene)s; oxidative polymerization)

INTRODUCTION

A great advance in the field of organic conducting polymers was the synthesis of long-chain poly(3-alkyl-2,5-thienylene)s[1–3] (PATs), which occupy a prominent position because of their high electrical conductivity in the oxidized state and their good processibility from solution and the melt in the neutral state[4–6]. Moreover, as a result of conjugation, these polymers exhibit significant third-order non-linear optical responses and other interesting physical properties[7–9] which make them promising materials for numerous applications in the near future[10–19].

It is now well known that either the chemical or electrochemical polymerizations which start from the conventional 3-alkyl monothiophene monomers or their 2,5-dibromo (or diiodo) derivatives, are regioselective methods, always leading to PATs containing mostly 60–90% head-to-tail (HT) coupled configurational dyads with varying amounts (40–10%) of tail-to-tail (TT) and head-to-head (HH) coupled dyads, as can be determined by ^1H n.m.r. spectroscopy[20,22].

Besides destroying the regioregularity of substitution, the HH coupled dyads also give rise to a distortion from planarity of the ring chain, due to the close vicinity of long-chain alkyl groups[23].

Recent significant examples[24–34], including regiospecific syntheses of almost 100% HT PATs, indicate that the dominant structural feature in determining improved electro-optical properties in PATs is not necessarily the regioregularity, but the absence, or at least a very small percentage, of HH coupled dyads. However, macroscopic conductivity data from some of the above examples[24–27] indicate that regioregularity in PATs is an attractive structural feature which may favour, despite a large number of HH interactions and shortened conjugation lengths, long-range order and stacking of polymer chains, thus acting as a driving force towards coplanarity in doped polymer films.

The above mentioned regiospecific syntheses[28–34] of PATs are based on the use of 3-alkyl-monothiophene monomers strategically derivatized at the 2- and 5-positions with different functionalities. The synthesis of these monomers and their cross-coupling polymerization are more difficult and time consuming processes when compared to the regioselective chemical oxidative coupling of readily accessible 3-alkylthiophenes by $FeCl_3$. However, it should be noted that when symmetrically β-substituted α-oligothiophenes are used as monomers, the oxidative coupling is forced to afford completely regioregular polymers, due to the chemical and geometrical equivalence of the coupling positions. Indeed, the oxidative polymerization of either of the two symmetrically β-disubstituted α-bithiophenes gave a full regioregular polymer, although it contained large amounts of HH coupled dyads[24–27]. In order to ensure that the oxidative coupling will lead to poly(alkylthiophene)s possessing not only regioregularity, but even a chain free from HH interaction, evidence indicates that two dialkyl-α terthiophenes, namely 3,3″- and 3′,4′-dialkyl–2,2′:5′,2″-terthiophene, may be chosen as monomers, provided that in each of them the two alkyl groups are the same. As shown in *Figure 1*, these monomers lead to poly(dialkyl-α-terthiophene)s with the expected structural features.

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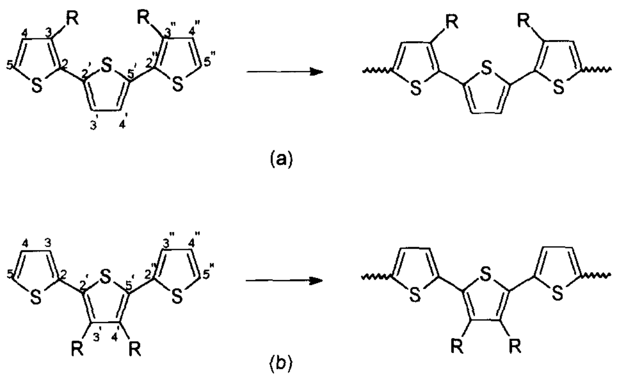

Figure 1 Atom numbering for the dialkyl-2,2′:5′,2″-terthiophene monomers and structures of the corresponding expected polymers: (a) 3,3″-dialkyl-; (b) 3′,4′-dialkyl-type

As far as the alkyl group is concerned, we have considered that the lower average density of alkyl groups per thiophene ring in poly(dialkyl-α-terthiophene)s (66.6%) when compared to PATs (100%), could lead, for a given alkyl chain length, to less soluble polymers. Therefore, to avoid the considerable drawbacks arising from poor solubility of these materials, we decided to study the synthesis and chemical oxidative polymerization of α-terthiophene monomers with rather long alkyl chains, namely 3,3″-dihexyl-, 3,3″-didodecyl-, 3′,4′-dihexyl- and 3′,4′-didodecyl-α-terthiophenes, 3,3″DHTT, 3,3″DDTT, 3′,4′DHTT and 3′,4′DDTT, respectively.

During the course of our studies, the synthesis of the polymer from 3,3″DHTT[35] and also, shortly afterwards, from 3′,4′-dibutyl-α-terthiophene[36] were reported. The polymerization of 3,3″DHTT was performed in $CHCl_3$ under rather unusual conditions (50°C and 20 h), but neither the concentrations of monomer and oxidant, nor the yields of polymerization or the fractionation have been reported. In our opinion, the omission of these significant data may reflect the fact that, under the drastic conditions used, large percentages of polymer were insoluble or, more likely, were refractory to the de-doping treatment used, as indicated by our preliminary investigations on the same polymerization performed in $CHCl_3$ at room temperature and for a shorter time.

As to poly(3′,4′-dibutyl-α-terthiophene), only a small oligomeric fraction (17% based on the monomer), corresponding to a heptamer rather than to a true polymer, was indeed soluble at room temperature.

These findings, together with our preliminary observations related to the use of $CHCl_3$ in the polymerization of 3,3″DHTT, encouraged us to continue our studies, not only on the previously planned polymerizations, but also on the de-doping process of the as-grown polymers. Our aim was to find the best possible polymerization conditions leading to the maximum amount of soluble neutral polymers with the highest molecular weights, which are relevant for the processibility and mechanical properties of conjugated polymeric materials.

EXPERIMENTAL

Characterization

The boiling points are uncorrected. Microanalytical results were supplied by Redox Laboratories (Cologno M., Milan, Italy). The ^{1}H-n.m.r. spectra were recorded in $CDCl_3$ on a Varian Gemini (200 MHz) Fourier transform spectrometer and are reported in ppm as δ relative to internal tetramethylsilane (TMS) at 0ppm. Mass spectrometry (m.s.) was carried out on a VG 7070 E spectrometer at 70 eV. The i.r. frequencies are reported in cm^{-1}, with the spectra being obtained on KBr discs, with a Perkin-Elmer 1750 Fourier transform infra-red spectrophotometer, by directly using neat samples for oily products or film samples for polymers. All literature compounds had physical and spectroscopic data agreeing with the results previously reported, with additional unpublished data concerning yields, i.r. or m.s. spectra being given below. All compounds first prepared in the course of this present study gave elemental analyses (C, H, S, Br and I) within 0.4% of theory, as well as i.r., ^{1}H n.m.r. and m.s. results which agreed with the assigned structures. Molecular weights were measured by gel permeation chromatography (g.p.c.) on a Waters Model 590 instrument equipped with a Shodex KF-804 column and a u.v.-vis Perkin-Elmer LC-95 sptectrophotometric detector. The molecular weights were obtained in the usual manner from the retention-time calibration curve using a series of polystyrene standards.

Synthesis of monomers

3-Alkyl- and 3,4-dialkylthiophenes were prepared by the general procedure of Kumada and coworkers[37], using the synthetic and purification details of Zimmer and coworkers[38] for 3-hexylthiophene [i.r.[39]; m.s. *m/e* 168 (M^+38.36%), Bäuerle *et al.*[40] for 3-dodecylthiophene (i.r.[3]; m.s.[29]), and Leclerc *et al.*[41] for 3,4-dihexylthiophene [yield 70%; i.r. 3101, 2956, 2927, 2871, 2857, 1466, 1378, 868, 784, 725; m.s. *m/e* 252 (M^+ 28.3%)]. 3,4-Didodecylthiophene was also prepared by this method [b.p. 208–210°C/0.3 mbar; yield 57%. ^{1}H n.m.r: 6.9, s, 2 H(2,5); 2.5, t, 4 H (αCH_2); 1.62, m, 4 H (βCH_2); 1.3, m, 36 H (CH_2); 0.89, t, 6 H (CH_3). I.r.: 3103, 2954, 2925, 2853, 1466, 1378, 868, 783, 721. M.s.: *m/e* 420 (M^+ 70.21%)].

Brominations of the alkylthiophenes were carried out with stoichiometric *N*-bromosuccinimide in *N,N*-dimethylformamide using the procedure of Mitchell *et al.*[42] for reactive aromatic compounds. Crude 2-bromo-3-hexylthiophene was purified as described for the product prepared by Br_2/CH_3COOH bromination[29] (yield 80%; i.r. 3107, 3080, 3055, 2955, 2927, 2870, 2856, 1539, 1466, 1457, 1410, 1378, 992, 874, 830, 713, 684, 636, 581). The two 3,4-dialkyl-2,5-dibromothiophenes were purified by chromatography on silica gel using n-hexane as eluent. 3,4-Dihexyl-2,5-dibromothiophene [yield 91%. ^{1}H n.m.r.: 2.53, t, 4 H (CH_2); 1.32, m, 16 H (CH_2); 0.89, t, 6 H (CH_3). I.r.: 2954, 2928, 2857, 1546, 1466, 1378, 1139, 1091, 948, 724. M.s.: *m/e* 410 (M^+ 40.26%). 3,4-Didodecyl-2,5-dibromothiophene [yield 93%. ^{1}H n.m.r.: 2.5, t, 4 H (αCH_2); 1.28, m, 40 H (CH_2); 0.89, t, 6 H (CH_3). I.r.: 2953, 2923, 2853, 1546, 1466, 1377, 1368, 1137, 1099, 946, 721. M.s: *m/e* 578 (M^+ 10.36%)]. 2-Iodo-3-dodecylthiophene was prepared by the method of Suzuki *et al.*[43], which was carried out at 75°C for 10 h. The oil which formed was extracted with ether and the ethereal solution washed with H_2O, 0.1 M NaOH, and then H_2O again. After drying over Na_2SO_4, the ether was removed and the crude product chromatographed on silica gel using n-hexane as eluent [yield:

88%. ^{1}H n.m.r.: 7.38, d, H$_5$, $J_{5-4} = 5.47$ Hz; 6.75, d, H$_4$, $J_{4-5} = 5.47$ Hz; 2.55, t, 2 H (αCH$_2$); 1.58, m, 2 H (βCH$_2$); 1.3, s, 18 H (CH$_2$); 0.89, t, 3 H (CH$_3$). I.r.: 3105, 3071, 2954, 2923, 2853, 1530, 1466, 1457, 1398, 1377, 967, 873, 829, 719, 685, 636, 579. M.s.: *m*/*e* 378 (M$^+$ 12.85%)].

The 3,3″-dialkyl monomers were prepared from the Grignard reagent of 2-bromo-3-hexylthiophene (2.5 equiv.) or 2-iodo-3-dodecylthiophene (2.5 equiv.) by the dichloro[1,3-bis(diphenylphosphino)propane] Ni (II) (13 mmol) catalysed coupling reaction with 2,5-dibromothiophene (1 equiv.). The 3′,4′-dialkyl monomers were prepared in an identical fashion to the 3,3″ monomers by the coupling of 2,5-dibromo-3,4-dihexylthiophene (1 equiv.) or 2,5-dibromo-3,4-didodecylthiophene (1 equiv.) with 2-thienylmagnesium bromide (4 equiv.), using 20 mmol of catalyst. The specific synthetic details outlined by Delabouglise *et al.*[44] were used for reaction conditions and crude product separation. 3,3″-Dialkylterthiophenes were directly purified by chromatography on silica gel using n-hexane as eluent; the 3′,4′-species were purified in the same way except that the crude monomers were first steam distilled in order to remove small amounts of 2,2′-bithiophene, thus improving the chromatographic separation. 3,3″DHTT [yield: 80%. ^{1}H n.m.r.: 7.18, d, 2 H (5,5″), $J = 5.19$ Hz; 7.05, s, 2 H (3′,4′); 6.94, d, 2 H (4,4″), $J = 5.19$ Hz; 2.8, t, 4 H (αCH$_2$); 1.64, m, 4 H (βCH$_2$); 1.32, m, 12 H (CH$_2$); 0.9, t, 6 H (CH$_3$). I.r.: 3102, 3066, 2953, 2927, 2856, 1466, 1422, 1377, 876, 834, 797, 723, 692, 656. M.s.: *m*/*e* 416 (M$^+$ 100%)]. 3,3″DDTT [yield: 72%. ^{1}H n.m.r.: 7.17, d, 2 H (5,5″), $J = 5.23$ Hz; 7.04, s, 2 H (3′,4′); 6.93, d, 2 H (4,4″), $J = 5.23$ Hz; 2.77, t, 4 H (αCH$_2$); 1.64, m, 4 H (βCH$_2$); 1.26, s, 36 H (CH$_2$); 0.86, t, 6 H (CH$_3$). I.r.: 3104, 3066, 2953, 2923, 2853, 1466, 1377, 875, 834, 796, 721, 692, 656. M.s.: *m*/*e* 584 (M$^+$ 100%)]. 3′,4′ DHTT [yield: 65%. ^{1}H n.m.r.: 7.31, dd, 2 H (5,5″), $J_{5-4} = 5.1$ Hz, $J_{5-3} = 1.25$ Hz; 7.14, dd, 2 H (3,3″), $J_{3-4} = 3.6$ Hz, $J_{3-5} = 1.25$ Hz; 7.07, dd, 2 H (4,4″), $J_{4-5} = 5.1$ Hz, $J_{4-3} = 3.6$ Hz; 2.7, t, 4 H (αCH$_2$); 1.56, m, 4 H (βCH$_2$); 1.35, m, 12 H (CH$_2$); 0.9, t, 6 H (CH$_3$). I.r.: 3106, 3070, 2954, 2927, 2856, 1501, 1465, 1429, 1417, 1377, 844, 828, 723, 691. M.s.: *m*/*e* 416 (M$^+$ 100%)]. 3′,4′ DDTT [yield: 62%. ^{1}H n.m.r.: 7.31, dd, 2 H (5,5″), $J_{5-4} = 5.1$ Hz, $J_{5-3} = 1.25$ Hz; 7.14, dd, 2 H (3,3″), $J_{3-4} = 3.6$ Hz, $J_{3-5} = 1.25$ Hz, 7.07, dd, 2 H (4,4″), $J_{4-5} = 5.1$ Hz, $J_{4-3} = 3.6$ Hz; 2.7, t, 4 H (αCH$_2$); 1.56, m, 4 H (βCH$_2$); 1.35, m, 36 H (CH$_2$); 0.9, t, 6 H (CH$_3$). I.r.: 3107, 3070, 2923, 2853, 1501, 1466, 1429, 1417, 1377, 845, 822, 721, 691. M.s.: *m*/*e* 584 (M$^+$ 100%)].

Spectroscopic characterization of the polymers

Poly (3,3″ DHTT) [^{1}H n.m.r.: 7.07, s, 2 H (3′,4′); 7.0, s, 2 H (4,4″); 2.76, t, 4 H (αCH$_2$); 1.68, m, 4 H (βCH$_2$); 1.37, s, 12 H (CH$_2$); 0.9, t, 6 H (CH$_3$). I.r.: 3063, 2953, 2925, 2869, 2855, 1498, 1467, 1435, 1377, 819, 777, 725]. Poly (3,3″DDTT) [^{1}H n.m.r.: 7.09, s, 2 H (3′,4′); 7.01, s, 2 H (4,4″); 2.77, t, 4 H (αCH$_2$); 1.68, m, 4 H (βCH$_2$); 1.27, s, 36 H (CH$_2$); 0.87, t, 6 H (CH$_3$). I.r.: 3063, 2952, 2921, 2851, 1500, 1467, 1378, 819, 790 (infl.), 776, 721]. Poly-(3′,4′ DHTT) [^{1}H n.m.r.: 7.15, dd, 2 H (3,3″), $J = 3.45$ Hz; 7.07, dd 2 H (4,4″), $J = 3.45$ Hz; 2.75 unresolved signal, 4 H (αCH$_2$); 1.37, m, 16 H (CH$_2$); 0.93, t, 6 H (CH$_3$). I.r.: 3064, 2955, 2927, 2870, 2857, 1495, 1466, 1432, 1378, 808, 795, 724]. Poly-(3′,4′DDTT) [^{1}H n.m.r.: 7.14, dd, 2 H (3,3″), $J = 3.48$ Hz; 7.06, dd, 2 H (4,4″), $J = 3.48$ Hz; 2.75 unresolved signal, 4 H (αCH$_2$); 1.27, m, 40 H (CH$_2$); 0.9, t, 6 H (CH$_3$). I.r.: 3062, 2955, 2922, 2852, 1493, 1467, 1378, 808, 794, 721].

RESULTS AND DISCUSSION

The monomers have been prepared by the Kumada reaction[37] and each monomer was oxidatively polymerized by anhydrous FeCl$_3$ in CHCl$_3$ or CCl$_4$. The other polymerization, de-doping, and fractionation conditions were kept constant for each of the eight runs and were standardized as follows: the FeCl$_3$ to monomer molar ratio was 4:1 and the weighed amount of oxidant was added all at once, as a solid, to the monomer (2–3 g) solution (7×10^{-2}M) in CHCl$_3$ or CCl$_4$ under a gently bubbling N$_2$ stream. The mixture was stirred at room temperature for 8 h, after which time the N$_2$ flow was stopped and methanol was added. The as-grown dark precipitated polymer was then exhaustively extracted in a Soxhlet unit, first with methanol, then with acetone, and dried. The red unextracted polymer was dissolved in CHCl$_3$ by stirring at room temperature and the insoluble material was removed by filtration, dried and considered as the insoluble polymer fraction. The red CHCl$_3$ solution was evaporated to dryness *in vacuo* to afford the soluble polymer fraction. Methanol and acetone were removed *in vacuo* from the combined Soxhlet extracts and the residue was partitioned between n-hexane and 1 N HCl. The organic layer was washed with water until neutral, dried and concentrated to afford the oligomeric fraction of the polymers.

After this procedure had been carried out, the polymers of the soluble fractions were always neutral, as evidenced by the elemental analyses showing very low amounts of Fe and Cl residues. For example, with poly(3′,4′-DDTT) we found the following: C 74.24, H 9.32 and S 16.45%, with Fe and Cl < 0.2%. The expected structural features of the final soluble polymers have been confirmed by the *FT* i.r. and ^{1}H n.m.r. spectroscopic data that have been reported in the Experimental section only for those polymers prepared in CCl$_4$, with the dependency of the spectra on the reaction medium being always negligible. Indeed, the *FT*i.r. spectrum of each polymer, compared with the spectrum of the corresponding monomer, showed only one aromatic absorption due to the C$_\beta$–H stretch and all the expected strong absorptions characteristic of the substitution pattern and due to the C$_\beta$–H out-of-plane bending vibrations, clearly indicating that the polymers possess well defined fully conjugated linear structures with an absence of mislinkages through the β-positions[4,24,25]. In addition, the expanded aromatic and aryl methylene regions of the ^{1}H n.m.r. spectra of the polymers always showed the expected major peaks, with these never accompanied by additional resonances. This reinforces the interpretation of the *FT* i.r. data and confirms that completely stereoregular polymers with rather high molecular weights have been obtained[29,33,41]. Thermal, electrical, optical, and X-ray characterizations of these polymers are in progress and will be reported in a later paper.

The polymers of the insoluble fractions, on the other hand, always showed in their i.r. spectra additional conspicuous absorption bands, mainly lying between

Table 1 Fractionation yields[a] and molecular weights of soluble fractions of poly(dialkylterthiophene)s prepared in $CHCl_3$ and CCl_4

	Insoluble fraction		Oligomeric fraction		Soluble fraction					
Polymer	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	M_w	M_n	CCl_4	M_w	M_n
Poly(3,3″DHTT)	85	29	2	28	14	16 000	7 800	41	15 800	8 800
Poly(3,3″DDTT)	13	0	38	43	48	22 700	11 000	54	17 000	9 600
Poly(3′,4′DHTT)	95	70	1	6	6	18 400	9 100	22	18 200	10 300
Poly(3′,4′DDTT)	71	0	3	29	26	36 800	18 000	67	31 400	17 200

[a] Weight of each fraction ×100/ weight of monomer

1350–1000 cm^{-1}, which were assigned[27,45] to residual doping impurities, with Fe and Cl content ranging from 3 to 5%. These significant amounts of residual doping seem to be strongly bonded to the polymer chains whose molecular weights exceed that of the recovered soluble neutral polymer. This, in turn, could have resulted in more soluble material (i.e. soluble at even higher molecular weights) if it had not been for the residual doping. Therefore, in our aim to attain additional amounts of higher-molecular-weight neutral soluble polymers, we submitted the insoluble polymers to further de-doping treatments. As a result, however, we found it impossible to reduce these polymers, to their neutral (either soluble or insoluble) forms, even when using reducing agents such as ammonia or hydrazine in the presence of CH_3OH or DMF as 'soaking' solvents for the insoluble polymers. Due to this exceptional and unexpected stability of the residual doping, the insoluble polymer fractions must be considered, together with the oligomeric fractions, as being part of the overall purification losses of the soluble polymers.

In *Table 1* the fractionation yields of the polymerization runs performed in $CHCl_3$ are listed and compared with the corresponding data from the CCl_4 runs. In this table, weight- and number-average molecular weights (M_w and M_n), as determined by g.p.c., are also given for the soluble polymers.

As far as the yields are concerned, the results presented indicate that higher yields of the insoluble fraction and lower yields of the oligomeric and soluble fractions have always been obtained in $CHCl_3$ runs compared to CCl_4 runs. However, one can notice that this drawback of $CHCl_3$ is more serious for dihexylsubstituted monomers when compared to didodecyl monomers, as well as for the 3′,4′-disubstitution pattern when compared to the 3,3″ one, with the lowest yield of soluble fraction being obtained from 3′,4′DHTT and highest from 3,3″DDTT.

As far as the molecular weights are concerned, it may be observed that each of the soluble polymers prepared in CCl_4 always shows a better polydispersity index (M_w/M_n) and a similar or slightly lower M_w value when compared to the same polymer prepared in $CHCl_3$. However, it should be noted here that it is always the case that significantly lower yields of insoluble fractions and, respectively, that higher yields of soluble polymers and unreacted materials (oligomeric fractions) have been obtained in the polymerization runs performed in CCl_4. This may indicate that when the insoluble fraction did not exist at all (3,3″DDTT and 3′,4′DDTT) due to good solubilities of the polymers, a reaction time longer than 8 h could have led to even larger percentages of possibly higher-molecular-weight soluble polymer. When, on the other hand, a significant insoluble fraction was formed (3,3″DHTT and 3′,4′DHTT) due to low solubilities of the polymers, a controlled shortening of the reaction time could have led to improved yields of soluble polymers without a significant lowering of the molecular weights. Overall, this may reflect the fact that, whereas in $CHCl_3$ a rather fast and uncontrollable process always took place with unfavourable results, in CCl_4, under the same experimental conditions, a slower and more profitable polymerization occurred, with this being susceptible to further improvements.

These results seem to be in keeping with the following interpretation. Although the mechanism of the oxidative coupling of thiophene monomers by $FeCl_3$ is still under discussion[46], it is reasonable to suppose that the polymerization rate is largely determined by the stability of the radical or radical cation formed from the monomer. Therefore, all other experimental conditions being equal, the monomer structure and polymerization medium become the main factors that determine the polymerization rate, thus affecting the fractionation yields and molecular weights. The previously noted differences between the polymerizations performed in CCl_4 and $CHCl_3$ may be attributed to either a slower formation or greater stability of the radical species involved in the polymerization processes performed in CCl_4 when compared to those performed in $CHCl_3$.

In our work we have *a priori* fixed the same experimental conditions for two different reaction media and four monomers differing in structure and alkyl chain length. As a consequence, neither in $CHCl_3$, nor in CCl_4, have the largest possible amounts of the highest-molecular-weight soluble polymers ever been achieved. In spite of this, some general concluding remarks can be summarized as follows. Although $CHCl_3$ and CCl_4, together with the other solvents, are known to be suitable reaction media for the chemical oxidative coupling of thiophene monomers by $FeCl_3$[46], $CHCl_3$ has almost exclusively been used up to now. Here we have demonstrated, however, that CCl_4 is far more suitable than $CHCl_3$ in at least two cases, namely (i) when the oxidative coupling is expected to be very fast, as suggested by either the use of high concentrations of reactants or a rapid formation of significant amounts of insoluble polymer in controlled experiments and (ii) when the polymers to be prepared are reasonably expected to be not very soluble, i.e. becoming insoluble at a rather low molecular weight. This may be the case for our poly(dialkylterthiophene)s when compared to PATs, as well as for polymers whose structure and substitution pattern are the same as that of a known polymer, but where the substituents are known to possess a reduced solubilizing power.

CONCLUSIONS

In conclusion, we have prepared new poly(3,3″- and 3′,4′-dialkyl-α-terthiophene)s possessing two desirable structural features of significant interest in the field of substituted polythiophenes, namely a full ordered regiochemistry (of bonding and substitution) as well as a chain free from head-to-head interactions. We have also reported here experimental conditions of special utility for attaining the soluble fraction of these polymers with the maximum yield and molecular weight. Our results argue for the new concept of the greater versatility and the wider scope for CCl_4 over $CHCl_3$ as the reaction medium for the chemical oxidative polymerizations promoted by $FeCl_3$. However, continued efforts should be devoted to the search for more examples that are able to further confirm this concept.

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REFERENCES

1 Jen, K. Y., Oobodi, R. and Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* 1985, **53**, 79

2 Elsenbaumer, R. L., Jen, K. Y. and Oobodi, R. *Synth. Met.* 1986, **15**, 169

3 Sato, M., Tanaka, S. and Kaeriyama, K. *Makromol. Chem.* 1987, **188**, 1763

4 Hotta, S., Rughooputh, S. D. D. V., Heeger, A. J. and Wudl, F. *Macromolecules* 1987, **20**, 212

5 Novak, M., Rughooputh, S. D. D. V., Hotta, S. and Heeger, A. J. *Macromolecules* 1987, **20**, 967

6 Hotta, S., Rughooputh, S. D. D. V. and Heeger, A. J. *Synth. Met.* 1987, **22**, 79

7 Tourillon, G. in 'Handbook of Conducting Polymers' (Ed. T. A. Skotheim), Vol. 1, Marcel Dekker, New York, 1986, Ch. 9, p. 293

8 Patil, A. O., Heeger, A. J. and Wudl, F. *Chem. Rev.* 1988, **88**, 183

9 Kanadzidis, M. G. *Chem. Eng. News* 1990 (Dec. 3), 36

10 Garnier, F., Tourillon, G., Gazard, M. and Dubois, J. C. *J. Electroanal. Chem. Interfacial Electrochem.* 1983, **148**, 299

11 Kaufman, J. H., Chung, T. C., Heeger, A. J. and Wudl, F. *J. Electrochem. Soc.* 1984, **131**, 2092

12 Biserni, M., Marinangeli, A. and Mastragostino, M. *J. Electrochem. Soc.* 1985, **132**, 1597

13 Tsumura, A., Koezuka, H. and Ando, T. *Synth. Met.* 1988, **25**, 11

14 Sinclair, M., McBranch, D., Moses, D. and Heeger, A. J. *Synth. Met.* 1989, **28**, D645

15 Houlding, V. H., Harata, A., Yardley, J. T. and Elsenbaumer, R. L. *Chem. Mater.* 1990, **2**, 169

16 Singh, B., Samoc, M., Nalwa, H. S. and Prasad, P. N. *J. Chem. Phys.* 1990, **92**, 2756

17 Braun, D., Gustafsson, G., McBranch, D. and Heeger, A. J. *J. Appl. Phys.* 1992, **72**, 564

18 Friend, R., Bradley, D. and Holmes, A. *Phys. World* 1992, (Nov.), 42

19 Bradley, D. D. C. *Synth. Met.* 1993, **54**, 401

20 Elsenbaumer, R. L., Jen, K. Y., Miller, G. G., Eckhardt, H., Shacklette, L. W. and Jow, R. in 'Springer Series in Solid-State Sciences', Vol. 76, 1987, p. 400

21 Sato, M. and Morii, H. *Polym. Commun.* 1991, **32**, 42

22 Sato, M. and Morii, H. *Macromolecules* 1991, **24**, 1196

23 Mao, H., Xu, B. and Holdcroft, S. *Macromolecules* 1993, **26**, 1163

24 Souto Maior, R. M., Hinkelman, K., Eckert, H. and Wudl, F. *Macromolecules* 1990, **23**, 1268

25 Zagórska, M. and Krische, B. *Polymer* 1990, **31**, 1379

26 Zagórska, M., Kulszewicz-Bajer, I., Pron, A., Firlej, L., Bernier, P. and Galtier, M. *Synth. Met.* 1991, **45**, 385

27 Louran, G., Kruszka, J., Lefrant, S., Zagórska, M., Kulszewicz-Bayer, I. and Pron, A. *Synth. Met.* 1993, **61**, 233

28 McCullough, R. D. and Lowe, R. D. *J. Chem. Soc. Chem. Commun.* 1992, 70

29 McCullough, R. D., Lowe, R. D., Jayaraman, M. and Anderson, D. L. *J. Org. Chem.* 1993, **58**, 904

30 McCullough, R. D., Lowe, R. D., Jayaraman, M., Ewbank, P. C., Anderson, D. L. and Tristam-Nagle, S. *Synth. Met.* 1993, **55–57**, 1198

31 McCullough, R. D., Tristam-Nagle, S., Williams, S. P., Lowe, R. D. and Jayaraman, M. *J. Am. Chem. Soc.* 1993, **115**, 4910

32 McCullough, R. D. and Williams, S. P. *J. Am. Chem. Soc.* 1993, **115**, 11608

33 Chen, T. A. and Rieke, R. D. *J. Am. Chem. Soc.* 1992, **114**, 10087

34 Chen, T. A. and Rieke, R. D. *Synth. Met.* 1993, **60**, 175

35 Gallazzi, M. C., Castellani, L., Marin, R. A. and Zerbi, G. *J. Polym. Sci. Polym. Chem. Edn.* 1993, **31**, 3339

36 Wang, C., Benz, M. E., LeGoff, E., Schindler, J. L., Albritton-Thomas, J., Kannewurf, C. R. and Kanatzidis, M. G. *Chem. Mater.* 1994, **6**, 401

37 Tamao, K., Kodama, S., Nakajima, J., Kumada, M., Minato, A. and Suzuki, K. *Tetrahedron* 1982, **38**, 3347

38 Van Pham, C., Mark Jr., H. B. and Zimmer, H. *Synth. Commun.* 1986, **16**, 689

39 Gautun, O. R., Carlsen, P. H. J., Samuelsen, E. J. and Mardalen, J. *Synth. Met.* 1993, **58**, 115

40 Bäuerle, P., Pfau, F., Schlupp, H., Würthner, F., Gaudl, K.-U., Caro, M. B., and Fischer, P. *J. Chem. Soc. Perkin Trans.* 2, 1993, 489

41 Leclerc, M., Diaz, F. M. and Wegner, G. *Makromol. Chem.* 1989, **190**, 3105

42 Mitchell, R. H., Lai, Y.-H. and Williams, R. V. *J. Org. Chem.* 1979, **44**, 4733

43 Suzuki, H., Nakamura, K. and Goto, R. *Bull. Chem. Soc. Jpn* 1966, **39**, 128

44 Delabouglise, D., Hmyene, M., Horowitz, G., Yassar, A. and Garnier, F. *Adv. Mater.* 1992, **4**, 107

45 Hotta, S., Shimotsuma, W. and Taketani, M. *Synth. Met.* 1984/85, **10**, 85

46 Niemi, V. M., Knuuttila, P., Österholm, J.-E. and Korvola, J. *Polymer* 1992, **33**, 1559