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New mechanistic aspects on the formation of poly(isothianaphthene) from P_4S_{10} and phthalic anhydride derivatives: carbon–carbon bond formation and cleavage via a cyclic reaction mechanism

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Abstract

Mechanistic studies on the formation of poly(isothianaphthene) (PITN) from phthalic anhydride and a thionating reagent (phosphorus pentasulphide or Lawessons' reagent) have shown that the thionating reagent is not crucial in the polymerization reaction itself; it only plays a role in the synthesis of the actual monomer, the tristhiophthalic anhydride. The polymerization process is not a classical polycondensation, but a process by which the very reactive tristhiophthalic anhydride monomer repeatedly attaches to the growing chain under expulsion of sulphur. We present new results obtained in studies on low molecular models, and we will focus on additional reactions induced by the thionating agent. A generalized mechanism will be proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymers; Poly(isothianaphthene); Mechanism

1. Introduction

Poly(isothianaphthene) (PITN) (9) (Fig. 1) has received substantial interest in the past years, since it is a low band-gap polymer [1,2]. In 12 years many synthetic routes to PITN (9) have been reported in the literature [3–8]. We could show that PITN can be derived from the reaction of phthalic anhydride (1) with a thionating reagent (phosphorus pentasulphide (P_4S_{10}) or Lawessons' reagent) [7]. Previous mechanistic studies based on the observed intermediates allowed us to propose a potential mechanism for the formation of PITN (9) from phthalic anhydride and P_4S_{10} [9] (Fig. 1).

Starting from phthalic anhydride (1), successive thionating and isomerization reactions yield tristhiophthalic anhydride (6). The latter compound might polymerize via a classical condensation process (dimer, trimer, etc.) under expulsion of sulphur (S_2) (Fig. 2). Although this mechanism is assumed throughout the paper, it cannot be excluded for the time being that a free radical or even ionic chain polymerization occurs to form a disulphide linked polymer, which subsequently undergoes rapid loss of sulphur.

This paper reports on our efforts to investigate the mechanism of this polymerization process in greater detail, with a focus on the role of the thionating agent.

2. Experimental

2.1. Instrumentation

Melting points were recorded with an Electrothermal IA9000 Digital Melting Point apparatus. The FT-IR and FT-Raman data were performed on an IFS 66 FT-IR spectrometer connected to a Bruker computer (ASPECT 1000) equipped with a Raman FRA 106 module. Mass spectroscopy was performed with a Finigan 1020 or a TSQ70 apparatus.

2.2. Liquid NMR

^1H and ^{13}C liquid NMR analyses were carried out in $CDCl_3$ at 25°C with a Varian Unity 400 spectrometer. Chemical shifts are expressed in δ (ppm) (internal shift reference for chloroform at 7.24 and 77.0 ppm, respectively). The spectral parameters used for the ^1H recordings were a spectral width of 4700 Hz, a 90° pulse width of 7.5 μs, an acquisition time of 2.498 s and four repetitions, while those of the ^{13}C recordings were a spectral width of 23 000 Hz, a 90° pulse width of 10 μs, an acquisition time of 0.701 s and 1000 repetitions.

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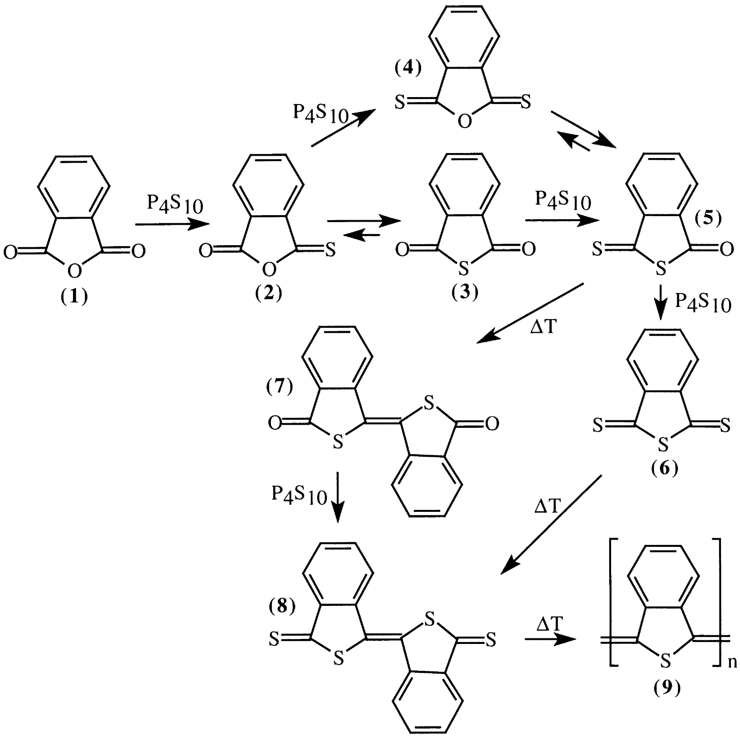


Fig. 1. Proposed mechanism for the formation of PITN (9) from the reaction of phthalic anhydride (1) with P_4S_{10}.

2.3. Solid state ^{13}C NMR

All solid state ^{13}C NMR spectra were recorded at room temperature on a Varian XL-200 instrument at 50.3 MHz. ^{13}C cross-polarization spectra are performed using cross-polarization contact times (T_{CT}) ranging from 1 to 9 ms, high-power (44 kHz) ^1H decoupling and a recycle delay of 2 s. The number of transients per spectrum was set to 8500, with an acquisition time of 0.0307 s, a 90° pulse width of 8.4 μs and a spectral width of 23 980 Hz. To minimize the effect of long-term drift, the NMR relaxation experiments were interleaved and block averaged with 32 acquisitions per block. Magic angle spinning was performed at 7 kHz using Si_3N_4 rotors. KBr was used to set the magic angle (54.7°) while the Hartman–Hahn condition was adjusted using the aromatic signal of hexamethylbenzene. This signal was also used to calibrate the chemical shift (132.1 ppm from TMS) and the π/2 pulse width (8.4 μs). Adamantane was used for shimming.

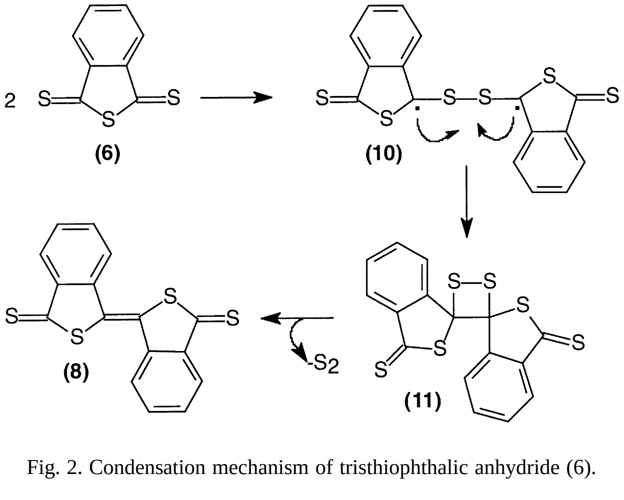


Fig. 2. Condensation mechanism of tristhiophthalic anhydride (6).

2.4. Synthetic procedures

All experiments were performed under a nitrogen atmosphere. Commercially available products were used without further purification.

2.4.1. Dimerization of benzylidenedithiophthalide (15a)

By thermal treatment: 0.5 g (1.96 mmol) benzylidenedithiophthalide (Fig. 4) was refluxed in 6.56 ml xylene (0.3 M) under nitrogen. After 20 h TLC indicated that no dimerization had occurred and that the benzylidenedithiophthalide remained unreacted.

By reaction with P_4S_{10}: 0.5 g (1.96 mmol) benzylidenedithiophthalide (15a) or 0.47 g (1.96 mmol) pentylidenedithiophthalide (15b) (Fig. 4) was reacted with 0.87 g (1.96 mmol) P_4S_{10} in 6.56 ml refluxing xylene (0.3 M) for 20 h. A black–blue powder (36% in case of benzylidenedithiophthalide; 28% in case of pentylidenedithiophthalide) was filtered and characterized as PITN (9) after Soxhlet extraction with THF and chloroform.

PITN: FT-IR (KBr, ν, cm^{-1}): 1585, 1453, 1263, 1124, 1041, 978, 875, 844, 734; FT-Raman (KBr, ν, cm^{-1}): 1463, 1447, 1302, 1231, 1194, 1166, 1053, 988, 885, 446; solid state NMR (ppm, relative to TMS): 139 (C_{3a}), 126 (C_3, C_4 and C_5).

By reaction with Lawessons' reagent: 0.5 g (1.96 mmol) benzylidenedithiophthalide or 0.47 g (1.96 mmol) pentylidenedithiophthalide are reacted with 0.80 g (1.96 mmol) Lawessons' reagent in 6.56 ml refluxing xylene (0.3 M) for 20 h. A black–blue powder (28% in case of benzylidenedithiophthalide; 15% in case of pentylidenedithiophthalide) was filtered and characterized as PITN (9) after Soxhlet extraction with THF and chloroform.

PITN: FT-IR (KBr, ν, cm^{-1}): 1584, 1453, 1265, 1124, 1041, 978, 875, 843, 734; FT-Raman (KBr, ν, cm^{-1}): 1463, 1445, 1302, 1231, 1191, 1167, 1053, 989, 885, 447; solid state NMR (ppm, relative to TMS): 139 (C_{3a}), 126 (C_3, C_4 and C_5), 40–15 ppm (pentyl/endgroup).

2.4.2. Synthesis of t-stilbene (25)

About 1 g (9.4 mmol) benzaldehyde (23) and 4.19 g (9.4 mmol) P_4S_{10} were refluxed in 31 ml xylene (0.3 M) for 20 h. The reaction mixture was purified by column chromatography (silica/hexane) and this yielded 5% *t*-stilbene.

m.p.: 121.6–122.8°C (lit: 122–124°C); FT-IR (KBr, ν, cm^{-1}): 3019 ($\nu_{\text{CH arom}}$), 2000–1600 ($_{\text{substitution pattern}}$), 1596 ($\nu_{\text{C=C arom}}$), 1494 ($\nu_{\text{C=C arom}}$), 1450 ($\nu_{\text{C=C arom}}$), 962 ($\nu_{\text{C=C } \textit{trans} \text{ alkene}}$), 764 ($_{\text{arom, monosubst.}}$), 692 ($_{\text{arom, monosubst.}}$); MS (EI, *m/e*): 180 ($M^+$, 100%).

2.4.3. Synthesis of tetraphenyl ethylene (26)

Via phosphor pentasulphide: 2 g (10.1 mmol) thiobenzophenone (24b) and 4.48 g (10.1 mmol) P_4S_{10} were refluxed for 20 h in 34 ml xylene (0.3 M). The reaction mixture was purified by column chromatography (silica; hexane/chloroform (90/10)) and this yielded 15% tetraphenyl ethylene.

m.p.: 226.4–227.6°C (lit: 227–228°C); FT-IR (KBr, ν, cm^{-1}): 3048 ($\nu_{\text{CH-arom}}$), 2000–1600 ($_{\text{substitution pattern}}$), 1594 w>($\nu_{\text{C=Carom}}$),1489($\nu_{\text{C=Carom}}$),1441($\nu_{\text{C=Carom}}$),746($_{\text{arom,monosubst.}}$), 699 ($_{\text{arom, monosubst.}}$); MS (EI, *m/e*): 332 ($M^+$, 100%).

Thiobenzophenone (24b): 5 g (27.4 mmol) benzophenone (24a), 18.3 g (1.5 mol eq.) P_4S_{10} and 13.84 g (6 mol eq.) $NaHCO_3$ were dissolved in 125 ml CH_3CN and reacted for 4 h at 30°C under nitrogen atmosphere. Afterwards ether was added and the reaction mixture was filtered. The filtrate was washed three times with 100 ml of a 5% $NaHCO_3$ solution and three times with water. The organic layers were combined and dried over $MgSO_4$. Purification was done by column filtration (silica; hexane/chloroform (75/25)). After evaporation under reduced pressure 71% of the blue crystalline thiobenzophenone was obtained.

FT-IR (KBr, ν, cm^{-1}): 3030 ($\nu_{\text{CH-arom}}$), 2000–1600 ($_{\text{substitution pattern}}$), 1583 ($\nu_{\text{C=C arom}}$), 1441 ($\nu_{\text{C=C arom}}$), 1265 ($\nu_{\text{C=S}}$), 1225 ($\nu_{\text{C=S}}$), 1046 ($\nu_{\text{C=S}}$), 777 ($_{\text{arom, monosubst.}}$), 758 ($_{\text{arom, monosubst.}}$), 690 ($_{\text{arom, monosubst.}}$); MS (EI, *m/e*): 198 ($M^+$, 100%); ^{1}H NMR ($CDCl_3$, 400 MHz, relative to TMS): 7.70 (d, 4H, $^3J = 7.27$ Hz), 7.55 (t, 2H, $^3J = 7.27$ Hz), 7.38 (t, 4H, $^3J = 8.18$ Hz).

Thermal: 0.35 g (1.76 mmol) thiobenzophenone (24b) was refluxed for 20 h in 5.9 ml xylene (0.3 M). Analysis of the reaction mixture indicated that in this case no tetraphenyl ethylene (26) was formed and that the thiobenzophenone (24b) remained unreacted.

2.4.4. Synthesis of dibenzylidenedithiophthalide (15c)

0.19 g (0.58 mmol) 1,1,3,3-tetrachlorothiophthalan, 1.11 g (5.8 mmol) thiobenzophenone (24b), 0.83 ml (7.36 mmol) *t*-butyl mercaptan and 0.028 ml (0.36 mmol) trifluoroacetic acid were refluxed for 20 h in methylene chloride (2.33 ml) (0.3 M). Purification of the reaction mixture via column chromatography (silica, hexane/chloroform (70/30)) yielded 45–50% dibenzylidenedithiophthalide (15c, yield versus 1,1,3,3-tetrachlorothiophthalan).

Dibenzylidenedithiophthalide: m.p.: 152.7–153.9°C; FT-IR (KBr, ν, cm^{-1}): 1588 ($\nu_{\text{C=C arom}}$), 1458 ($\nu_{\text{C–S}}$), 1263 ($\nu_{\text{C–S}}$), 1217 ($\nu_{\text{C=S}}$), 1047 ($\nu_{\text{C=S}}$), 763 ($\nu_{\text{C=C arom}}$), 702 ($\nu_{\text{C=C arom}}$); MS (*m/e*): 330 (M^+, 100%), 254 ($M^+–CS_2$, 18%); ^{1}H NMR ($CDCl_3$, 400 MHz, relative to TMS): 8.09 (d, $^3J = 4$ Hz, 1H, H_7), 7.44 (t, $^3J = 5.33$ Hz, 1H, H_5), 7.36 (m, 10H, H_{10-12} and $H_{10'-12'}$), 7.27 (t, $^3J = 5.33$ Hz, 1H, H_6), 6.84 (d, $^3J = 4$ Hz, 1H, H_4); ^{13}C NMR ($CDCl_3$, 400 MHz, relative to TMS): 219.58 (C_1), 144.27, 142.25, 141.18, 140.79, 131.68, 129.84 (2C), 129.70 (2C), 129.20 (2C), 129.11, 129.08, 129.06, 128.72, 128.46 (2C), 124.73, 123.87.

2.4.5. Dimerization of dibenzylidenedithiophthalide (15c)

Thermal: About 1 g (3 mmol) dibenzylidenedithiophthalide (15c) is refluxed for 20 h in 12.27 ml xylene (0.3 M). TLC indicated that the dibenzylidenedithiophthalide (15c) remained unreacted.

Via P_4S_{10}: About 1 g (3 mmol) dibenzylidenedithiophthalide (15c) and 1.33 g (3 mmol) P_4S_{10} were refluxed for 20 h in 12.27 ml xylene (0.3 M). TLC indicated that the dibenzylidenedithiophthalide (15c) has quasi not reacted. Mass spectroscopy indicated that traces of dibenzylidenedithiophthalide dimer were formed.

2.4.6. Synthesis of PITN (9) from trans-3,3′-bibenzo(c)thienylidene-1,1′-dione (7)

1 g (3.36 mmol) *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dione (7) and 1.48 g (3.36 mmol) P_4S_{10} were refluxed for 20 h in 11.2 ml xylene (0.3 M). After evaporation of the xylene under reduced pressure, the black residue was refluxed in MeOH for 1 h. The precipitate was purified via Soxhlet extraction with THF and chloroform. After drying under vacuum 48% of PITN (9) was obtained.

FT-IR (KBr, ν, cm^{-1}): 1583, 1451, 1260, 1131, 1040, 977, 872, 841, 729; FT-Raman (KBr, ν, cm^{-1}): 1463, 1451, 1302, 1228, 1197, 1164, 1058, 991, 885, 446; solid state NMR (ppm, relative to TMS): 139 (C_{3a}), 126 (C_3, C_4 and C_5).

2.4.7. Synthesis of PITN from trans-3,3′-bibenzo(c)thienylidene-1,1′-dithioketone (8)

Thermal: 0.43 g (1.31 mmol) *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dithioketone (8) was refluxed for 20 h in

4.4 ml xylene (0.3 M). TLC shows that no reaction occurs and that the *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dithioketone (8) is left unreacted.

2.4.8. *trans-3,3′-Bibenzo(c)thienylidene-1,1′-dithioketone*

1 g (3.4 mmol) *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dione (7) and 1.37 g (3.4 mmol) Lawessons' reagent were refluxed for 2 h in 200 ml chlorobenzene. After refluxing with MeOH, the purification was done by column filtration (silica; hexane/chloroform (75/25)). Evaporation under reduced pressure yields 0.47 g *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dithioketone (8) (41%). MS (EI, *m/e*): 328 (M^+, 100%), 264 (M^+–2S, 76%).

2.4.9. *Trapping experiment in the reaction of trans-3,3′-bibenzo(c)thienylidene-1,1′dione (7)*

0.5 g (2.5 mmol) *trans*-3,3′-bibenzo(c)thienylidene-1,1′dione (7), 11.1 g (25 mmol) P_4S_{10} and 4.55 g (25 mmol) benzophenone were refluxed in 8.33 ml xylene under nitrogen. After 20 h the xylene was evaporated under reduced pressure, the residue was refluxed for 1 h in 25 ml of methanol to destroy the excess of P_4S_{10}. After filtration the filtrate is concentrated under reduced pressure and purified by column chromatography (silica; hexane/chloroform (90/10)) and this yields 18% dibenzylidenedithiophthalide (15c) and 17% tetraphenyl ethylene (26). The residue of the filtration was further purified by Soxlet extraction with THF and chloroform and yielded 29% PITN.

2.4.10. *Trapping experiment in the reaction of benzylidenedithiophthalide (15a)*

About 0.63 g (2.5 mmol) benzylidenedithiophthalide (15a), 11.1 g (25 mmol) P_4S_{10} and 4.55 g (25 mmol) benzophenone were refluxed in 8.33 ml xylene under nitrogen. After 20 h the xylene is evaporated under reduced pressure, the residue is refluxed for 1 h in 25 ml methanol to destroy the excess of P_4S_{10}. After filtration the filtrate is concentrated under reduced pressure and purified by column chromatography (silica; hexane/chloroform (90/10)) and this yields 11% dibenzylidenedithiophthalide (15c) and 33% tetraphenyl ethylene (26) Formation of only slight amounts of PITN could be observed in this experiment.

3. Results and discussion

It is known that the formation of PITN (9) from phthalic anhydride (1) or derivatives with a thionating reagent might proceed via a polycondensation reaction of tristhiophthalic anhydride (6) under expulsion of sulphur (S_2) [9].

In this paper we want to investigate whether this mechanism is an ordinary polycondensation reaction or if the thionating reagent plays a specific role in the polymerization process itself. In other words: does a bisthiolacton group (S–C=S) show enough reactivity to dimerize under thermal conditions? We therefore tried to dimerize benzylidenedithiophthalide (15a) by refluxing it for 20 h in xylene. The synthesis of the latter compound is described earlier [10].

However, no dimerization of the benzylidenedithiophthalide occurred. This made us think that the thionating reagent (P_4S_{10} or Lawessons' reagent) was crucial in the polymerization reaction. Reaction of the benzylidenedithiophthalide (15a) or pentylidenedithiophthalide (15b) with an equimolar amount of P_4S_{10} for 20 h in refluxing xylene gave a blue–black insoluble powder which—to our surprise—was characterized to be PITN (9) instead of the expected dimer. Similar results were obtained when Lawessons' reagent was used instead of P_4S_{10}. This already indicates that we are dealing with a complex process, since no bifunctional monomers were initially present. The following question arises: is there an explanation for the formation of PITN from dithiophthalides (15a or 15b)?

The fact that the dithiophthalides (15a or 15b) polymerize via reaction with the thionating reagent, implies that a reaction has to occur between the benzylidene double bond and the thionating reagent. In literature it is known that Lawessons' reagent in solution undergoes the following monomer–dimer equilibrium [11] (Fig. 3).

For phosphorus pentasulphide (P_4S_{10}) an analogous equilibrium might exist. Taking the existence of such a monomeric unit from the thionating reagent into consideration, this might provide a potential mechanism for the formation of PITN (9) from dithiophthalides (15a or 15b) (Fig. 4).

Reaction of the monomeric thionating reagent with the C_3–C_8 double bond (Fig. 4) would lead to the formation of a phosphonium ylide (17) and tristhiophthalic anhydride (6). Since the latter compound gives rise to PITN (9) (its monomer tristhiophthalic anhydride can be generated in situ from 1,1,3,3-tetrachlorophthalan without addition of P_4S_{10}) [12], this might be a possible explanation for the formation of PITN from benzylidenedithiophthalide (15a). The reaction sequence presented in Fig. 4 can be seen as a retro-synthetic process from the reaction of a phosphonium ylide with a thiocarbonylic functional group. Such "thio-Wittig" reactions are known in literature [13].

This chemistry, which might explain the PITN formation from dithiophthalides (15a or 15b), again leads to the question of what the exact role of the thionating reagent is

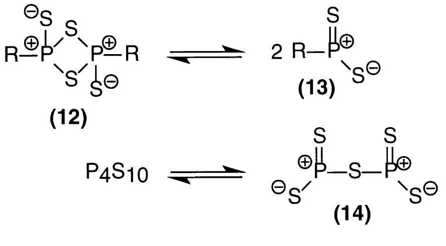
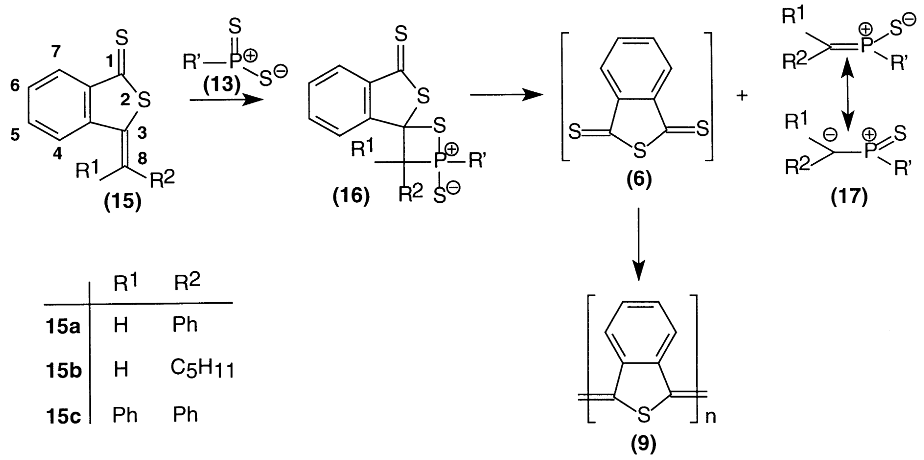


Fig. 3. Dimer–monomer equilibrium for Lawessons' reagent (R = $PhOCH_3$) and P_4S_{10}.



	R1	R2
15a	H	Ph
15b	H	C_5H_{11}
15c	Ph	Ph

Fig. 4. Formation of PITN (9) from the reaction of benzylidenedithiophthalides (15a–c) and a thionating reagent.

in the formation of PITN (9) from phthalic anhydride derivatives.

Indeed, one can construct a sequence (Fig. 5) in which a reaction between the thionating reagent (13) and the thiocarbonylic group (18) leads, via the intermediate (19), to a phosphonium ylide (20) under expulsion of sulphur. Such a phosphonium ylide can attack a thiocarbonyl group (18) which yields the intermediate (21) and finally a C=C double bond (22) setting the thionating reagent free.

The proposed cyclic mechanism might be an explanation for the overall polymerization process where PITN (9) is derived from the reaction of phthalic anhydride (1) with a thionating reagent. On the other hand we established in earlier work [12] that the thionating agent is not necessary to induce the polymerization of the tristhiophthalic anhydride intermediate. So, how do these conflicting data relate to each other? To investigate whether via this cyclic mechanism other C=C coupled products could be obtained from reaction of (thio)carbonyls and thionating agents, we carried out the following tests. We reacted benzaldehyde (23) with P_4S_{10} for 20 h in refluxing xylene (0.3 M); thiobenzophenone (24b) was treated the same way. The expected products, according to the cyclic reaction mechanism, are *t*-stilbene (25) and tetraphenyl ethylene (26), respectively (Fig. 6).

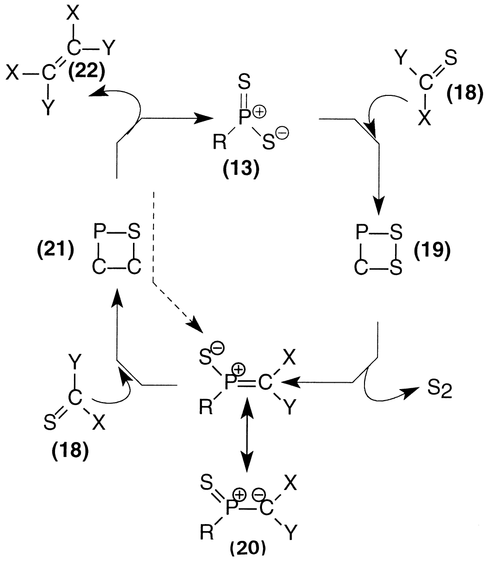


Fig. 5. Proposal for a cyclic polymerization mechanism for the synthesis of PITN.

Spectroscopic analysis points out that *t*-stilbene (25) and tetraphenyl ethylene (26) are indeed formed. The yield after column chromatography is 5 and 15%, respectively. The formation of tetraphenyl ethylene (26) was proven by comparison of the FT-IR spectra of a commercial and the synthesized tetraphenyl ethylene (26).

These experiments show that the thionating reagent might participate in the reaction process. To investigate this we performed the second experiment thermally, in absence of P_4S_{10}. In this case no tetraphenyl ethylene (26) is formed and only unreacted thiobenzophenone (24b) and benzophenone (24a, by a hydrolysis reaction) are determined in the reaction mixture. So, thiocarbonyl compounds can be coupled by reaction with P_4S_{10}, possibly via the cyclic process and dithiophthalides (15a or 15b) may give PITN (9) via the counter-clockwise cyclic process. As a consequence of former work we could synthesize the sterically more hindered dibenzylidenedithiophthalide (15c) which allows us to test the reactions discussed here further. We may expect, given the processes as described above, that bond cleavage might be inhibited by steric hindrance, and if P_4S_{10} would then couple the bisthiolactones instead we should obtain a dimeric model for PITN. As was mentioned before for (15a), dibenzylidenedithiophthalide (15c) also does not dimerize thermally. Under the same reaction conditions but in the presence of P_4S_{10} no PITN or dimers were formed, in contrast to the less hindered benzylidenedithiophthalide (15a). This implies that bond scission induced by P_4S_{10} at C_3–C_8 is indeed sterically hindered, and that P_4S_{10} is unable to couple the bisthiolactone groups.

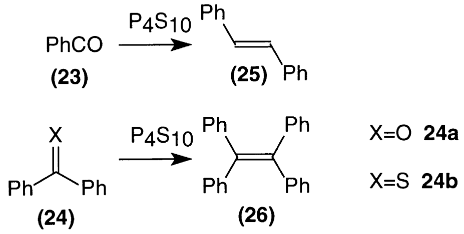


Fig. 6. Reaction of benzaldehyde (23) or thiobenzophenone (24b) with P_4S_{10}, respectively, yielding *t*-stilbene (25) and tetraphenyl ethylene (26).

Another test we considered to unravel the chemistry involved here was to perform reactions with *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dithioketone (8). This product could be obtained by reaction of *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dione (7) [14] with Lawessons' reagent or P_4S_{10} in the presence of $NaHCO_3$ in CH_3CN at 30°C. Thermal treatment of (8) in the absence of P_4S_{10} under the conditions that apply for the polymerization of phthalic anhydride derivatives, leaves (8) unreacted. In contrast with this, reaction of *trans*-3,3′-bibenzo(c)thienylidene-1,1′-dione (7) with P_4S_{10} under the same conditions as above, gives rise to PITN. Since P_4S_{10} cannot couple bisthiolactone functional groups, the latter observation suggests a scission process in (8) yielding (6) which then gives PITN. If we were able to trap (6) we would be able to substantiate the latter assumption. Indeed (6) can be trapped in the presence of thiobenzophenone (24b) yielding the dibenzylidenes (15c) as trapping products. As thiobenzophenone (24b) can be formed in situ from benzophenone and P_4S_{10}, we performed an experiment in which we reacted (15a) or (7) in refluxing xylene with an excess of P_4S_{10} and benzophenone. Next to PITN in both cases the trapping product (15c) could be isolated, thus proving not only the scission of the double bond in (15a) and (7), but also the formation of tristhiophthalic anhydride (6). In conclusion, the results indicated that P_4S_{10} is responsible for side reactions and not for the polymerization itself. The polymerization seems to originate from (6), which dimerizes to (8), which itself is unreactive under the used conditions. Rather the tristhiophthalic anhydride (6) is highly reactive and attaches repeatedly to the dimer and the growing chain thus formed. In other words, it is not a classical polycondensation, since in that case dimers, trimers and higher oligomers would also be reactive. Finally, the relations between (6), (8) and (9) (as in Fig. 1) are now elucidated.

The last question that arises concerns about the aforementioned high reactivity of the tristhiophthalic anhydride (6). A possible explanation might be the contribution of the di-radical resonance structure (29). Fig. 7 compares the di-radical contribution of (6) with the ones of tristhiomaleic anhydride (27) and tristhionaphthalic anhydride (30). The last two compounds are known in literature [15]. Let us start by assuming, just hypothetically, that for the tristhiophthalic acid (6) the relative contribution of the two alternative resonance structures (6) and (29) are more or less equal. The presence of aromatic topologies ("arylene" like in (6) and (30); "thienylene" like in (28), (29) and (31)) will induce a shift towards either a higher contribution of the di-radical structure (28) or a lower contribution of the di-radical structure (31), relative to the situation for (6).

Indeed, comparison of the resonance structures (27), (6) and (30) tells us that the aromaticity rises in the direction of the arrow. The structural comparison of the di-radical structures (28), (29) and (31) to one another shows that the relative contribution may weaken in the direction of the arrow as a consequence of the fact that the thiophene-aromaticity, which is responsible for the substantial

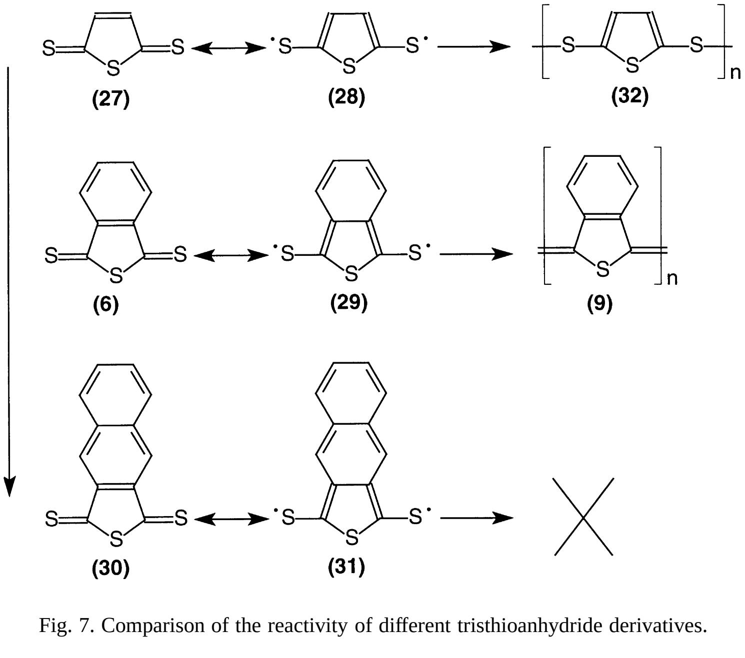


Fig. 7. Comparison of the reactivity of different tristhioanhydride derivatives.

contribution of structure (28) to the geometry of tristhiomaleic anhydride, is “diluted” in this direction. In accordance, Cava [15] mentions that the tristhionaphthalic anhydride (30) can be isolated and behaves as a stable compound in contrast to the tristhiophthalic anhydride (6) and the tristhiomaleic anhydride (27). In addition, the latter compound polymerizes to a polymer in which the thiophene-rings are connected via disulphide-bridges (32)[16].

4. Conclusion

We can conclude that the thionating reagent in the synthesis of PITN (9) plays a role only in the formation of tristhiophthalic anhydride (6), either via successive thionation and isomerization processes when we start from phthalic anhydride (1), or via a breakthrough of a C=C double bond (counter-clockwise cyclic process) as in the case of dithiophthalides (15a or 15b) and *t*-3,3′-dibenzo(c)thienylidene-1,1′-dione (7). The thionating reagent is not involved in the polymerization reaction itself. It seems that the tristhiophthalic anhydride (6) is reactive enough to attach repeatedly to the growing chain, although in a reactive pathway unlike that of a classical polycondensation.

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