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Oxidative Degradation of Poly(3-octylthiophene)

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ABSTRACT: This report concerns oxidation mechanisms of undoped poly(3-octylthiophene) (POT). Thermal oxidation of POT films has been carried out under conditions relevant to processing. The films have also been exposed to accelerated aging. Samples were heated in air or nitrogen atmospheres at temperatures ranging from 180 to 220 °C. The molecular weight changes with oxidation time were studied by size exclusion chromatography (SEC). An increase of molecular weight occurred at high temperatures, which, in the presence of air, led to the formation of insoluble gel. Carbon-13 NMR and infrared spectroscopy were used for the identification of the key products and showed that the major oxygen-containing group is ketone in the α-carbon position of the alkyl side chain. Hence, the mechanism for thermal oxidation at processing temperatures indicated mainly a side chain degradation. Photooxidation by UV light of short wavelengths gave five new modes between 1080 and 1330 cm^{-1} and a different carbonyl pattern when compared to thermooxidation. These new modes have the same shifts as the doping–induced bands of POT. Thus, photooxidation indicated a chain scission or a ring–opening mechanism.

Introduction

The finding that polyacetylene could become electrically conductive on oxidation or reduction has initiated intense research on conducting polymers.[1] An ultimate goal has been to combine metallic behavior with the low weight and the good processability of polymers. However, problems with poor stability in air and difficulties to process polyacetylene soon became obvious. Later on, polymers with increased stability, e.g. polymers with aromatic units,[2] appeared. The processing of conducting polymers, however, was still a major problem.

One way to overcome the processing problem is to use a precursor route, as in Durham polyacetylene.[3] By introducing flexible side chains to the conjugated and stiff main chains, soluble and melting polymers could be achieved. A typical example of this approach is polythiophene with alkyl side chains (PATs), where an alkyl substituent of four or more carbons leads to a soluble polymer.[4–6] With processable conducting polymers such as poly(3-alkylthiophenes) (P3ATs), conventional processing techniques such as injection molding and solution casting can be used. It is thus possible to produce blends with common polymers to combine conductivity with the mechanical properties of the added polymers and to reduce the price of the blend.[7–9]

During processing, polymers are exposed to high temperatures and shear forces and often also to oxygen. This may initiate different degradation reactions, ultimately leading to chain scission or cross-linking, and thus to impaired properties.[10]

In the case of conducting polymers, the conditions prevailing under processing may also influence conductivity negatively. For some processable conducting polymers, it is known that thermal treatment of the doped polymer will cause a rapid decrease in conductivity: thermal undoping.[11] Hence, in these cases processing at high temperatures must be done with undoped polymer. There is, however, very little known about the extent to which processing initiates degradation reactions of this kind of polymer. Long time exposures to medium-high temperatures as well as UV exposure will also age the polymer and lead to degradation. Again, the behavior of conducting polymers in these respects is not well-known.

The structure of the degraded polymer must be examined for an understanding of the degradation mechanisms which is necessary for the design of polymer stabilization. We have examined thin films of undoped poly(3-octylthiophene) (POT) after exposure to temperatures and atmospheres similar to processing conditions. For comparison, we have also examined the degraded products obtained after exposing the polymer to accelerated aging in UV light of high dose rates and at moderate temperatures. We have used chemical treatments and a model compound as a help to identify oxidation products. Characterization has been performed with FTIR, NMR, and GPC. We have also attempted to stabilize POT with antioxidants (AO) normally used for common bulk polymers.

Experimental Section

Sample Preparation. Poly(3-octylthiophene) synthesized by the method developed by Sugimoto was used.[12] The weight average molecular weight, M_w, of the polymer was 147×10^3, and the number average molecular weight, M_n, 19×10^3, and it had an iron content of 0.016% by weight. The polymer was dissolved in chloroform, undissolved parts were filtered off, and the polymer was subsequently cast to give thin films, 20–40 μm. These films were vacuum pumped at room temperature for 48 h and then exposed to thermal degradation, photooxidation, chemical treatment, and FTIR and SEC characterization.

In order to complement the degradation study of POT, the low molecular weight model compound 2,5-diphenyl-3-octylthiophene, DPhOT, was prepared. This compound was synthesized with a Grignard coupling reaction catalyzed by a nickel–phosphine complex according to the method of Kumada et al.[13] The halide used to synthesize DPhOT was 2,5-dibromo-3-octylthiophene[14] and as Grignard reagent phenylmagnesium bromide was used. The product (overall yield: about 30%) had an oil-like consistency and was confirmed to be DPhOT by NMR and IR spectroscopy. ^{13}C NMR ($CDCl_3$, 25 °C): δ (ppm) 14.2 (CH_2); 22.8, 29–30, 31, 32 (CH_2, 7C); 125.6, 127.3, 128.5–129.2, 142.1 (C_6H_5, 12C); 134.4–134.6, 137.4, 139.7 (thiophene, 4C). DPhOT was then thermooxidized in the same way as the polymer, and the degraded compound was studied with FTIR and ^{13}C NMR.

Thermal treatment was performed in a ventilated oven, designed to allow good control of atmosphere and temperature as well as to give a rapid heating of the sample.[15] POT films,

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30–40 μm thick, were heated at temperatures ranging from 180 to 220 °C with heating times from 10 to 30 min. The atmospheres used were air or high-purity nitrogen (<0.0005% oxygen) delivered by AGA AB.

Accelerated aging, with 20 μm thick POT films, was performed in an air atmosphere with three different methods: in the ventilated oven at 100° for 24–72 h; with a mercury lamp at room temperature; in a Suga Test Instrument Weather-o-meter with a xenon lamp as the radiation source and with a black panel temperature of 60 °C. After each exposure, the films were studied with FTIR.

The degraded films were treated at room temperature with ammonia (g), sodium hydroxide in 2-propanol (1 M), and hydrogen chloride in 2-propanol (1 M). The exposure times used ranged from 6 h to 1 week.

Antioxidants (AO) were received from Ciba-Geigy and Shell in the form of powders and incorporated by dissolving 0.5–1.0 weight % AO together with POT and thereafter casting films as with pure POT. Infrared spectroscopy confirmed the presence of AO in dried films. The AO used were 2,6-di-*tert*-butyl-*p*-methylphenol (Ionol T, Shell); stearyl β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Irganox 1076, Ciba Geigy); pentaerythrityl tetrakis[(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate] (Irganox 1010, Ciba Geigy); 2,2″-methylenebis(4-methyl-6-*tert*-butylphenyl monoacrylate) (Irganox 3052, Ciba-Geigy); tris(2,4-di-*tert*-butylphenyl) phosphite (Irgafos 168); Irganox B 561, Ciba-Geigy (4 parts Irgafos 168 + 1 part Irganox 1010); Irganox B 900, Ciba-Geigy (4 parts Irgafos 168 + 1 part Irganox (1076); *N,N′*-bis[(β-3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyl]hydrazide (Irganox 1024, Ciba-Geigy); bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (Tinuvin 770, Ciba-Geigy) (HALS 1).

Analysis. Size exclusion chromatography, SEC, analysis was used to determine the molecular weight distribution. A Waters Associates SEC Model 200 operating at 25 °C with tetrahydrofuran, THF, as solvent was used for the determination. The calibration was based on narrow polystyrene standards and tested with well-defined broad molecular weight samples. To ensure dissolution, 1 g samples were heated at 120 °C in 1 L of solvent for 3 h under nitrogen. The solutions were filtered on a poly(tetrafluoroethylene) filter (0.45 μm) to remove undissolved parts. The amount of insoluble material, gel, was determined by weighing the material remaining on the filter pad.

FTIR measurements were performed on degraded and chemically treated samples using a Perkin-Elmer model 1710 spectrometer. The spectra were taken with a resolution of 4 cm^{-1}.

Proton-decoupled ^{13}C-NMR spectra were recorded in 5–10 % (w/v) solutions in $CDCl_3$ on a Varian VXR-300 spectrometer (75 MHz, tetramethylsilane as an internal standard). The acquisition time was 1.8 s, and the pulse delay, 2 s. The number of scans accumulated was 58 000.

Results and Discussion

A. Chemical Identification of Oxidation Products by Infrared Spectroscopy.

Exposure of POT films to air for different temperatures and times led to the development of a complex IR absorption in the 1600–1800 cm^{-1} region, as seen in Figure 1, which indicates the presence of several types of carbonyl groups. Several maxima or shoulders were observed in this carbonyl region at or around 1635–1650, 1670, 1715–1725, and 1770 cm^{-1}. The intensity of these bands increased with the time and temperature of exposure. No change could be seen in the hydroxyl region or in other regions except for the decrease of three weak absorption bands: 1306, 1150, and 1084 cm^{-1} (see Figure 1). These bands are attributed to bands induced by doping,[16] which appeared in spite of the low content of $FeCl_3$ remaining in the sample, indicating very light or no doping. The decrease in the intensity of these peaks, observed also for treatment in a nitrogen atmosphere, is due to the undoping normally obtained with doped PATs exposed to high temperatures.[11]

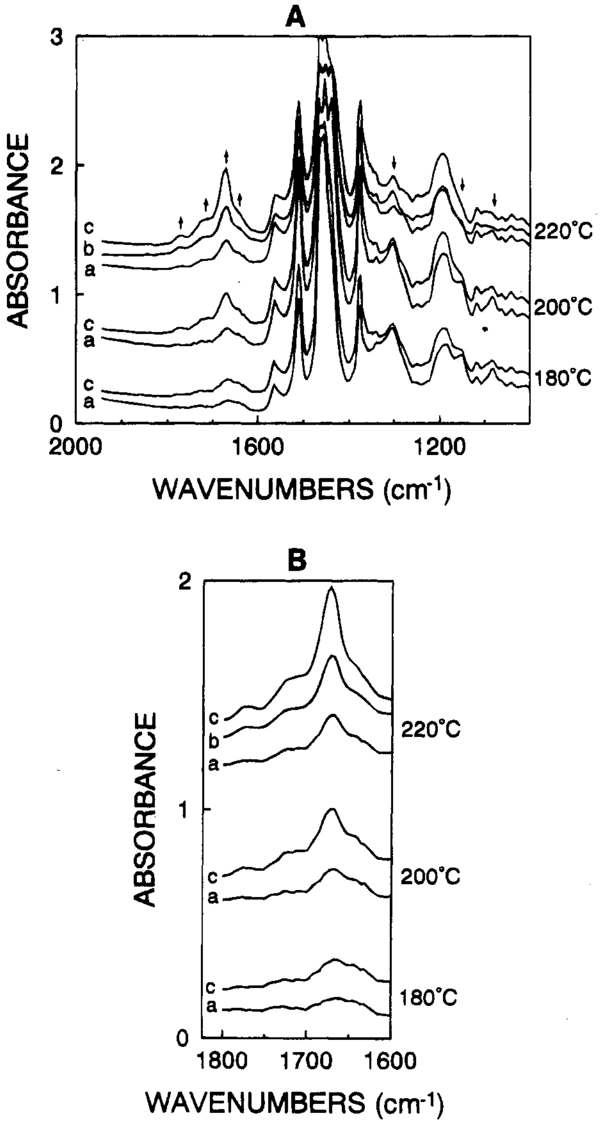
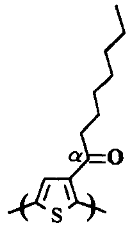


Figure 1. Changes in IR spectra of the POT film thermooxidized at 180–220 °C for (a) 10 min, (b) 20 min, and (c) 30 min: (A) 1000–2000 cm^{-1}; (B) carbonyl range.

Table 1. C═O Frequency of Monosubstituted Thiophenes

substituent	position 3 C═O frequency (cm^{-1})
═O	1634
–CHO	1691
$-COCH_3$	1674
–COOH	1690

The identification of the carbonyl groups obtained after oxidation was undertaken with the help of a comparison with low molecular weight reference compounds;[17–19] see Table 1. The main peak at 1670 cm^{-1} is similar to that of 3-acetylthiophene. This indicates ketone in the α-carbon position of the alkyl side chain.



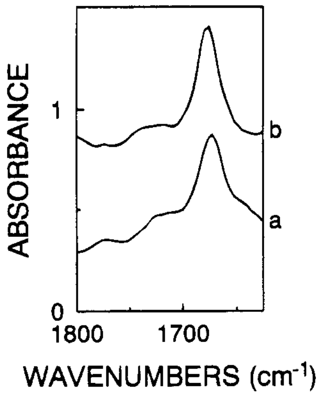


Figure 2. Changes in carbonyl IR absorption during thermooxidation at 220 °C in air for (a) POT, 30 min, and (b) DPhOT, 1 h.

The shoulders around 1640 cm^{-1} can be assigned either to olefin unsaturations situated on the side chain or created after ring opening of the thiophene ring or to a carbonyl oxygen bonded directly to the ring. However, no change was seen in the range 800–1000 cm^{-1}, as could be expected for unsaturated compounds.[20,21] This leads us to assume a carbonyl oxygen connected to the ring. This oxygen should be either in the 4-position or in the 2- or 5-position after chain scission.

The shoulders around 1720 cm^{-1} can be assigned to ketone in positions of the alkyl group other than in the α-position.[20,21] At 1680–1690 cm^{-1}, a possible shoulder due to aldehydes or acids, probably at the α–carbon, can neither be seen clearly nor excluded.[17] The shoulder at 1770 cm^{-1} can be due to peracids, lactones, esters, or peresters.[20,21] Base treatment converts acids, esters, and lactones to carboxylates, leaving aldehyde and ketone unchanges.[22,23] However, the chemical treatment of oxidized samples with KOH in 2-propanol or with NH_3(g) gave no observable changes in the carbonyl peak region and no peak at 1585 cm^{-1} due to the appearance of carboxylate. Assuming that the reacting agent has penetrated the film, this indicates no lactones or carboxylic or ester groups. Thus, infrared spectroscopy indicates that thermooxidation of POT at 180–220 °C mainly oxidizes the alkyl side chains.

Chemical Identification of Oxidation Products of the Model Compound. The model compound DPhOT was oxidized at 220 °C in air. The oxidized samples showed carbonyl patterns in the IR spectra similar to those of the polymer, with the exception of the shoulders observed for POT around 1640 and 1770 cm^{-1}; see Figure 2. Small peaks at 1743, 1776, and 1805 cm^{-1} are due to the phenyl groups in DPhOT. The bond strength between the thiophene rings in POT should be similar to the bond strength between the phenyl group and the thiophene ring in DPhOT. However, in DPhOT the steric hindrance between the α-hydrogen in the alkyl group and the *o*-hydrogen in the phenyl group is more pronounced than in POT between the α-hydrogen and the sulfur of the thiophene ring. The oxidation potential should thus be lower in POT, and the reactivity toward oxidation of ring carbons, higher. Furthermore, if oxidation and subsequent chain scission would occur for DPhOT, it is likely that the fragments are volatilized at 220 °C. Thus, it is reasonable to suggest that carbonyl structures observed after oxidation of DPhOT can be related to the alkyl side chain. The shoulders around 1640 and 1770 cm^{-1}, which are developed after oxidation of POT only, can thus be related to the polymer backbone and possibly are formed after chain scission. The peaks and shoulders at 1670 and 1720 cm^{-1} are present in both the polymer and the model compound. This confirms that these peaks are associated with side chain oxidation.

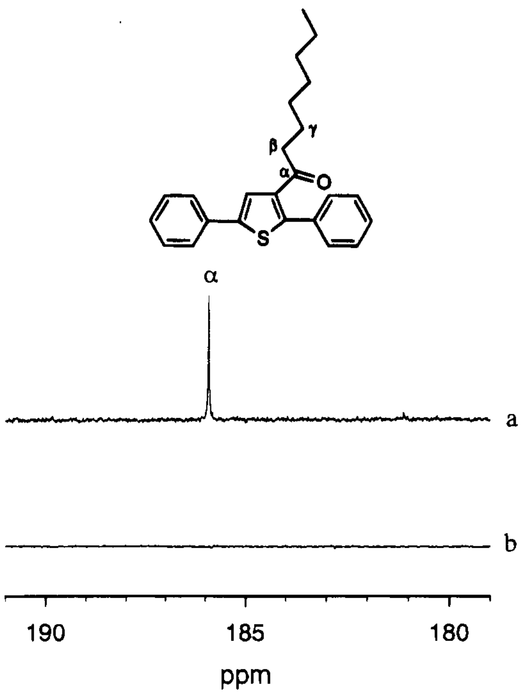


Figure 3. Carbon-13 NMR spectra of the C:O region (α-carbon) of the alkyl group of (a) oxidized and (b) unoxidized DPhOT.

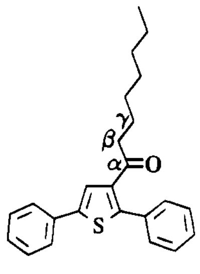


Figure 3 shows carbon-13 NMR spectra of unoxidized and oxidized DPhOT. The signal at 186 ppm is, in accordance with low molecular weight thiophenes, assigned to ketone or aldehyde formation in the α-carbon position of the alkyl side chain.[24] The signals at 25 and 42 ppm, Figure 4, are further evidence that a ketone in the 3-position is formed after thermooxidation.[25] These signals are associated with the neighboring carbon atoms on the side chain. Moreover, no signs of carboxylic acids or alcohols can be seen with carbon-13 NMR. This confirms that these structures are either not present or present only in small traces.

Size Exclusion Chromatography. In earlier examinations of the heat stability of POT,[7,26] thermogravimetric analysis, TGA, has been used. It was stated that no degradation took place below 400 °C. However, size exclusion chromatography, SEC, has shown that cross-linking reactions of POT take place at 180 °C.[26] Also, iron remaining from the polymerization influences the formation of insoluble gel when oxygen is present. In the present study, exposure of the polymer chains to processing conditions caused a change in the molecular weight. In the presence of air, cross-linking will lead to the formation of insoluble gel (Table 2). When the

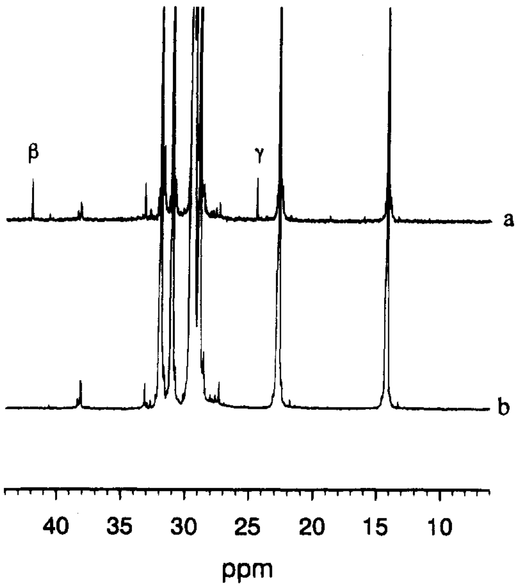


Figure 4. Carbon-13 NMR spectra of the CH_2 region of the alkyl group of (a) oxidized (top) and (b) unoxidized (bottom) DPhOT.

Table 2. Calculated Amount of Gel Formed in the Samples after Thermooxidation in Air

	gel content (%)			
oxid time (min)	180 °C	200 °C	210 °C	220 °C
10		45	48	78
20	3	63	76	86
30	5–10	80	83	94

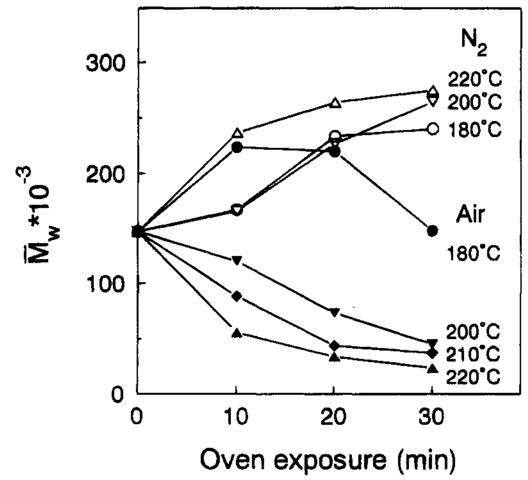


Figure 5. Molecular weight (M_w) changes of POT heat treated at 180–220 °C for 10–30 min in air and nitrogen.

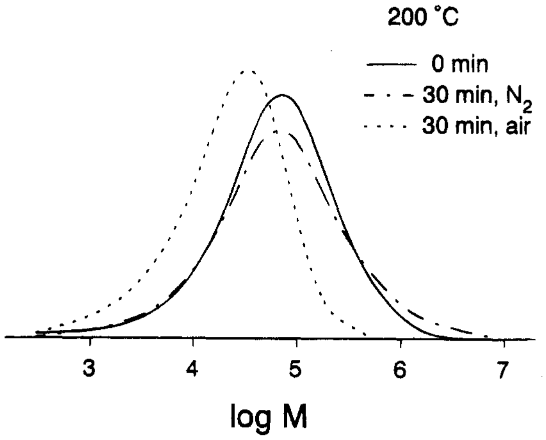


Figure 6. Changes in MWD of POT before and after heat treatment at 200 °C for 30 min in air and nitrogen atmospheres.

content of gel is large enough, a decrease in the molecular weight of the soluble part is seen (Figure 5) since the probability of cross-linking reactions is higher for the high molecular weight material. This decrease is also seen for POT thermooxidized at 200–220 °C. However, for samples thermooxidized at 180 °C with an oxidation time of 10–20 min, cross-linking only leads to a small amount of gel and an increase in the molecular weight is seen. When the oxidation time increases to 30 min, the amount of gel increases and the molecular weight of the soluble part decreases.

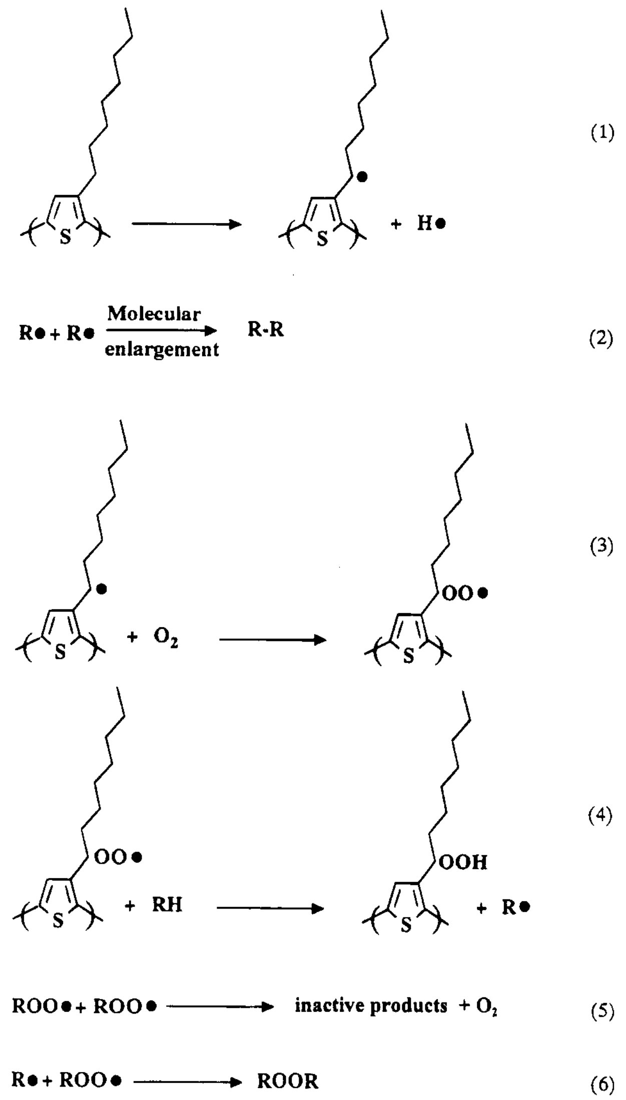
However, degradation under nitrogen only leads to a few percent of gel, and only an increase in the molecular weight is seen. The leveling off in the molecular weight indicates that a mechanism other than that in oxidized samples is involved. This molecular enlargement may be due to reactions between end groups of the polymer chains which do not lead to the formation of insoluble gel. Molecular weight distributions, MWD, of samples treated at 200 °C (see Figure 6) further illustrate the difference in reactions responsible for the molecular enlargement in different atmospheres. The shift toward lower MW when air is used is a result of extensive gel formation only leaving low molecular weight material soluble. For the degradation in nitrogen the molecular enlargement, independent of mechanism, is much slower. It might also be possible that chain scission reactions occur which also would contribute to the limited increase in molecular weight.

Degradation Reaction Mechanisms. It is a well-known fact that the α-position of unsaturated polymers is a sensible point for radical formation.[10] Earlier it was proposed that, after thermooxidation, POT should undergo hydrogen abstraction in the α-carbon position of the alkyl group;[26] see Scheme 1, reaction 1. The radical formed could thereafter be the site for further reactions and induce cross-linking when two radicals, designated R•, combine with each other, reaction 2. This is probably the main cause for molecular enlargement leading to insoluble material by degradation in oxygen. The combination could, in principle, also occur in a nitrogen atmosphere. The absence of gel formation indicates, however, that the number of radicals formed in limited by degradation in nitrogen. Investigations of polythiophenes with substituents other than alkyl side chains show less tendency for insoluble gel formation.[27]

When oxygen is present, hydroperoxides should be the key substance according to the classical chain mechanism found earlier for, e.g., polyethylene.[10] In the first step, thus, a peroxy radical is formed from the alkyl radical as in reaction 3. Hydroperoxides may then be formed in a second step both by inter- and intramolecular hydrogen abstraction. Intermolecular hydrogen abstraction is shown in reaction 4. The peroxy radicals can also compete in reactions leading to inactive products, reaction 5, or cross-linking, reaction 6.

At high temperatures, e.g. above 150 °C, as is the case for polyethylene, however, homolytic cleavage of these hydroperoxides is likely to occur with alkoxy and hydroxy radicals as decomposition products,[28] Scheme 2 reaction 7. Thus, hydroperoxides accelerate radical formation. Furthermore, an increased number of radicals increases the termination reactions which finally leads to an increase in cross-linking and gel formation. It is also known that metals might affect cleavage of

Scheme 1

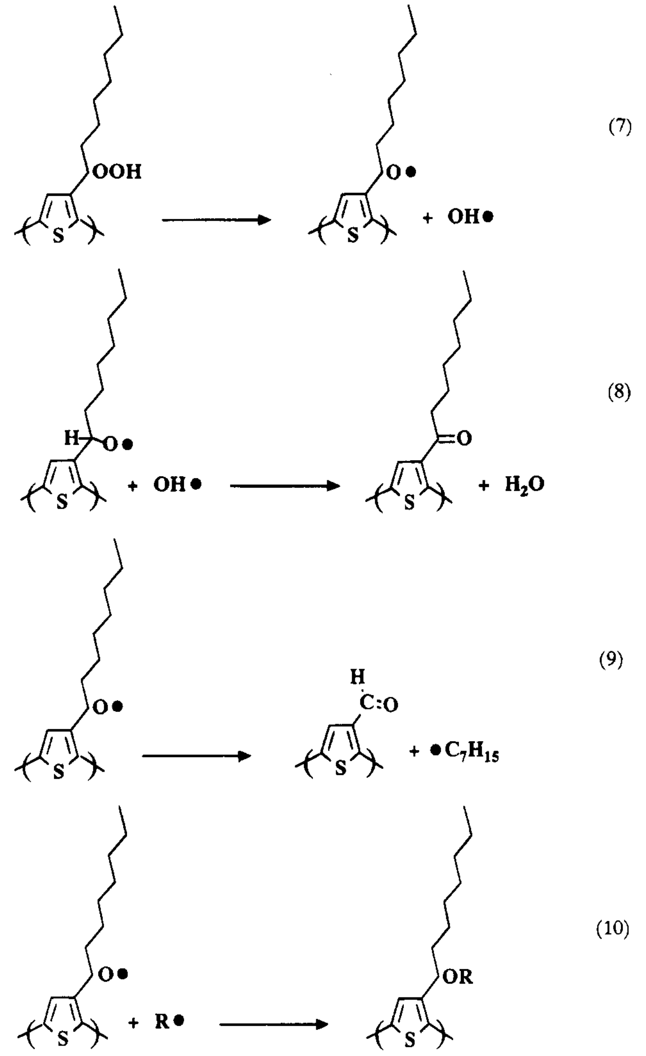


$$R\bullet + R\bullet \xrightarrow[\text{enlargement}]{\text{Molecular}} R\text{-}R \qquad (2)$$

$$ROO\bullet + ROO\bullet \longrightarrow \text{inactive products} + O_2 \qquad (5)$$

$$R\bullet + ROO\bullet \longrightarrow ROOR \qquad (6)$$

Scheme 2



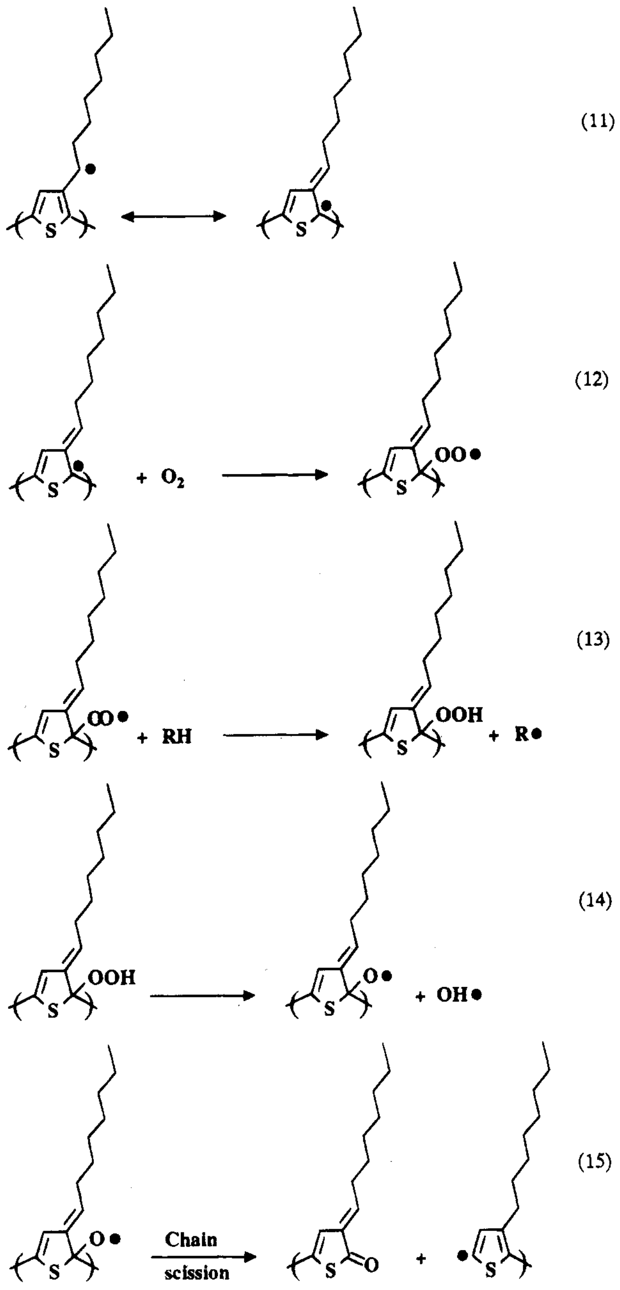
hydroperoxides and further accelerate degradation.[10] Thus, $FeCl_3$, used as the oxidant for polymerization of alkylthiophenes, might cause problems during processing and use of the polymer. Earlier, it has been seen that even quite small amounts of iron residues in POT will increase cross-linking and the amount of gel.[26]

The alkoxy and hydroxy radicals formed in reaction 7 could abstract hydrogen and form new polymer radicals together with water and hydroxyl groups. However, IR spectra show no change in the hydroxyl region, which indicates that the content of hydroxyl groups must be low. Instead, it has also been found that ketone in the α-carbon position is the main product after oxidation. This strongly supports that ketone is formed from an alkoxy radical through hydrogen abstraction in a cage reaction,[10] reaction 8. Another common reaction for an alkoxy radical is β-scission,[10] which in this case would lead to 3-thiophene aldehyde, reaction 9. This aldehyde should be seen in the carbonyl region at 1680–1690 cm^{-1}. However, no peak can clearly be seen in this region even if a small peak cannot be excluded. This indicates, at the most, only small traces of aldehydes which may react further to, e.g., peracids, acids, or esters. It is also reasonable to anticipate that cross-linking reactions can take part from the alkoxy radical after reaction with an alkyl radical, reaction 10. In some POT units, hydrogen abstraction in positions other than in the α-carbon position will lead to reactions similar to (1)–(10). The main product from these reactions should also be ketone, which also is supported by the presence of carbonyls at 1720 cm^{-1}.

Scheme 3 shows that carbonyls situated directly on the thiophene ring and unsaturated structures can be formed from a resonance structure to the radical in the α-carbon position, (11). This radical may thereafter reaction as earlier, with the formation and cleavage of hydroperoxides, reactions 12–14. The carbonyl is formed after chain scission of the polymer chain, reaction 15. Similar reactions have earlier been suggested by Holdcroft et al. after photodegradation of poly(3-alkylthiophenes) in solution.[29]

Stabilizers. The effect of stabilizer on the POT degradation, normally used for common polymers such as polyethylene, was studied. The following classes of stabilizer, divided according to their mode of action, were used: primary antioxidants interfering with the peroxy radicals, secondary antioxidants reacting with hydroperoxide groups, antioxidants reacting with nonoxygenated radicals, metal deactivators, and light stabilizers in the form of radical scavengers. The stabilizers could be subdivided into the following: phenolic antioxidants; monophenols (Ionol, Irganox 1076) and polyphenols (Irganox 1010), synergistic antioxidants; phosphites (Irgafos 168) and phenols (Irganox 3052), UV stabilizers; hindered amines (Tinuvin 770)), metal deactivators (Irganox 1024), and mixtures (Irganox B 900, Irganox B 561).

Scheme 3



As indicated with FTIR and SEC, however, these antioxidants showed no obvious effects on the degradation rate or course. This might be due to the extremely high sensitivity of hydrogen abstraction from the α-carbon position of POT with a possible radical site in every alkyl group of the polymer. In polymers such as polyethylene, the radicals are formed in connection to weak link structures, e.g. chain branches, and unsaturated structures which are not so frequent.[10] Concentrations of antioxidants far above those used for common polymers might then be needed for POT.

B. Aging of POT Films. Accelerated aging in the form of moderate temperature (100 °C), weather-o-meter (60 °C and xenon lamp), and ultraviolet radiation (mercury lamp and 25 °C) was performed in the presence of air. Thermooxidation of POT films at 100 °C gives similar carbonyl spectra as for films oxidized at processing temperatures. However, only small traces of gel are observed. Exposure to 60 °C and xenon lamp gave IR spectra which can be seen in Figure 7. New strong modes appeared at 1083, 1150, 1184, 1309, and 1333 cm^{-1}. These modes are the same as obtained for doped POT and can be related to doping-induced bands.[16] As could be seen earlier, these bands were reduced after exposure to high temperature, with or without oxygen atmosphere. Earlier, IR investigation of doped poly(2,5-thienylene) films has shown four conspicuous absorption bands, between 1020 and 1330 cm^{-1}, which are independent of the difference in the dopant species and content.[30] The question, however, whether these bands are related to the positively charged polymer backbone or due to the remaining doping ions, remains unsettled. These results indicate, nevertheless, that these bands can be related to the polymer.

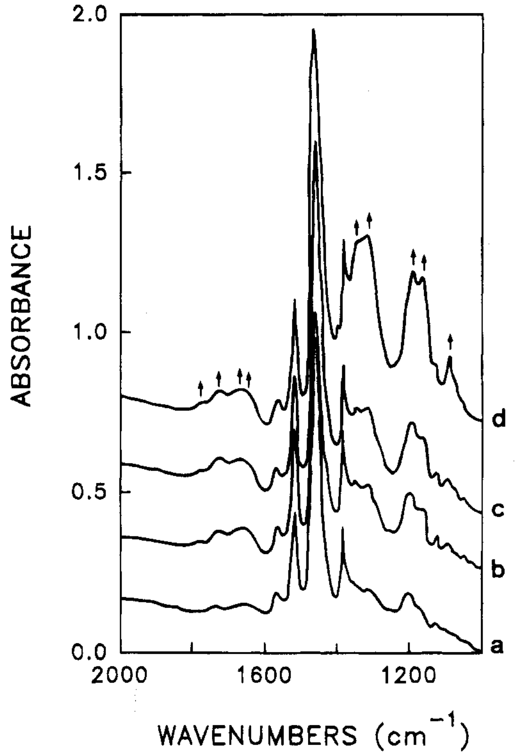


Figure 7. IR changes, 1000–2000 cm^{-1}, during photooxidation of the POT film, 20 μm thickness, irradiation in air with a xenon lamp at 60 °C, for (a) 0 h; (b) 48 h, (d) 72 h.

In the carbonyl region, there are mainly four bands at or around 1630–1655, 1670, 1720, and 1770 cm^{-1}, Figure 8. Holdcroft has found that poly(3-hexylthiophene) undergoes chain scission in organic solvents when irradiated with UV–vis light after singlet oxygen addition at the 2-position of the thiophene ring.[29,31,32] According to his proposed mechanisms and the carbonyl shifts obtained in this investigation, it is reasonable to believe that the bands or shoulders around 1630–1655 cm^{-1} can be assigned to a carbonyl situated directly on the thiophene ring and formed after chain scission. A peak at 1654 cm^{-1} also seems to dominate in the carbonyl region after photooxidation with a mercury lamp at room temperature. With increasing photooxidation and temperature, however, the bands at 1670, 1720, and 1770 cm^{-1} seem to increase in intensity relatively to the shoulders around 1630–1650 cm^{-1}. This can be due to an increasing attack by free radicals on the α-carbon atom of the alkyl group.

Aging in weather-o-meter with a xenon lamp and a temperature of 60 °C gives IR patterns similar to those from photooxidation with the mercury lamp. Hence, it is reasonable to believe that the mechanisms caused by photooxidation can be related mainly to the polymer

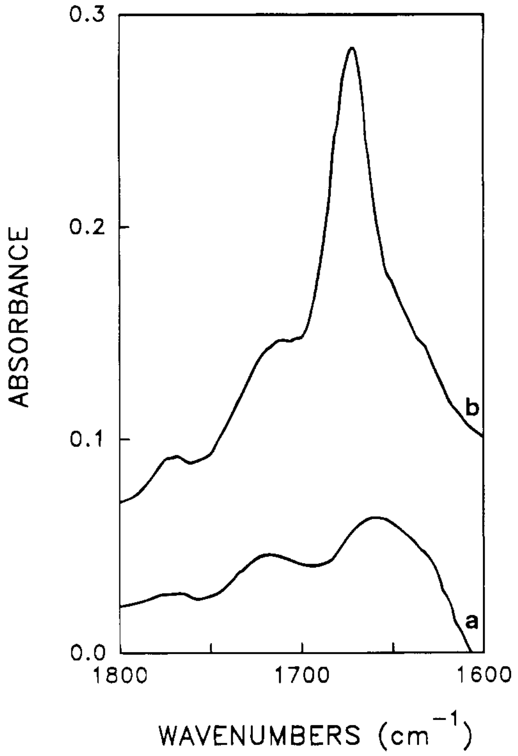


Figure 8. Carbonyl absorptions of oxidized POT films: (a) photooxidized with a xenon lamp at 60 °C for 48 h, 20 μm thickness; (b) thermally oxidized at 220 °C for 30 min, 40 μm thickness.

backbone and to chain scission. However, some side chain degradation as in thermal oxidation also seems to occur.

Conclusions

This examination shows that POT during thermooxidation mainly undergoes hydrogen abstraction from the α-carbon of the alkyl side chain and that this position then becomes the site for the oxidation products. The same results should also be expected from poly(alkylthiophenes) with other alkyl side chains.

After thermooxidation at processing temperatures, α-unsaturated ketone structures are the dominant carbonyl group. At these temperatures, molecular enlargement occurs in both air and nitrogen atmospheres but leads to gel formation only in the presence of oxygen. This difference indicates enlarging reactions which depend on the atmosphere used.

It was found that a low molecular weight model compound can be used as a tool to understand the degradation mechanisms of poly(alkylthiophenes). The low molecular weight compound simplified characterization of the degradation products and FTIR and NMR results presented here are in excellent agreement for both POT and DPhOT.

Photooxidation of thin films of POT showed four new strong modes in FTIR between 1080 and 1330 cm^{-1} similar to those of doped POT. These modes together with a different carbonyl pattern indicate a degradation mechanism which differs from thermal oxidation and which is more connected to the degradation of the polymer backbone and to chain scission instead of to side chain degradation, as in the case for thermooxidation.

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