

Synthesis of poly(isothianaphthene) from 1,1,3,3-tetrachlorothiophthalan and tert-butylmercaptan: mechanism and quantitative analysis by solid state n.m.r.

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A new synthetic route to the low bandgap polymer poly(isothianaphthene) (PITN) is presented. This new route comprises the reaction of 1,1,3,3-tetrachlorothiophthalan with tert-butylmercaptan and trifluoroacetic acid as a catalyst. This reaction clarifies the mechanism proposed for the synthesis of PITN from phthalic anhydride and phosphorus pentasulfide. The obtained product was analysed by elemental analysis, FTi.r., FT Raman and solid state n.m.r. spectroscopy. Electrical conductivity after synthesis equals approximately $10^{-2} \text{ S cm}^{-1}$. All experimental data are consistent with those of PITN obtained via other synthetic procedures. An indication of the number average molecular weight of PITN is given by quantitative end group analysing using CP/MAS n.m.r. © 1997 Elsevier Science Ltd.

(Keywords: poly(isothianaphthene); CP/MAS n.m.r.; end group analysis)

INTRODUCTION

The low bandgap polymers form an interesting domain in the field of electrically conducting organic polymers. Extensive interest has been drawn to these polymers because they might display intrinsic conductivity without the use of a dopant^{1–5}. Furthermore, these polymers show a nearly colourless transparency after doping due to a shift of the absorption maximum from the visible to the near infra-red (i.r.)^{2,3}.

Poly(isothianaphthene) (PITN) is such a polymer with a narrow bandgap of 1 eV. Several synthetic pathways to PITN are described in the literature. PITN can be synthesized by electrochemical polymerization of isothianaphthene, resulting in a deposited film on an electrode surface^{1,6}, or by oxidation of 1,3-dihydrobenzo(c)thiophene with FeCl_3 ⁷ or *N*-chlorosuccinimide⁴, or by reaction of phthalide or phthalic anhydride with phosphorus pentasulfide or Lawesson's Reagent⁸. Recently, another pathway was described by Chen and Lee⁹ in which SO_2Cl_2 was used for the dehydrogenation of the precursor poly(1,3-dihydroisothianaphthene).

Mechanistic studies¹⁰ upon the formation of PITN from phthalic anhydride and a thionating reagent (phosphorus pentasulfide or Lawesson's Reagent) have pointed out that trithiophthalic anhydride (**6**) might be the essential intermediate in the synthesis of PITN by this method.

EXPERIMENTAL

Instrumentation

Melting points (m.p.) were recorded with an Electrothermal IA9000 Digital Melting Point apparatus. Fourier transform (FT)i.r. and FT Raman data were recorded on an IFS 66 FTi.r. spectrometer connected to a Bruker computer (ASPECT 1000) equipped with a Raman FRA 106 module. Mass spectroscopy (m.s.) was performed with a Finigan 1020 or a TSQ70 apparatus. Conductivity measurements after synthesis were performed by the four-point method with a 1.5 mm distance between the inner electrodes.

Liquid nuclear magnetic resonance (n.m.r.)

The ^1H and ^{13}C liquid n.m.r. 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 $7.5 \mu\text{s}$, 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 $10 \mu\text{s}$, an acquisition time of 0.701 s and 1000 repetitions. An attached proton test (APT) spectrum was acquired to discriminate between methyl and methine (positive signals), and non-protonated and methylene (negative signals) carbon resonances¹¹.

Solid state ^{13}C n.m.r.

All solid state ^{13}C n.m.r. spectra were recorded at room temperature on a Varian XL-200 instrument at

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50.3 MHz. ^{13}C (cross polarization (CP)) spectra were recorded using CP 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, and an acquisition time of 0.0307 s, a 90° pulse width of 8.4 μs and a spectral width of 23980 Hz were used. To minimize the effect of long term drift, the n.m.r. relaxation experiments were interleaved block averaged with 32 acquisitions per block. Magic angle spinning (MAS) 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 tetramethylsilane (TMS)] and the $\pi/2$ pulse width (8.4 μs). Adamantane was used for shimming.

Synthetic procedures

All experiments were performed in a nitrogen atmosphere. Commercially available products were used without further purification. The polymerization reactions were performed in methylene chloride, benzene and 1,1,2,2-tetrachloroethane.

Polymerization of 1,1,3,3-tetrachlorothiophthalan

To a solution of 1 g (3.7 mmol) of 1,1,3,3-tetrachlorothiophthalan¹² (**9**) in 12.24 ml of CH_2Cl_2 (0.3 M) was added 4.36 ml (39 mmol) of 2-methyl-2-propanethiol and 0.15 ml (1.95 mmol) of trifluoroacetic acid. The mixture was refluxed ($39\text{--}40^\circ\text{C}$) for 20 h and became gradually darker in colour. After 20 h the mixture was cooled to room temperature. After evaporation under reduced pressure the black solid material was refluxed in methanol (30 ml) during 1 h and filtered off. The solid material was then extracted in a Soxhlet apparatus with tetrahydrofuran and chloroform until the solution became colourless. The yield after drying *in vacuo* was 52% black material.

Analytical data: $\text{C}_{8.0}\text{H}_{4.03}\text{S}_{1.06}\text{Cl}_{0.13}$ (C: 68.39%; H: 2.87%; S: 24.23%; Cl: 3.36%; rest 1.15%) (calc.: $\text{C}_{8.0}\text{H}_{4.0}\text{S}_{1.0}$ (C: 72.7%; H: 3.1%; S: 24.3%)); FT i.r. (KBr, ν , cm^{-1}): 1586, 1452, 1263, 1126, 1040, 978, 872, 845, 734; FT Raman (KBr, ν , cm^{-1}): 1464, 1447, 1304, 1230, 1194, 1167, 1058, 990, 885, 447; solid state n.m.r. (ppm, relative to TMS): 209.86 (C=S end group), 189.03 (C=O end group), 139 (C_{3a}), 126 (C_3 , C_4 and C_5), 31.41 (CH_3); conductivity: $\sigma = 5 \times 10^{-3} \text{ S cm}^{-1}$.

The polymerization in benzene (0.3 M) (reflex temperature 80°C) was performed analogously and yielded 23% PITN.

Analytical data: $\text{C}_{8.0}\text{H}_{4.1}\text{S}_{1.02}\text{Cl}_{0.14}$ (C: 67.96%; H: 2.91%; S: 23.08%; Cl: 3.35%; rest 2.7%); FT i.r. (KBr, ν , cm^{-1}): 1584, 1451, 1376, 1261, 1136, 967, 730; FT Raman (KBr, ν , cm^{-1}): 1458, 1443, 1304, 1229, 1195, 1167, 1057, 989, 884, 446; solid state n.m.r. (ppm, relative to TMS): 139 (C_{3a}), 126 (C_3 , C_4 and C_5); conductivity: $\sigma = 8 \times 10^{-3} \text{ S cm}^{-1}$.

The polymerization in 1,1,2,2-tetrachloroethane (0.3 M) (reflux temperature 147°C) was performed in the same way and yielded 27% PITN.

Analytical data: $\text{C}_{8.0}\text{H}_{4.3}\text{S}_{0.99}\text{Cl}_{0.04}$ (C: 70.72%; H: 3.19%; S: 23.36%; Cl: 1.13%; rest 1.60%); FT i.r. (KBr, ν , cm^{-1}): 1586, 1452, 1376, 1260, 1136, 968, 730; FT Raman (KBr, ν , cm^{-1}): 1458, 1442, 1305, 1230, 1195, 1167, 1058, 990, 884, 446; solid state n.m.r. (ppm, relative

to TMS): 139 (C_{3a}), 126 (C_3 , C_4 and C_5); conductivity: $\sigma = 10^{-2} \text{ S cm}^{-1}$.

Synthesis of dibenzylidenedithiophthalide (**11**) and 1,1-diphenyl methyl tert-butyl thioether (**13**)

1,1,3,3-Tetrachlorothiophthalan¹² (**9**) (0.29 g, 1.06 mmol), 0.63 g (3.18 mmol) of thiobenzophenone (**10**), 1.27 ml (11.25 mmol) of tert-butyl mercaptan and 0.043 ml (0.56 mmol) of trifluoroacetic acid were refluxed for 20 h in methylene chloride (3.55 ml). Purification of the reaction mixture by column chromatography (silica; gel, hexane/chloroform (7/3)) yielded 25% dibenzylidenedithiophthalide (**11**) (yield *versus* 1,1,3,3-tetrachlorothiophthalan) and 19% 1,1'-diphenyl methyl tert-butyl thioether (**13**) (yield *versus* thiobenzophenone) as a side product.

Dibenzylidenedithiophthalide. M.p.: $152.7\text{--}153.9^\circ\text{C}$; FT i.r. (KBr, ν , cm^{-1}): 1588 ($\nu_{\text{C}=\text{C}_{\text{arom}}}$), 1458 ($\nu_{\text{C}=\text{S}}$), 1263 ($\nu_{\text{C}=\text{S}}$), 1217 ($\nu_{\text{C}=\text{S}}$), 1047 ($\nu_{\text{C}=\text{S}}$), 763 ($\nu_{\text{C}=\text{C}_{\text{arom}}}$), 702 ($\nu_{\text{C}=\text{C}_{\text{arom}}}$); m.s. (m/e): 330 (M^+ , 100%), 254 ($\text{M}^+ - \text{CS}_2$, 18%); ^1H n.m.r. (CDCl_3 , 400 MHz, relative to TMS): 8.09 (*d*, $^3J = 4 \text{ Hz}$, 1H, H_7), 7.44 (*t*, $^3J = 5.33 \text{ Hz}$, 1H, H_5), 7.36 (*m*, 10H, H_{10-12} and $\text{H}_{10'-12'}$), 7.27 (*t*, $^3J = 5.33 \text{ Hz}$, 1H, H_6), 6.84 (*d*, $^3J = 4 \text{ Hz}$, 1H, H_4); ^{13}C n.m.r. (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

1,1-Diphenyl methyl tert. butyl thioether. M.p.: $82.8\text{--}83.4^\circ\text{C}$; FT i.r. (KBr, ν , cm^{-1}): 3023 ($\nu_{\text{CH}_{\text{arom}}}$), 2957 (ν_{asCH_3}), 1598 ($\nu_{\text{C}=\text{C}_{\text{arom}}}$), 1494 ($\nu_{\text{C}=\text{C}_{\text{arom}}}$), 1467 (δ_{asCH_3}), 702 ($\nu_{\text{C}=\text{C}_{\text{arom}}}$); m.s. (EI, m/e): 257 (MH^+ , 10%), 168 ($\text{MH}^+ - \text{SC}(\text{CH}_3)_3$, 100%); ^1H n.m.r. (CDCl_3 , 400 MHz, relative to TMS): 7.39 (*d*, $^3J = 7.76 \text{ Hz}$, 4H, H_3 and H_3), 7.32 (*t*, $^3J = 7.46 \text{ Hz}$, 4H, H_4 and H_4), 7.25 (*t*, $^3J = 7.22 \text{ Hz}$, 2H, H_5 and H_5), 5.22 (*s*, 1H, H_1), 1.32 (*s*, 9H, H_7); ^{13}C n.m.r. (CDCl_3 , 400 MHz, relative to TMS): 140.60 (C_2 and C_2'), 128.76 (C_3 and C_3' or C_4 and C_4'), 128.48 (C_3 and C_3' or C_4 and C_4'), 127.40 (C_5 and C_5'), 62.00 (C_1), 48.36 (C_6), 30.02 (C_7).

RESULTS AND DISCUSSION

Mechanistic studies on the formation of PITN from the reaction of phthalic anhydride (**1**) with a thionating reagent (e.g. P_4S_{10}) indicate that this reaction occurs by a sequence of thionation, isomerization and polymerization processes¹⁰.

The first step in the reaction of **1** with P_4S_{10} is the conversion of the C=O into C=S (**2**). P_4S_{10} is a well known reagent for the synthesis of thiocarbonyls from carbonyls¹³⁻¹⁵. The product formed in this way readily isomerizes to the more stable thiophthalic anhydride (**3**). Further thionation yields the thiothiophthalic anhydride (**5**), which may also come from the isomerization of the bithiophthalic anhydride (**4**)¹⁶. The former can be converted in its turn into trithiophthalic anhydride (**6**), which finally yields PITN (**8**) (Figure 1).

Since the mechanism implies that trithiophthalic anhydride (**6**) is an intermediate in the synthesis of PITN the following question arises: does **6** directly give rise to PITN or is the thionating reagent involved in the polymerization reaction itself?

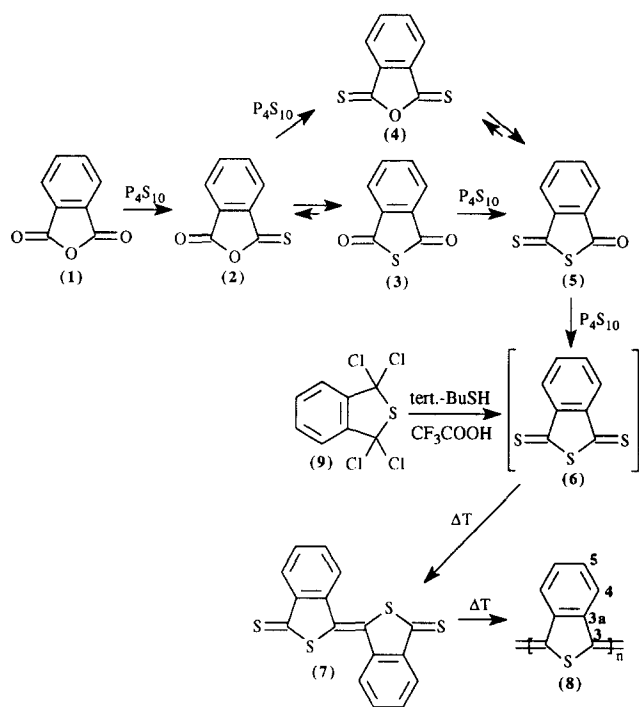


Figure 1 Proposed mechanism for the polymerization of phthalic anhydride (1) with P_4S_{10} and the synthesis of PITN from 1,1,3,3-tetrachlorothiophthalan (9) via the *in situ* formation of the trithiophthalic anhydride (6)

To answer this question one should be able to study **6** in a more direct way. Cava and Lakshmikantham¹⁶ tried to isolate **6** by thionation of the thiothionophthalic anhydride (5) with Lawesson's Reagent. Instead, a black insoluble product, which was not further characterized, and 30% *trans*-3,3'-bibenzo(c)thienylidene-1,1'-dithioketone (7) were obtained. Since Cava and Lakshmikantham illustrate also in this work that geminal dihalides can be converted into thioketones by use of 2-methyl-2-propanethiol in the presence of a catalyst such as trifluoroacetic acid, a procedure which is known in the literature¹⁷, we tried to obtain **6** from 1,1,3,3-tetrachlorothiophthalan (9)¹², using this synthetic procedure (Figure 1).

Although Cava and Lakshmikantham did not characterize the black product they obtained nor did they specify the experimental conditions used, it is very acceptable from our experience using phthalic anhydride (1) and P_4S_{10} that this black precipitate might be PITN. Since we know that only substantial amounts of PITN can be obtained if the monomer concentration is at least 0.3 M^{10,18}, we performed our experiment using 0.3 M of 1,1,3,3-tetrachlorothiophthalan (9) and a reaction time of 20 h. In this case, 52% of a black precipitate was isolated. This black product was characterized to be PITN by elemental analysis, spectroscopy and conductivity. The i.r., Raman and solid state n.m.r. spectra obtained via this method are identical with those of the dedoped samples obtained via other synthetic procedures⁸. We performed this reaction in methylene chloride, benzene and 1,1,2,2-tetrachloroethane. When methylene chloride ($T = 39\text{--}40^\circ\text{C}$) is used as the solvent a somewhat higher yield (52%) is obtained, compared to the process in benzene (yield = 23% $T = 80^\circ\text{C}$) or 1,1,2,2-tetrachloroethane ($T = 147^\circ\text{C}$, yield = 27%). The conductivities of the materials after synthesis ($\sim 10^{-2} \text{ S cm}^{-1}$) are similar to those of PITN synthesized

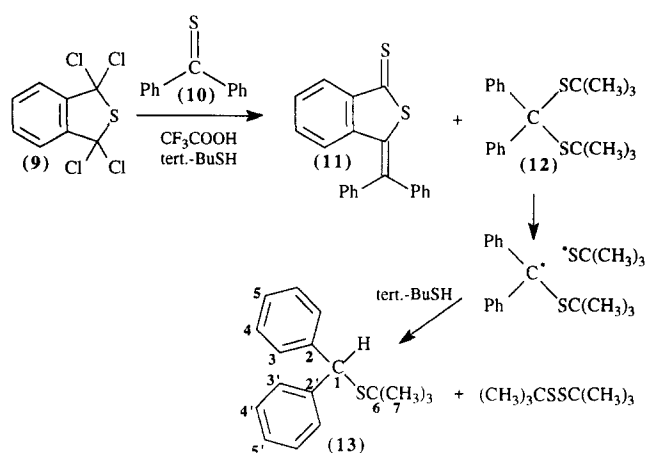


Figure 2 Synthesis of dibenzylidenedithiophthalide (11) and 1,1-diphenyl methyl tert-butyl thioether (13)

via other pathways. These results point to a polymerization mechanism in which trithiophthalic anhydride (6) polymerizes by condensation with expulsion of sulfur (S_2) without the necessity of a thionating reagent*. This type of condensation reaction may also occur between the intermediate (6) and other thiocarbonyl functional groups. In this way the presence of **6** may be proven by trapping with, for instance, thiobenzophenone. Performing the polymerization reaction in methylene chloride in the presence of 3 equiv of thiobenzophenone (10)¹³ indeed leads to the formation of dibenzylidenedithiophthalide (11) in a yield of 25%, and no formation of PITN is observed. Besides **11**, a side product was also obtained in a yield of 19% and identified as 1,1-diphenyl methyl tert-butyl thioether (13) after isolation by column chromatography (Figure 2). The formation of **13** can be explained as follows: attack of the tert-butyl mercaptan on the thiobenzophenone results in the formation of diphenyl methyl bis(tert-butyl thioether) (12). Since the C–S bond is relatively weak, radical scavenging can take place. In this way a stable radical is formed at the 1-position of **12**. It is known that thiols can act as radical scavengers with formation of the corresponding disulfide¹⁹. Mass spectroscopy indicates the formation of tert-butyl disulfide ($M^+ = 178$).

Since the formation of the disulfide implies that the radical scavenging is accompanied by a hydrogen atom transfer from the excess of thiol (tert-butyl mercaptan) present in the reaction mixture, the formation of 1,1-diphenyl methyl tert-butyl thioether (13) is explained.

The structure of the side product was established by 1H and ^{13}C liquid n.m.r. The chemical shift resonance at 5.22 ppm indeed corresponds with the proton on C_1 . Moreover, integration of the proton signals indicates that the doublet at 7.39 ppm and the triplet at 7.32 ppm correspond with each four protons, the triplet at 7.25 ppm with two protons while the singlet signals at 5.22 ppm and 1.32 ppm integrate for one and nine protons, respectively.

Further verification is obtained from the ^{13}C liquid spectra. The APT spectrum allows discrimination between

* The possibility that a dichlorothioloactone intermediate is involved as the actual monomer in the polymerization reaction is rejected by the authors because the tetrachlorothiophthalan (9) does not react with thiobenzophenone in the absence of the tert-butyl thiol and the acid catalyst

protonated (positive signals) and non-protonated (negative signals) carbon resonances. In this way we can assign the signals at 140.60 and 48.36 ppm to the quaternary aromatic atom C_2' and to the aliphatic carbon C_6 , respectively. Based on their intensity we can assign the aromatic protonated signals at 128.76 and 128.48 ppm to C_3/C_3' and C_4/C_4' . The three methyl carbon atoms correspond to the signal at 30.02 ppm. The remaining aromatic signal at 127.40 ppm belongs to C_5/C_5' , and C_1 (62.00 ppm) is the remaining protonated carbon. The C–H coupled spectrum confirms these assignments and shows that C_1 indeed carries only one proton.

Solid state n.m.r.

A complete analysis of the structure of PITN was accomplished earlier by our group, with the use of solid state ^{13}C n.m.r.⁵ The chemical shift assignments are completely in agreement with the results published earlier, based on a study on model compounds, and by the use of a multipurpose pulse sequence²⁰.

In the region between 125 and 140 ppm, distinction was made between four overlapping resonances, arising from two protonated (C_4 and C_5) and two non-protonated carbons (C_3 and C_{3a}), respectively. The signal at 139.0 ± 0.5 ppm is assigned to the non-protonated carbon, C_{3a} . The broad peak around 126.0 ppm is a superposition of three signals coming from the second quaternary carbon, C_3 at 126.0 ± 0.5 ppm and the two protonated carbons, C_4 and C_5 at 125.0 and 128.5 ± 1 ppm, respectively.

The spinning rate was chosen as 7 kHz. This is required to spin out the chemical shift anisotropy conveniently and move the spinning side bands out of the desired region of isotropic carbon resonances of PITN and to avoid peak overlap (Figure 3a). In the spectrum of the PITN synthesized at 40°C in methylene chloride, three minor peaks were noticed at 209.86, 189.03 and 31.41 ppm. (Figure 3a). The two former resonances can be assigned to the possible end groups of this PITN compound, namely a thiocarbonyl (C=S), which is the expected end group in this condensation reaction, and a carbonyl (C=O) end group, which might be the result of the hydrolysis of a C=S end group, respectively. The latter signal at 31.41 ppm might correspond with the methyl resonance of a tert-butyl

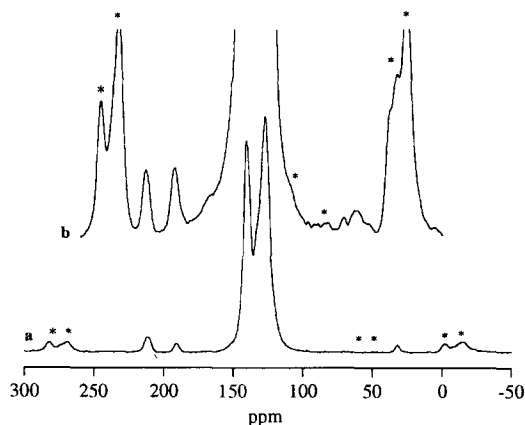


Figure 3 CP/MAS ^{13}C n.m.r. spectrum of PITN synthesized at 40°C (the signals marked with an asterisk are spinning side bands): (a) spinning rate at 7 kHz, (b) spinning rate at 5 kHz

thioether end group. An explanation for this hypothesis might be found in the fact that tert-butyl mercaptan can react with thiocarbonyls as is described above. Since the polymerization reaction also occurs in an excess of tert-butyl mercaptan, a similar reaction can happen here. In order to investigate whether the polymer chain ends in two tert-butyl thioether groups [$> \text{C}(\text{StBu})_2$] or in one tert-butyl thioether group and a hydrogen atom ($> \text{HCStBu}$) we compared the solid state spectrum of PITN synthesized in methylene chloride with the ^{13}C liquid n.m.r. spectrum of 1,1-diphenyl methyl tert-butyl thioether (13).

At a spinning rate of 7000 Hz only the CH_3 signal at 31.41 ppm can be observed because the possible signals at 62.00 and 48.36 ppm are obscured by the spinning side bands of the C=S and C=O end groups. Therefore we repeated the experiment at a lower spinning rate of 5000 Hz (Figure 3b; vertical scale is enlarged). Since the signal at 62.00 ppm indeed can be seen now, we may conclude that a C=S end group can be transformed into a HCStBu end group.

The detection of these three end groups allows the determination of the number average molecular weight.

End group analysis

A determination of the degree of polymerization is possible by high resolution ^{13}C CP/MAS solid state n.m.r. Since a quantitative determination of intensities is usually not possible at one contact time²¹ a series of spectra of PITN were obtained from normal CP/MAS experiments with contact times varied between 1 and 9 ms. The transfer of magnetization from protons to carbons is characterized by the cross polarization time (T_{CH}) of the observed carbon atom and the spin lattice relaxation time ($T_{1\rho\text{H}}$) of the protons in the rotating frame. Generally T_{CH} is much shorter than $T_{1\rho\text{H}}$. The evolution of the integrated intensity (M) with the contact time T_{CT} is dominated by T_{CH} at short T_{CT} and by $T_{1\rho\text{H}}$ at long T_{CT} :

$$M = M_0[1 - \exp(-T_{\text{CT}}/T_{\text{CH}})] \exp(-T_{\text{CT}}/T_{1\rho\text{H}}) \quad (1)$$

For a quantitative analysis, the tail of the variable contact time curve ($T_{\text{CT}} > 5T_{\text{CH}}$) was fitted to a single decaying exponential. By extrapolating this monoexponential function to $T_{\text{CT}} = 0$ (monologarithmic scale) the quantitative M_0 value, proportional to the number of carbons, was obtained.

Figure 4 shows the linear least square fitting of the integrated end groups ($M_{0\text{End}}$) and aromatic ($M_{0\text{Arom}}$) intensities for $T_{\text{CT}} \geq 3.5$ ms and extrapolated to $T_{\text{CT}} = 0$. Notice that the total end group intensity is a combination of the intensity of the C=S end group, the C=O end group and 1/3 of the intensity of the methyl signal.

The ratio between the extrapolated intensities of the end groups ($M_{0\text{End}}$) and the other aromatic carbons ($M_{0\text{Arom}}$) can now be determined. The experimental value is 1/39. This will be a measure for the degree of polymerization, when comparing this ratio with our model (14) (Figure 4). For $n = 8$ in this model we obtain a theoretical ratio of 2/78 or 1/39 ($M_{0\text{End}}/M_{0\text{Arom}}$), completely in agreement with the measured value. Since for $n = 8$ the degree of polymerization is 10, the number average molecular weight for PITN synthesized at 40°C can be calculated:

$$M_n = (\text{DP} \times M_{\text{W}(\text{r.u.})}) + X \quad (2)$$

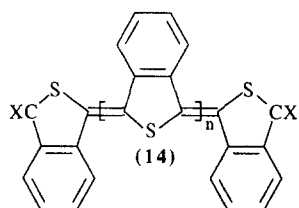
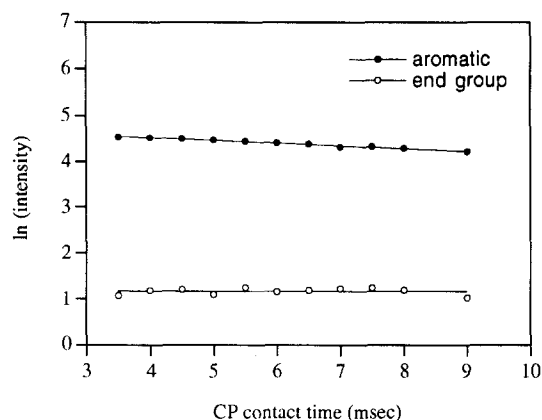


Figure 4 Linear least square fitting of (○) the integrated end groups and (●) aromatic intensities for $T_{CH} \geq 3.5$ ms and extrapolated to $T_{CH} = 0$ ms and the model (14) used for calculation of the number average molecular weight of PITN

where DP is the degree of polymerization, $M_{W(r.u.)}$ is the molecular weight of the repeating unit, and X is a constant representing the molecular weight of the end groups. Calculation of the number average molecular weight gives $M_n = (10 \times 132) + X$. Taking the separate contributions of the three end groups into account, we find a value of 1380 for M_n .

Since no end groups can be seen in the CP/MAS n.m.r. experiment at higher polymerization temperatures we may conclude that the molecular weight is even higher in these cases.

Another possible end group might be $>CCl_2$ due to insufficient thioketone formation. This can be derived from the result of the elemental analysis where at a 40°C reaction temperature 3.36% of Cl can be found. The corresponding carbon is not visible in the CP/MAS spectrum. Taking this fourth end group into account does not change the value of the DP derived from CP/MAS substantially.

CONCLUSIONS

Reaction of 1,1,3,3-tetrachlorothiophthalan (9) with 2-methyl-2-propanethiol and trifluoroacetic acid as a catalyst leads to the formation of PITN (8). The chemistry used implies the formation of trithiophthalic anhydride (6), although isolation of 6 is not possible due to its high reactivity. On the other hand, the formation of this intermediate (6) was proven by trapping with thiobenzophenone (10). The fact that PITN can be obtained by this route confirms that 6 is the actual monomer in the process by which PITN is formed from phthalic anhydride (1) and phosphorus pentasulfide or

Lawessons' Reagent. Moreover, these experiments show that the thionating reagent is not a necessity in the polymerization reaction itself.

An indication of the degree of polymerization and hence the number average molecular weight of PITN is given, based on quantitative end group analysis by CP/MAS n.m.r. For PITN synthesized at 40°C DP = 10 and $M_n = 1380$. Since at higher temperatures no end groups can be seen, we may conclude that in this case the molecular weight is even higher.

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