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An Efficient Acid-Induced Conversion of Dithiocarbamate Precursor Polymers into Conjugated Materials

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ABSTRACT: An acid-induced conversion method for dithiocarbamate precursor poly(thienylenevinylene) (PTV) and poly(phenylenevinylene) (PPV) derivatives is presented, which has the advantage that it can be executed at moderate temperatures. The lower conversion temperature avoids possible thermal degradation of the polymer chromophore structure, and therefore conjugated polymers with a higher effective conjugation length can be obtained. This process was studied using UV−vis and FTIR spectroscopy. The obtained results indicate that trifluoroacetic acid yields a more defect-free structure as compared to benzenesulfonic acid which induces degradation after prolonged reaction times. A tentative mechanism is proposed in which the formation of an intermediate carbenium ion is part of the rate-limiting step. It also implicates a competition between elimination and substitution reactions depending on specific reaction conditions.

Introduction

Nowadays, conjugated polymers find application in various optical and electronic devices such as light-emitting diodes (LED),[1] field effect transistors (FET),[2] photovoltaic cells,[3] and sensors.[4] Because of their interesting optoelectronic and electrical properties, a considerable amount of research has been performed on poly(arylenevinylene) derivatives.[5,6] These polymers have been typically synthesized via precursor routes in which a *p*-quinodimethane system acts as the actual monomer. This monomer will polymerize into the precursor polymer via a self-initiating radical chain mechanism.[7−11] In a second step, the obtained precursor polymers can be transformed into the conjugated form in situ or ex situ. The major advantage of such precursor routes is the ease by which high molecular weight materials are obtained. Over the past 50 years several different precursor routes have been developed such as the sulfonium route,[12−15] the Gilch route,[16] the xanthate route,[17−19] and the, in our research group developed, sulfinyl[20,21] and dithiocarbamate route.[22−27] All these routes differ by the identity of the polarizer (P) and leaving (L) functional group in the premonomer structure, the polymerization conditions, whether conversion to the conjugated structure occurs in situ or ex situ, and to what extent the conversion is thermal induced or reagent induced (Scheme 1). Furthermore, the characteristics of the obtained polymers can vary along the different precursor routes.

For instance, the xanthate precursor route yields typically broad polydispersities (PD) and shows structural defects in the final conjugated system. On the other hand, the sulfinyl and the, in this study discussed, dithiocarbamate precursor route lead to the formation of precursor polymers with low structural defect levels.[28,29] Furthermore, in the case of the sulfinyl route the conversion from the precursor polymer toward the conjugated polymer already starts at 65 °C.[30] However, the implementation of the non-symmetrical P and L groups into the premonomer is quite challenging.[31] For the dithiocarbamate precursor route the opposite situation occurs; here the monomer synthesis is rather simple and results into highly stable monomers. However higher conversion temperatures (180 °C) are necessary to reach fully conjugated polymers, and therefore degradation of the polymer chromophore structure is a realistic threat.[32] In a serendipitous way, we discovered that the dithiocarbamate functional group in the precursor is eliminated, inducing the formation of the conjugated system, in the presence of acid. Typically, a temperature of 70 °C can be used, but also at ambient temperature conversion occurs. Such low conversion temperatures may avoid the degradation of the polymeric chromophore and therefore guarantee the formation of conjugated structures with optimal electronic properties.

Specifically in this study, poly(3-octyl-2,5-thienylenevinylene) (O-PTV) and poly[(2-methoxy-5-(3′,7′-dimethyloctyloxy))-1,4-phenylenevinylene] (MDMO-PPV) have been synthesized using the dithiocarbamate precursor route.[28] Furthermore, to combine the advantages of both the sulfinyl and dithiocarbamate routes, e.g., low conversion temperatures and easy monomer synthesis, a new conversion process for dithiocarbamate precursor polymers has been developed. After synthesis and characterization of the precursor polymer, the thermal conversion as well as the acid induced conversion process toward O-PTV and MDMO-PPV is studied via FT-IR and UV−vis spectroscopy. Finally, a tentative reaction mechanism is proposed, and preliminary results are presented concerning the specific characteristics of the acid-induced elimination reaction of dithiocarbamate groups.

Experimental Section

General. Unless otherwise stated, all reagents and chemicals were obtained from commercial sources (Acros and Aldrich) and used without further purification. A xanthate precursor toward plane PTV was synthesized according to a literature preocedure.[19] Tetrahydrofuran (THF) was dried by distillation

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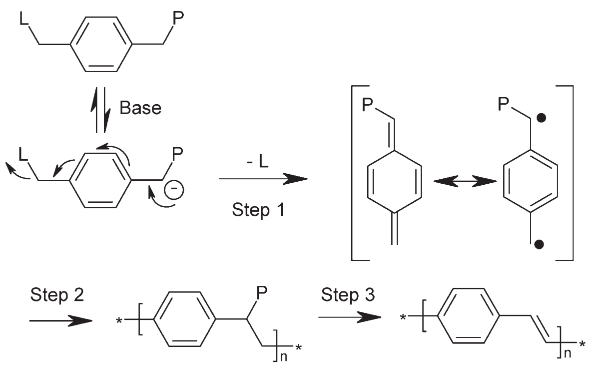
Scheme 1. Precursor Routes toward Poly(*p*-phenylenevinylene) Derivatives



Gilch route:	L=P= Cl or Br
Sulfonium route:	L=P= R_2S-
Sulfinyl route:	L= Cl or Br ; P= RS(O)-
Xanthate route:	L=P= RO-C(S)-S-
Dithiocarbamate route:	L=P= R_2N-C(S)-S-

from sodium/benzophenone. NMR spectra were recorded with a Varian Inova 300 spectrometer at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR using a 5 mm probe. Gas chromatography/mass spectrometry (GC/MS) analyses were carried out with TSQ-70 and Voyager mass spectrometers (Thermoquest); the capillary column was a Chrompack Cpsil5CB or Cpsil8CB. Analytical size exclusion chromatography (SEC) was performed using a Spectra series P100 (Spectra Physics) pump equipped with two mixed-B columns (10 μm, 0.75 cm × 30 cm, Polymer Laboratories) and a refractive index detector (Shodex) at 70 °C. Chlorobenzene was used as the eluent at a flow rate of 1.0 mL/min. Molecular weight distributions are given relative to polystyrene standards. FT-IR spectra were collected with a Perkin-Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1}, summation of 16 scans). UV−vis spectroscopy was performed on a VARIAN CARY 500 UV−vis−NIR spectrophotometer (scan rate: 600 nm/min). Samples for temperature-dependent thin-film FT-IR and UV−vis characterization were prepared by dropcasting the precursor polymer from a $CHCl_3$ solution (10 mg/mL) onto NaCl disks or quartz disks. The disks were heated in a Harrick high-temperature cell (heating rate: 2 °C/min), which was positioned in the beam of either the FT-IR or the UV−vis spectrometer to allow in situ measurements. Spectra were taken continuously under a continuous flow of N_2 during which the samples were in direct contact with the heating element. "Timebase software" supplied by Perkin-Elmer and "Scanning Kinetics software" supplied by Varian were used to investigate regions of interest.

Synthesis. *Monomer Synthesis.* The synthetic routes toward the MDMO-PPV bisdithiocarbamate premonomer **1** and the O-PTV bisdithiocarbamate premonomer **4** have been reported earlier.[22,33,34]

Polymer Synthesis

MDMO-PPV

Synthesis of MDMO Precursor PPV **2**. Premonomer **1** (500 mg, 0.851 mmol) was dissolved in dry THF (4.2 mL) giving a concentration of 0.2 M. The mixture was stirred at 35 °C under a continuous flow of nitrogen. 1.5 equiv of a LHMDS solution (1 M in THF) was added in one go to the stirred monomer solution. The reaction proceeded for 1.5 h at 35 °C under a nitrogen atmosphere, and the mixture was subsequently quenched in ice water (100 mL). The excess of base was neutralized with HCl (1 M). The aqueous phase was extracted with $CHCl_3$ (3 × 40 mL). After combination of the organic phases and evaporation of the solvent, the obtained crude polymer was again dissolved in $CHCl_3$ (2 mL) and precipitated in stirred cold methanol (100 mL). The mixture was filtered, and the polymer was collected and dried in vacuo. The residual fractions contained only premonomer and oligomers (yield 64%, 239 mg). ^{1}H NMR ($CDCl_3$): 6.97−6.45 (br m, 2H), 5.87−5.50 (br s, 1H), 4.23−3.05 (br m, 11H), 1.95−1.02 (br m, 16H), 1.02−0.74 (m, 9H). ^{13}C NMR ($CDCl_3$): 195.76, 150.85, 127.68, 114.11, 113.09, 67.10, 56.39, 51.98, 49.08, 46.38, 39.27, 37.54, 36.60, 34.45, 29.91, 27.92, 24.67, 22.69, 22.58, 19.66, 12.47, 11.55. IR (NaCl, cm^{-1}): 2953, 2929, 1504, 1484, 1462, 1413, 1267, 1210, 1140, 1041. SEC: $M_w = 220 \times 10^3$; PD = 2.3.

Thermal Conversion of Precursor Polymer to Conjugated MDMO-PPV ***3a***. From a solution of **2** (50 mg, 0.114 mmol) in *o*-dichlorobenzene (25 mL) oxygen was removed by purging for 1 h with nitrogen. Subsequently, the solution was heated to 180 °C and stirred for 3 h. After cooling to room temperature, the *o*-dichlorobenzene was evaporated, and the crude polymer mixture was dissolved in chloroform (2 mL). The solution was precipitated dropwise in cold methanol (50 mL). The polymer was filtered off, washed with cold methanol, and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3a** was obtained as a red polymer. The elimination procedure was performed a second time to ensure complete elimination (yield: 97%, 32 mg). ^{1}H NMR ($C_2D_2Cl_4$): 7.5 (br, 2H), 7.2 (br, 2H), 4.6−3.2 (br m, 5H), 2.1−0.6 (br m; 19H). ^{13}C NMR ($CDCl_3$): 151.4, 127.0, 123.3, 110.5, 108.8, 67.9, 56.4, 39.2, 37.4, 36.6, 30.2, 27.9, 24.6, 22.6, 19.8. IR (KBr, cm^{-1}): 2957, 2925, 2860, 1510, 1469, 1395, 1217, 1028, 872. UV−vis: λ_{max} (thin film) = 530 nm. SEC: $M_w = 351 \times 10^3$; PD = 3.0.

Benzenesulfonic Acid-Induced Conversion of Precursor Polymer to Conjugated MDMO-PPV ***3b***. From a solution of **2** (50 mg, 0.114 mmol) in chlorobenzene (25 mL) oxygen was removed by purging for 1 h with nitrogen. Subsequently, the solution was heated to 70 °C, and 1.5 equiv (based on the amount of dithiocarbamate moieties in the precursor polymer) of a benzenesulfonic acid solution (0.342 M in chlorobenzene) was added. After stirring for 30 min, the excess of acid was neutralized with $NaHCO_3$ and the mixture was extracted with $CHCl_3$. The solvent was evaporated, and the crude polymer mixture was redissolved in chloroform (2 mL). The solution was precipitated dropwise in cold methanol (50 mL). The polymer was filtered off, washed with cold methanol, and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3b** was obtained as a red polymer (yield: 97%, 32 mg). UV−vis: λ_{max} (thin film) = 534 nm. SEC: $M_w = 284 \times 10^3$; PD = 4.1.

Trifluoroacetic Acid-Induced Conversion of Precursor Polymer to Conjugated MDMO-PPV ***3b***. From a solution of **2** (200 mg, 0.456 mmol) in chlorobenzene (100 mL) oxygen was removed by purging for 1 h with nitrogen. Subsequently, the solution was heated to 70 °C, and 1.5 equiv (based on the amount of dithiocarbamate moieties in the precursor polymer) of trifluoroacetic was added. After stirring for 8 h, the excess of acid was neutralized with $NaHCO_3$, and the mixture was extracted with $CHCl_3$. The solvent was evaporated, and the crude polymer mixture was redissolved in chloroform (8 mL). The solution was precipitated dropwise in cold methanol (200 mL). The polymer was filtered off, washed with cold methanol, and dried at room temperature under reduced pressure. The conjugated MDMO-PPV **3b** was obtained as a red polymer (yield: 98%, 130 mg). UV−vis: λ_{max} (thin film) = 538 nm. SEC: $M_w = 385 \times 10^3$; PD = 2.8.

O-PTV

Synthesis of the Octyl Precursor PTV **5**. The premonomer **4** (2.8 g, 5.4 mmol) was previously freeze-dried. A solution, with a premonomer concentration of 0.4 M, in dry THF (13.5 mL) was degassed by passing through a continuous nitrogen flow. The solution was cooled to 0 °C. Sodium bis(trimethylsilyl)amide (NaHMDS) (11 mL of a 1 M solution in THF) was added in one go to the stirred monomer solution. The resulting mixture was stirred for 90 min under continuous nitrogen flow at 0 °C. The polymer was precipitated in ice water, and the water layer was neutralized with diluted HCl before extraction with chloroform.

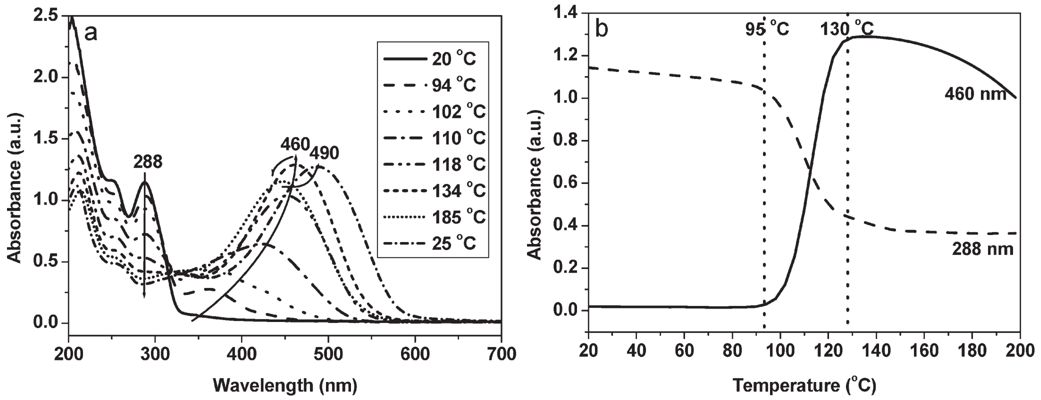
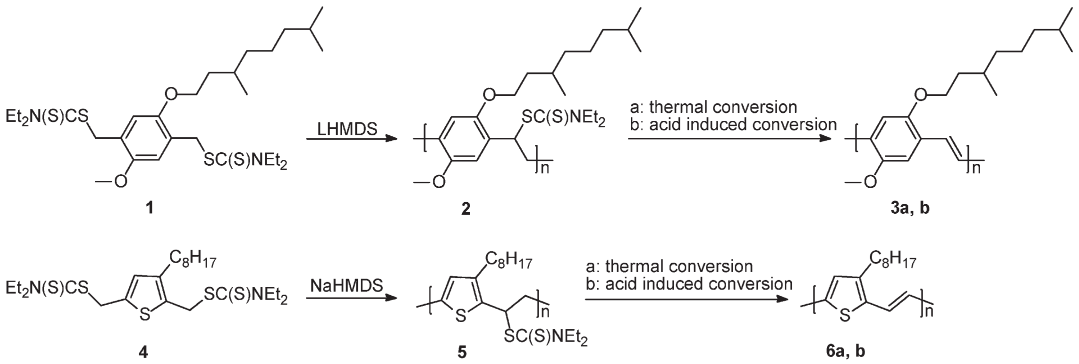


Figure 1. (a) UV−vis spectra of precursor polymer **2** at different temperatures. (b) UV−vis absorbance profiles at 288 and 460 nm at different temperatures for **2**.

Scheme 2. Synthesis of MDMO-PPV and O-PTV via the Dithiocarbamate Precursor Route, Followed by the Thermal or Acid-Induced Elimination



The solvent of the combined organic layers was evaporated under reduced pressure, and a second precipitation was performed in pure cold methanol. The precursor polymer **5** was collected and dried in vacuo (yield 56%, 1.1 g). ^{1}H NMR (CDCl$_3$): 6.57 (br, 1H), 5.46 (br, 1H), 3.96 (br, 2H), 3.66 (br, 4H), 2.27 (br, 2H), 1.21 (br, 18H), 0.85 (br, 3H). ^{13}C NMR (CDCl$_3$): 193.96, 139.5, 138.8, 133.8, 127.6, 52.7, 48.9, 46.6, 31.8, 30.7, 29.5, 29.3, 28.2, 22.6, 14.0, 12.5, 11.5. UV−vis: λ_{max} = 261 nm (in film). IR: 2931, 2846, 1486, 1415, 1268, 1206 cm^{-1}. SEC: $M_w = 86 \times 10^3$; PD = 3.1.

*Thermal Conversion of the Octyl Precursor PTV **5** toward Octyl-PTV **6a**.* The precursor polymer **5** (51 mg, 0.14 mmol) was dissolved in *o*-dichlorobenzene (2.8 mL) and refluxed for 4.5 h. After being cooled, the obtained slurry was precipitated in methanol. The precipitate was filtered off, washed several times with methanol, and dried in vacuo. A purple/black solid has been obtained (yield 92%, 28 mg). ^{1}H NMR (CDCl$_3$): 6.97 (s, 1H), 5.00 (s, 1H), 2.26 (br, 2H), 1.24 (br, 12H), 0.85 (br, 3H). ^{13}C NMR (CDCl$_3$): 140.2, 139.3, 134.4, 128.4, 121.1, 53.3, 37.2, 32.7, 31.6, 30.4, 30.1, 29.0, 23.4, 14.9. UV−vis: λ_{max} = 548 nm (in solution). IR (cm^{-1}): 2931, 2846, 1460, 1250, 1016, 926. SEC: $M_w = 47 \times 10^3$; PD = 3.3.

*Benzenesulfonic Acid-Induced Conversion of the Octyl Precursor PTV **5** toward Octyl-PTV **6b**.* The precursor polymer **5** (30 mg, 0.1 mmol) was dissolved in chlorobenzene (5 mL) and heated until 70 °C before benzenesulfonic acid (0.019 g, 0.12 mmol) was added. The solution was stirred for 10 min at 70 °C. After being cooled, the solution was poured into H$_2$O and extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the obtained slurry was precipitated in MeOH, filtered off, and dried in vacuo. A purple/black solid was obtained (17 mg, yield 93%). UV−vis: λ_{max} = 580 nm. SEC: $M_w = 72 \times 10^3$; PD = 3.7.

*Trifluoroacetic Acid-Induced Conversion of the Octyl Precursor PTV **5** toward Octyl-PTV **6b**.* The precursor polymer **5** (36 mg, 0.1 mmol) was dissolved in chlorobenzene (5 mL) and heated until 70 °C before trifluoroacetic acid (0.011 mL, 0.15 mmol) was added. The solution was stirred for 10 min at 70 °C. After being cooled, the solution was poured into H$_2$O and extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the obtained slurry was precipitated in MeOH, filtered off, and dried in vacuo. A purple/black solid was obtained (21 mg, yield 95%). UV−vis: λ_{max} = 583 nm (shoulder: 628 nm). SEC: $M_w = 57 \times 10^3$; PD = 3.4.

Results and Discussion

Precursor Polymers. The synthetic routes toward the MDMO-PPV bisdithiocarbamate premonomer **1** and the O-PTV bisdithiocarbamate premonomer **4** have been reported earlier.[22,33,34] The polymerizations are performed under a nitrogen atmosphere. To this end, the monomers are dissolved in dry THF (0.2 M for MDMO-PPV premonomer and 0.4 M for the O-PTV premonomer), and the base is added (Scheme 2). In case of the MDMO-PPV premonomer an amount of 1.5 equiv of lithium hexamethyldisilazide (LHMDS) and for the O-PTV monomer 2.0 equiv of sodium hexamethyldizilazide (NaHMDS) have been used. After polymerization both reaction mixtures are poured into ice water, neutralized by hydrochloric acid (1 M) and extracted with CHCl$_3$. The precursor polymers **2** and **5** are isolated by precipitation in cold methanol.

In-Situ Thermal Conversion in Thin Film. To examine the conversion conditions for dithiocarbamate precursor polymers, the thermal elimination was studied in thin films by in-situ UV−vis and FT-IR spectroscopy. Thin films were obtained by dropcoating a solution of the precursor polymers in CHCl$_3$ on quartz or NaCl disks, these films have been placed into a Harrick high-temperature cell under a

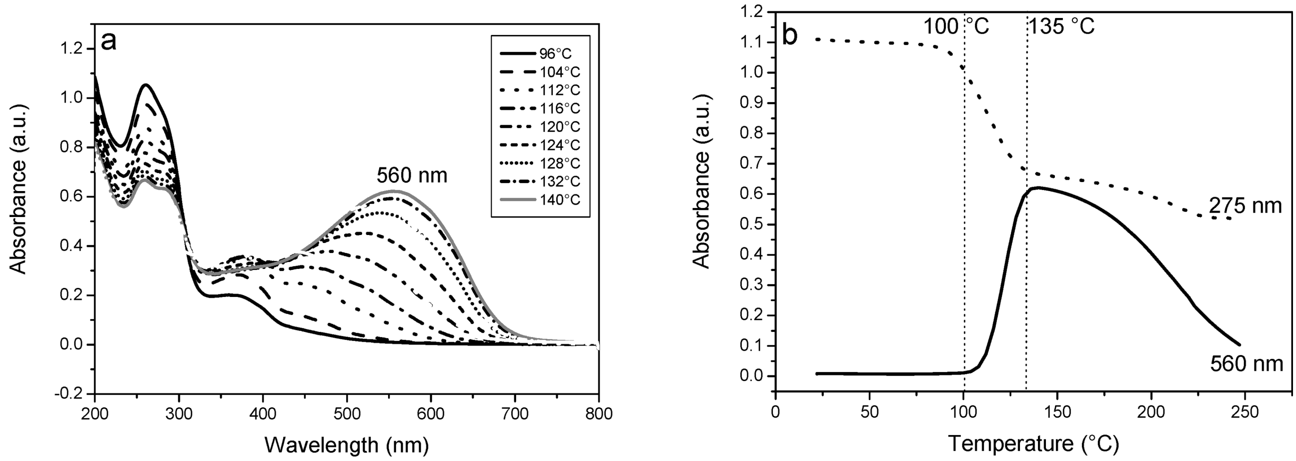


Figure 2. (a) UV−vis spectra of **5** at different temperatures. (b) UV−vis absorbance profiles at 275 and 560 nm at different temperatures for **5**.

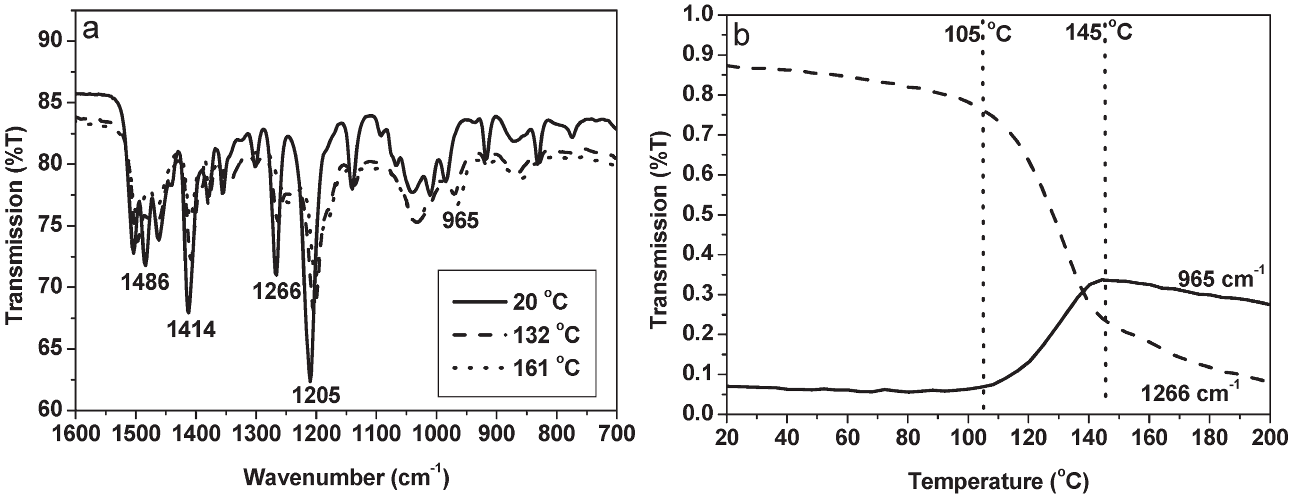


Figure 3. (a) FT-IR spectra of **2** at different temperatures. (b) IR absorption profiles at 965 and 1266 cm^{-1} at different temperatures for **2**.

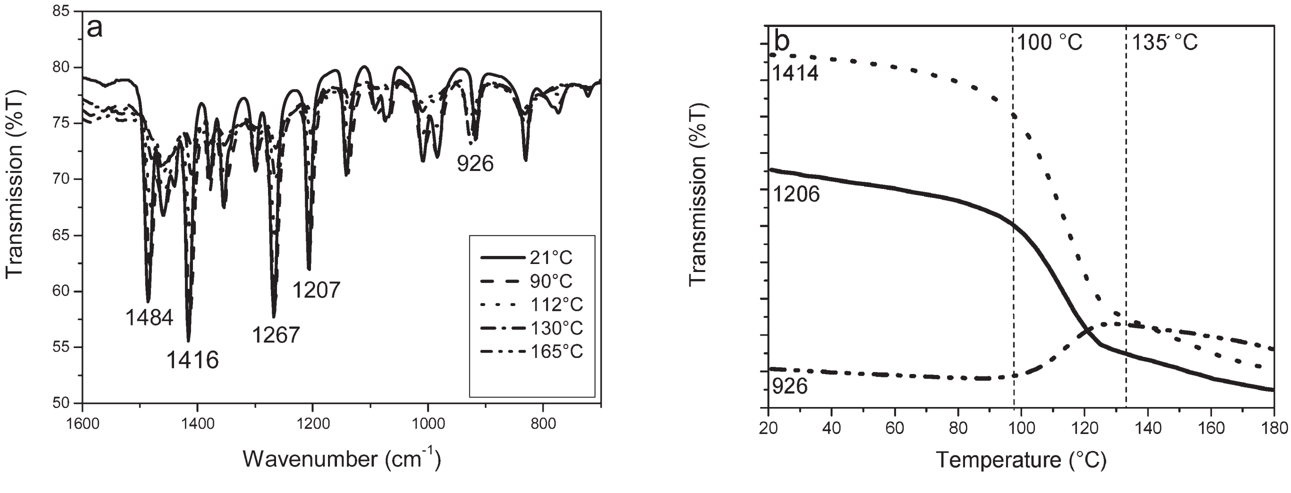


Figure 4. (a) FT-IR spectra of **5** at different temperatures. (b) IR absorption profiles at 926, 1206, and 1414 cm^{-1} at different temperatures for **5**.

continuous nitrogen flow, which was positioned in the beam of either the UV−vis or the FT-IR spectrometer, respectively. The thin precursor polymer films were heated at 2 °C/min from ambient temperature to 200 °C, and spectra were collected at different temperatures.

Upon heating, a new absorption band appears in the UV−vis absorption spectra, associated with the formation of the conjugated system. Concomitantly, the absorption band associated with the precursor polymer decreases. For the MDMO-PPV the precursor band is situated at 288 nm (Figure 1a). The absorption maximum ($\lambda_{\max}$ 460 nm) at 134 °C is lower as compared to this observed ($\lambda_{\max}$ 490 nm) after cooling to room temperature due to the thermochromic effect.[26] The elimination process can be

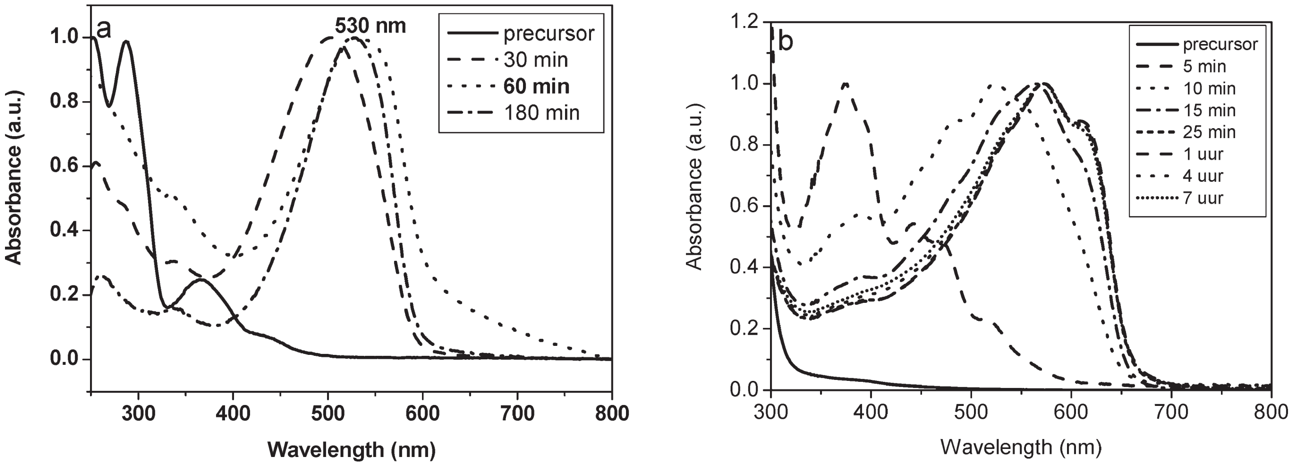


Figure 5. UV−vis absorption spectra for the thermal conversion (180 °C, *o*-DCB) in solution of (a) MDMO precursor PPV and (b) octyl precursor PTV.

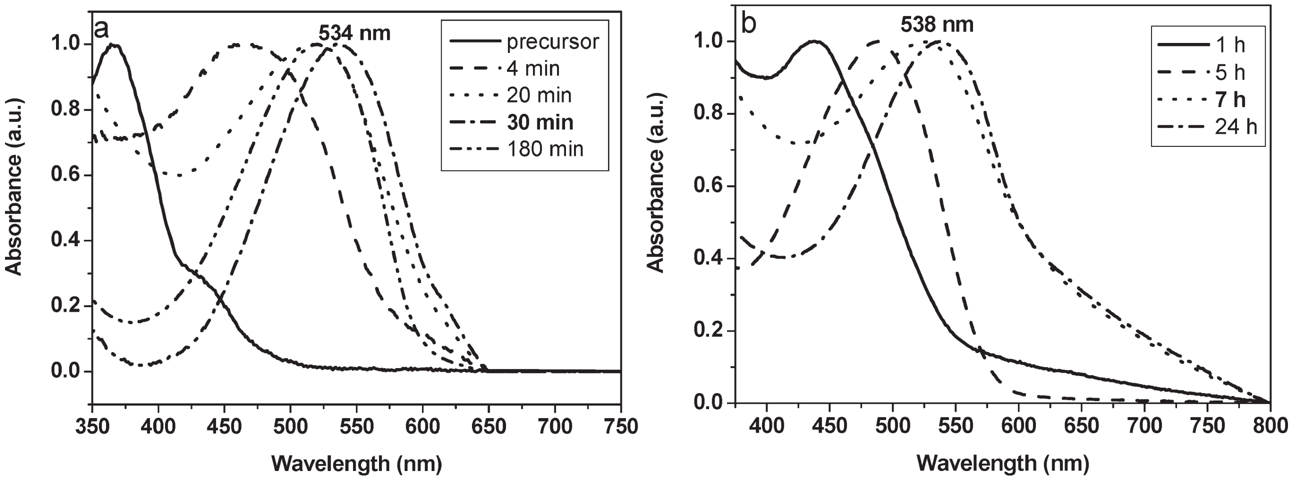


Figure 6. UV−vis absorption spectra for the acid induced conversion (70 °C in CB) of MDMO precursor PPV with (a) benzenesulfonic acid and (b) trifluoroacetic acid.

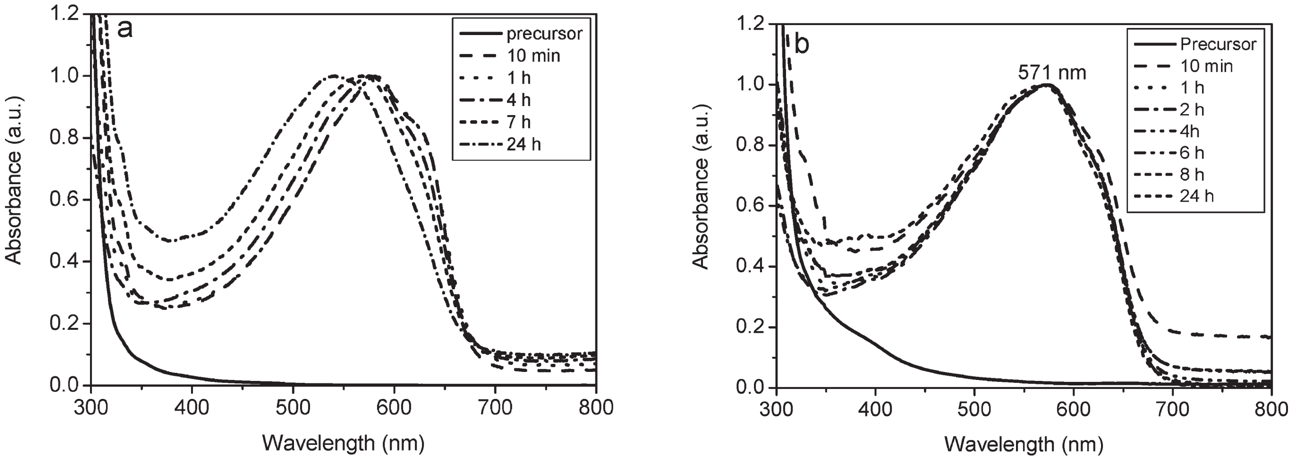


Figure 7. UV−vis absorption spectra for the acid induced conversion (70° in CB) of octyl precursor PTV with (a) benzenesulfonic acid and (b) trifluoroacetic acid.

more thoroughly analyzed by plotting the absorption profiles at 460 and 288 nm as a function of temperature (Figure 1b). In these profiles an increase of the absorbance at 460 nm can be noticed between 95 °C and 130 °C under these heating conditions (2 °C/min). In the same temperature range, a decrease in the absorbance at 288 nm takes place.

For the O-PTV a similar behavior is observed. The absorption at 275 nm, corresponding to the precursor polymer, decreases during the reaction. Simultaneously, the absorption consistent with the conjugated system appears around 560 nm. From the absorbance profiles, it can be concluded that under these heating conditions (2 °C/min) the formation of the conjugated system starts above 100 °C.

These processes can also be monitored using in situ FT-IR spectroscopy. Using this technique, upon heating a decrease is observed of the absorption bands at 1205, 1266, 1414, and 1486 cm^{-1}, which can be assigned to vibrations of the dithiocarbamate functional group. At the same time, a new absorption band appears (at 965 cm^{-1}, for MDMO-PPV)[35] which originates from the *trans*-vinylene double bonds formed during thermal elimination. Concerning MDMO-PPV, it can be noticed from the FT-IR transmission profiles at 965 and 1266 cm^{-1} that the elimination starts at 105 °C and is completed at 145 °C, under the heating conditions used. These results are consistent with the UV−vis profiles.

Also for O-PTV the disappearance of the dithiocarbamate functional group and the formation of the *trans*-vinylene double bond (at 926 cm^{-1}) can be observed (Figure 4a) using FT-IR spectroscopy. From the absorption profiles, results are obtained totally consistent with the UV−vis profiles (Figure 4b).

Thermal Conversion in Solution. The dithiocarbamate precursor polymers can also be converted into their conjugated form by means of a thermal conversion in solution, which is typically done at a temperature of 180 °C. To determine the time period necessary for a complete conversion in solution, the polymers are dissolved in *o*-dichlorobenzene (*o*-DCB) and heated at 180 °C. Samples were taken with regular intervals and studied with UV−vis spectroscopy (Figure 5a,b). From these spectra it can be concluded that the MDMO-PPV precursor polymer is fully converted under these heating conditions within 60 min.

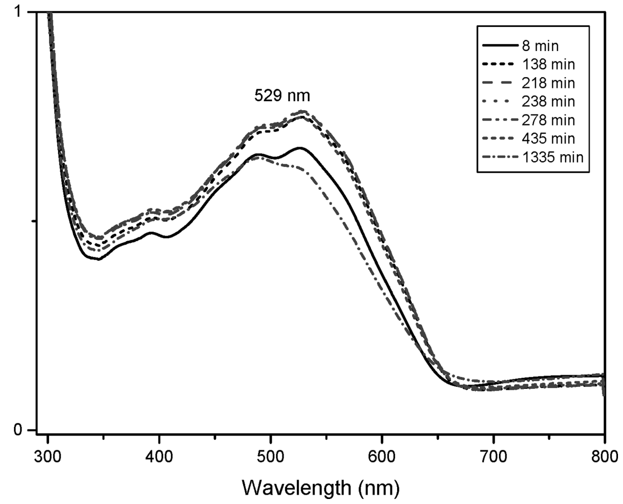


Figure 8. UV−vis spectra for the acid induced conversion of octyl precursor PTV with benzenesulfonic acid at room temperature.

In case of the O-PTV precursor, the conversion proceeds faster. Already after 25 min, the maximum wavelength (573 nm) has been reached (Figure 5b). However, elimination at 180 °C may lead to degradation of the polymer chromophore structure (conjugated system).[32] Prolonged heating (> 4 h) of the O-PTV leads to a blue shift in the UV−vis spectra, which is indicative for a thermal degradation of the conjugated system. This underlines the necessity to find alternative conversion processes to avoid detrimental degradation of the conjugated system.

Acid-Induced Conversion. Recently, a haphazard observation in our research group showed that dithiocarbamate precursor polymers have the tendency to change color in "acid" solvents, e.g., chloroform.[36] As this might refer to a partial conversion of the precursor polymer to the conjugated form, a study of the influence of acids on the conversion of dithiocarbamate precursor polymers was started.

The acid-induced elimination is studied in solution using UV−vis spectroscopy. Hereto, the precursor polymers are dissolved in chlorobenzene (CB) and heated at 70 °C in the presence of 1.5 equiv of either benzenesulfonic acid or trifluoroacetic acid, and the reaction is followed by taking samples at regular intervals. When no further changes in the UV−vis spectra are observed, the reaction mixture is neutralized and extracted with $CHCl_3$. If possible (sufficient quantity), the polymers are isolated via precipitation in cold methanol.

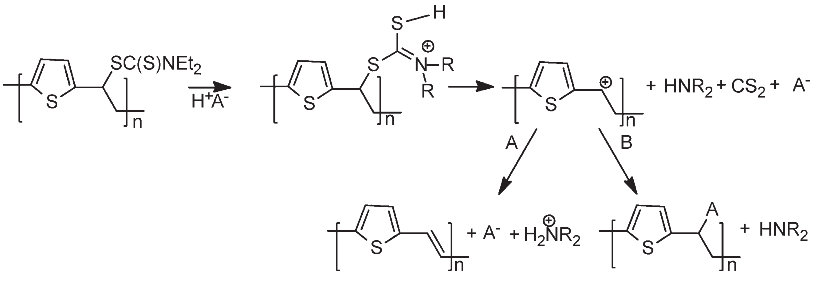
When the MDMO-PPV precursor is treated with benzenesulfonic acid, the conversion seems to be very fast. It takes only 30 min to convert the precursor polymer and reach the maximum absorption wavelength (Figure 6a). This is not the case for the conversion with trifluoroacetic acid. Here it takes about 7 h before the conversion is complete (Figure 6b). The distinction between these two experiments can simply be explained by the acid strength; e.g., benzenesulfonic acid has a pK_a value of −6.5 (at 25 °C). Trifluoroacetic acid is a much weaker acid with a pK_a value of 0.5 (at 25 °C). The obtained absorption maxima (λ_{max}) are similar (534 and 538 nm) to those obtained after thermal elimination (530 nm).

In case of precursor O-PTV, the acid-induced conversion with benzenesulfonic acid is extremely fast, the new absorption maximum is reached almost instantaneously, already after 10 min the maximum value of 580 nm has been reached (Figure 7a).

If the weaker trifluoroacetic acid is used, the reaction is still very fast (Figure 7b). Upon addition of the acid, instant color change (from orange to purple) occurs. Already the first sample (after 10 min) shows a fully conjugated polymer.

For longer reaction times however, a clear difference between the two acids can be observed. With benzenesulfonic acid as reagent, it can be stated that the absorption maximum after 7 h and especially after 24 h (Figure 7a)

Scheme 3. Proposed Mechanism for the Acid-Induced Conversion Reaction of DTC Precursor Polymers



shows a clear hypsochromic shift, which is probably due to partial degradation of the polymer. A similar effect is observed for MDMO-PPV when benzenesulfonic acid is used (Figure 6a, spectrum at 180 min). So, in the case of benzenesulfonic acid, it is very important to avoid long exposure to acid to avoid degradation of the conjugated system. In the case of trifluoroacetic acid the degradation process is much slower and is not observed within a time frame of 24 h (Figures 6b and 7b). Seemingly because of the lower acidity, the kinetic separation between the elimination process and the degradation process is large enough to limit the reaction to the first process.

Next, the conversion process of precursor O-PTV is studied at room temperature for which the conversion with benzenesulfonic acid was still quite fast. The maximal absorption wavelength reached is, however, about 50 nm lower than the one at 70 °C (Figure 8). Longer exposure to acid only leads to degradation. A very similar result was obtained when using trifluoroacetic acid at room temperature. Seemingly at room temperature a side reaction limits the extent to which the conjugation in the O-PTV system develops.

To achieve a deeper understanding of the acid-induced elimination of the dithiocarbamate functional group in the corresponding precursor polymers, a mechanistic scheme is proposed as presented in Scheme 3. This mechanism assumes as a first step the protonation of the dithiocarbamate group converting it to a better leaving group. Next, the dithiocarbamate group is expelled and decomposes in carbon disulfide and a secondary amine. At the same time a carbenium ion is formed in the precursor polymer structure. This opens a path for two competitive reactions, e.g., an elimination reaction (A) forming a double bond and a substitution reaction (B) with the conjugated base of the acid used, onto the carbenium ion site. In the former reaction the secondary amine will trap the proton liberated during the elimination reaction. This implies that the acid does not act as a catalyst but is effectively consumed. Given this mechanism, it should be expected that higher temperatures favor elimination, lower temperature, or added nucleophiles would make the substitution reaction more competitive.[37]

To test the latter effect a nucleophile reagent, i.e., 1 equiv of octanethiol, has been added at room temperature to the reaction mixture with trifluoroacetic acid (Figure 9). Here, it can be observed that the conjugated system did not develop fully, even if the mixture was allowed to react for 24 h. It may be assumed that the addition of octanethiol favors a nucleophilic substitution and creates a collection of oligomeric conjugated fragments.

Another experiment evaluates the influence of the acid concentration. On addition of only 0.3 equiv of trifluoroacetic acid instead of 1.5 (Figure 10), it is observed that the conjugation length is limited again to oligomeric fragments of the conjugated system.[38] This demonstrates that the acid is effectively consumed during the conversion and does not act as a catalyst.

Consistent with the proposed reaction mechanism in Scheme 3, the acid-induced conversion of the PTV precursor polymer is much faster than for the PPV precursor polymer. If it is assumed that the reaction proceeds via an intermediate carbenium ion, this carbenium ion will be stabilized by the aromatic core next to it. In the case of PTV, the aromatic core is a thiophene unit which is much more electron-rich than the core of the PPV precursor polymer. Therefore, the thiophene ring gives raise to a better stabilization of the intermediate and so a faster reaction.

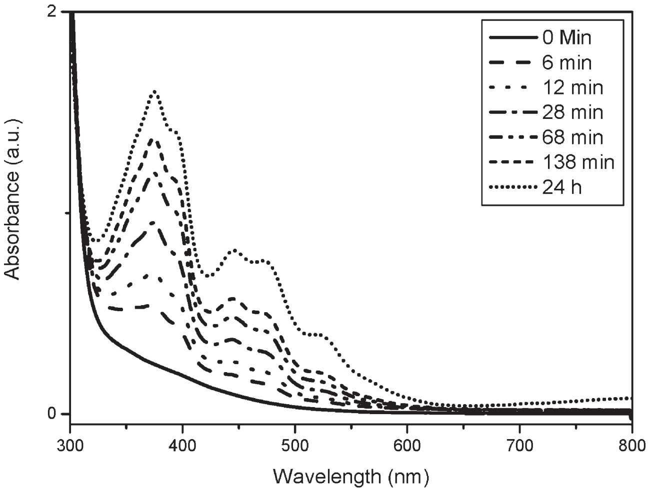


Figure 9. UV−vis spectra of the trifluoroacetic acid-induced conversion of octyl precursor PTV at room temperature in the presence of octanethiol.

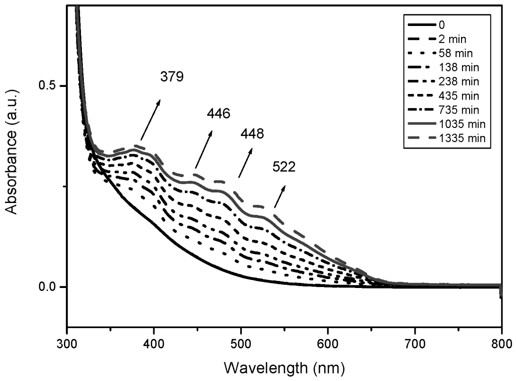
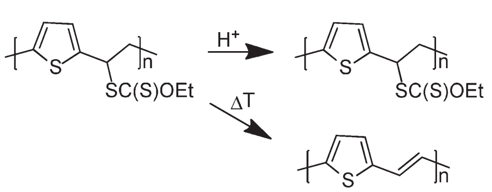


Figure 10. UV−vis spectra of the acid-induced conversion of octyl precursor PTV with 0.3 equiv of trifluoroacetic acid.

Scheme 4. Acid-Induced and Thermal Conversion of a Xanthate Precursor Polymer



To explore the unique character of this method for dithiocarbamate precursor polymers, a comparison with another precursor route has been performed. A xanthate precursor toward plain PTV[19] has been converted in the presence of 1.5 equiv benzenesulfonic acid at room temperature in CB, and the reaction is monitored by UV−vis spectroscopy in solution (Scheme 4). The spectra (Figure 11a) only show the absorption band of the precursor polymer, and there is no indication for the formation of the conjugated system. For comparison, the results from in situ UV-vis spectroscopy for a thermal elimination of a thin film of the xanthate precursor polymer are shown in Figure 11b. A film of the precursor polymer has been heated with a ramping temperature of 2 °C/min from room temperature up to 350 °C. Clearly said behavior, i.e., acid-induced elimination, is only displayed for the dithiocarbamate precursor polymers and is unprecedented in the literature for this class of functional groups. Future work is in progress in which we focus on a detailed NMR study using ^{13}C-labeled PTVs to

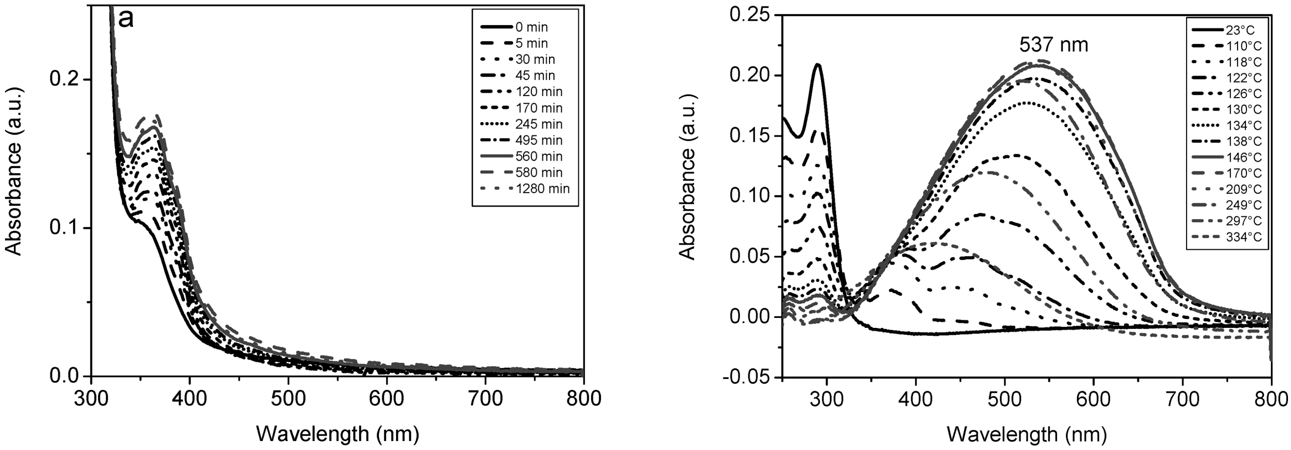


Figure 11. (a) UV-vis spectra of the benzenesulfonic acid-induced conversion of the xanthate precursor polymers, at room temperature in CB. (b) In-situ UV−vis experiment of thermal conversion of xanthate precursor polymer.

unravel details of the defect structures present in thermal and acid-induced converted PTV precursors. Furthermore, a study has been started to gain a deeper insight in the chemistry of dithiocarbamate functional groups using model compounds. This work will be reported in due time.

Conclusion

Two conversion processes for dithiocarbamate precursor polymers have been studied and compared: the thermal conversion and the acid-induced conversion. The acid-induced conversion allows lowering the conversion temperature from 180 to 70 °C. The concentration and the nature (strength) of the acid are of importance to avoid degradation and therefore defects. By tuning the reaction conditions, the competition between an elimination and a substitution reaction can be controlled in favor of elimination. Finally, a mechanistic framework is presented to explain the main features observed for the acid-induced elimination.

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