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EFFECTS OF TEMPERATURE AND OXYGEN ON THE DEGRADATION OF DOPED AND UNDOPED POLYPHENYLACETYLENE

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ABSTRACT

The thermal oxidation and pyrolysis of pristine polyphenylacetylene (PPA) and PPA–electron acceptor complexes were studied. Thermogravimetric and differential thermal analyses of pristine PPA reveal that in the presence of substantial amounts of O_2, an initial exothermic process first leads to a weight gain followed by a two-step weight loss process. The initial weight gain is attributed to the formation of oxygen-containing groups in the polymer and the presence of these groups has been confirmed by XPS and IR absorption spectroscopy. Halogen and organic electron acceptor dopants interfere with the formation of these groups and promote char formation during pyrolysis. During heating, even when no weight change is discernible, the degree of effective conjugation will decrease which in turn will adversely affect the photoconductive properties of PPA.

INTRODUCTION

Recent results have shown that solution cast films of *trans*-polyphenylacetylene (PPA) are semiconducting photoconductors when undoped, when doped with certain inorganic and organic electron acceptors and when sensitized with organic dyes [1–4]. Phenylacetylene has long been known to polymerize by a variety of mechanisms and in the presence of many different catalysts [1]. Most of these catalysts have not yet been demonstrated to yield a pure isomer, although a recent study has shown that stereoregular PPA can be prepared using Rh(I) catalysts [5]. *Trans*-rich PPA can be prepared in the presence of $W(CO)_6$ catalyst [6] and has been found to exhibit the best photoconductive properties [2,4].

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Since *trans*-PPA and its charge-transfer complexes were shown to be promising photoconductors, it would be of interest to explore their stability under various conditions. We have recently reported on the stability of *trans*-PPA in solution and under light illumination [7]. In this paper we address the effects of O_2 and temperature on the degradation of both doped and undoped *trans*-PPA.

EXPERIMENTAL

The *trans*-PPA samples used in this study were prepared using the method described by Masuda et al. [8]. Polymerization was carried out in the presence of $W(CO)_6$ catalyst in CCl_4 solution under irradiation by a Xe arc lamp. The polymer sample obtained had an average molecular weight of about 80000. For comparison purposes some *cis*-PPA samples were also examined. *Cis*-rich PPA was prepared in the presence of ferric acetylacetonate and triethylaluminium [9] in the laboratory of Professor P. Ehrlich, State University of New York, Buffalo, and was obtained through his courtesy.

PPA–acceptor complexes were easily prepared by mixing the solutions of both components in a nitrogen atmosphere [10,11]. The electron acceptors used were iodine (sublimed, Merck), bromine (BDH Chemicals), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), tetrachloro-*o*-benzoquinone (chloranil) and tetrafluoro-*p*-benzoquinone (fluoranil). All the organic acceptors used were from Aldrich. The organic solvents used were chloroform, toluene or methylene chloride. Since PPA deconjugates and degrades slowly in organic solvents [7], the solvents in all cases were removed quickly by pumping under reduced pressure.

A Netzsch STA 409 simultaneous thermogravimetric (TG)–differential thermal analyzer (DTA) unit was used to monitor the degradation of the PPA samples under heating. A heating rate of $10\,^{\circ}C\ min^{-1}$ and a gas flow rate of $100\ ml\ min^{-1}$ were used. The oxygen concentration, in the N_2–O_2 gas mixtures used, ranged from 0 to 75%. The following analytical techniques were used to characterize the PPA samples before and after heat treatment: elemental analysis; UV-visible absorption spectroscopy using a Shimadzu UV-260 spectrophotometer; IR absorption spectroscopy on a Perkin–Elmer model 682 spectrophotometer with the PPA samples dispersed in KBr pellets, and X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB MK II spectrometer with a Mg $K\alpha$ X-ray source (1253.6 eV photons). In the XPS measurements, the powdered polymer samples were mounted on standard sample studs using double-sided adhesive tape. All core-level spectra were referenced to the C 1s neutral carbon peak at 284.6 eV.

RESULTS AND DISCUSSION

Thermogravimetric and differential thermal analysis

The TG scans of undoped *trans*-PPA in various N_2–O_2 mixtures are shown in Fig. 1. In N_2, the sample does not show any weight loss below 275 °C. In contrast, *cis*-PPA showed the onset of weight loss at about 120 °C. This is consistent with the results obtained by other investigators [1,12]. In the presence of O_2, the *trans*-PPA samples showed weight changes commencing at lower temperatures. When the O_2 content is high, a small weight gain may be observed before the weight loss occurs. In air, the weight loss commences at a temperature about 50 °C lower than in N_2. An initial weight gain may be attributed to the formation of oxygen-containing groups (see below). This initial weight gain has also been observed when polyacetylene is heated in air above 100 °C [13]. At temperatures greater than 400 °C, the differences between PPA heated in N_2 and in the presence of O_2 become very significant. In the presence of O_2, the weight loss slows down considerably between 450 and 520 °C before a second rapid weight loss step occurs. In this temperature region, the weight of the PPA sample is about 50% of the original weight. In N_2, the weight of the PPA samples at 520 °C

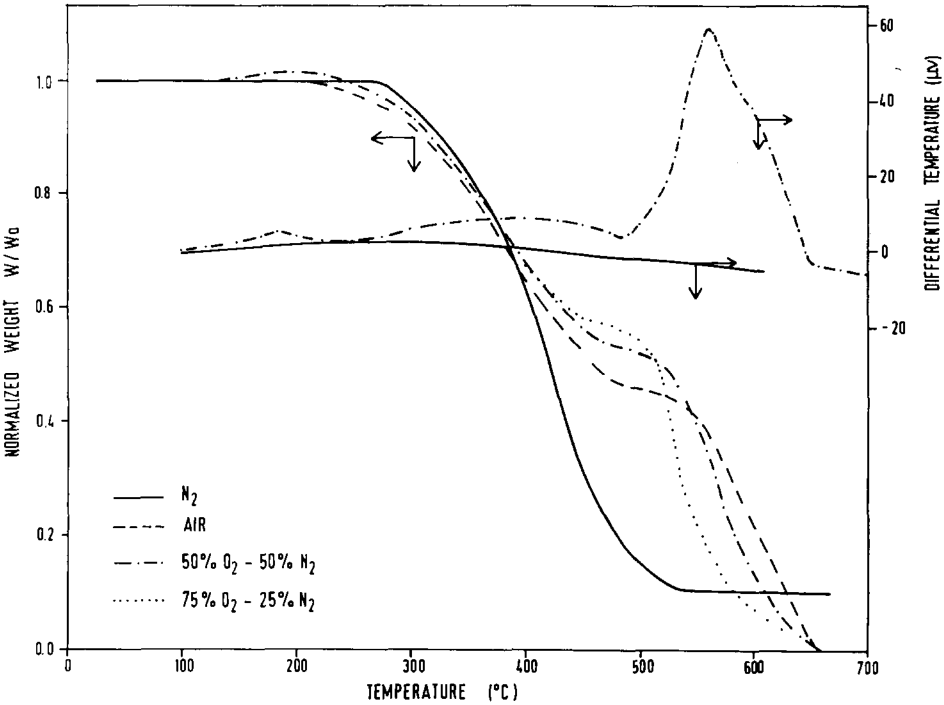

Fig. 1. TG and DTA curves for pristine PPA in N_2 and N_2–O_2 mixtures.

is about 12% of the original value and is approaching an asymptotic value. The temperature at which the plateau occurs and the rate of the subsequent rapid weight loss are dependent on O_2 concentration. At high O_2 concentration, the plateau is higher and is achieved at a lower temperature but the subsequent weight loss is also more rapid. For *cis*-PPA, the presence of O_2 also accelerates the initial weight loss which commences at about 100 °C. The weight loss characteristics at higher temperatures in the presence of O_2 are also similar to those of *trans*-PPA, with a plateau at around 450 °C followed by rapid weight loss. The weight remaining at the plateau region is also higher than that at the same temperature when N_2 is used. Masuda et al. [14] have carried out TG runs of *trans*-PPA in both air and N_2 up to 500 °C but did not address the differences between them.

Isothermal TG runs were also carried out either in N_2 or O_2 with the sample being maintained at 110–113 °C for 1 h. The N_2 runs do not show any weight changes while the O_2 runs show a weight gain of 4–5%. This increase in weight is probably due to the uptake of O_2 resulting in the formation of C=O or C–O type species. The presence of these groups was determined from XPS and IR absorption spectra (see below). The weight increase at about 185 °C, observed in the non-isothermal TG runs (Fig. 1), is probably due to the same phenomenon. Simultaneous TG–DTA scans show that this weight gain at 185 °C is accompanied by a small exothermic peak (Fig. 1). These scans also show that in the presence of O_2, the initial rapid weight loss step commencing at 250 °C is accompanied by minor energy changes, while the second rapid weight loss step is highly exothermic. In N_2, the energy changes associated with the PPA decomposition are much less prominent than when O_2 is present.

The thermal oxidation and pyrolysis mechanisms postulated for polyacetylene and polymethylacetylene [13,15,16] may also be representative of the processes occurring with PPA. Even at room temperature, PPA probably undergoes doping by oxygen to some extent as shown by the presence of oxygen-containing groups in the XPS C 1s core-level spectra of the pristine PPA (see later section). As the temperature increases, the oxidative attack on the polymer increases with the formation of ether, ketone, hydroxyl or perhydroxyl groups, and hence the observed weight gain as shown in the TG curves. As the temperature rises above about 200 °C, the formation of volatile products results in net weight loss. Since in the presence of O_2 the weight loss occurs at a lower temperature than in N_2, it may be possible that O_2 catalyses the formation of defects in the polymer chain and/or the oxygen-containing groups are less stable than the hydrocarbon products from chain scission and rearrangement during pyrolysis in N_2. At temperatures between 450 and 520 °C, slowing down of the weight loss in the presence of O_2 may indicate an increase in the stability of the residue. One possible explanation would be that O_2 promotes a certain degree of linkage formation between chains or condensation reactions in the residue. Above

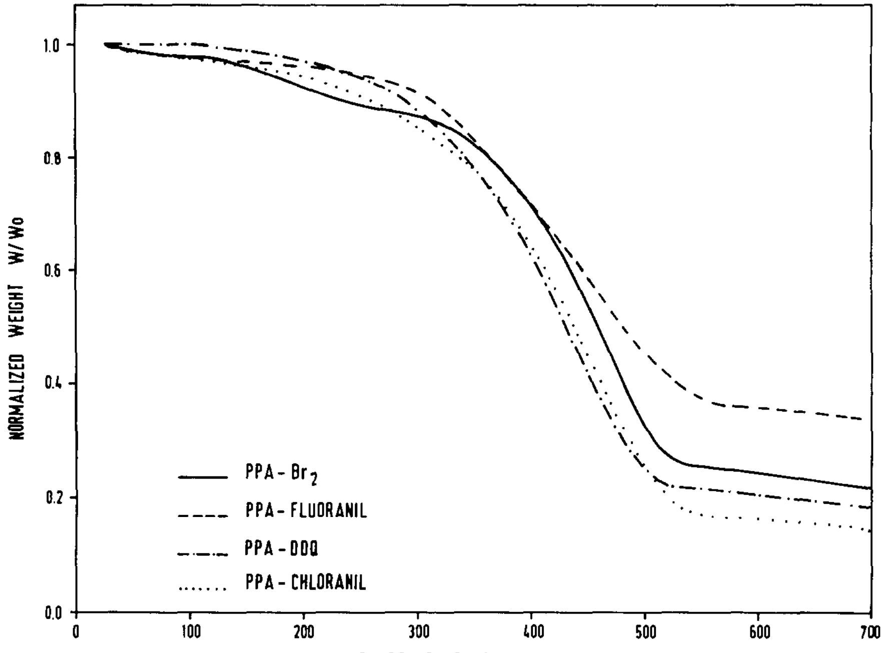

Fig. 2. TG curves for PPA–acceptor complexes in N_2.

550 ° C, the rapid weight loss is due to the combustion of the residue which results in volatile oxygenated products and heat evolution. In the presence of O_2, no carbonaceous char remains at 660 ° C.

The six different types of PPA–acceptor complexes generally show an initial lower degree of stability under heating than the pristine PPA. The TG curves for PPA–Br_2, PPA–fluoranil, PPA–DDQ and PPA–chloranil complexes in N_2 are shown in Fig. 2. The data shown in this figure are for an initial PPA : electron acceptor mole ratio of 1 : 0.10 in the case of Br_2, fluoranil and chloranil, and 1 : 0.18 for DDQ. The PPA–acceptor complexes generally show a gradual weight loss commencing below 150 ° C. The major weight loss still occurs after 270 ° C. The amount of residue remaining at 700 ° C is much higher with doped PPA. For example, with 10% fluoranil as much as 30% of the original sample is left as residue, compared with about 10% residue for pristine PPA. TG runs of the pure dopants show that no residue will remain at 700 ° C. The effect of dopants in increasing carbonaceous char yield has also been observed in the thermal pyrolysis of A_sF_5-doped and I_2-doped polyacetylene [15]. These dopants appear to facilitate the electron–proton exchange process and enhance the formation of proton-enriched products [15].

The TG curves for the PPA–acceptor complexes in air show a similar two-step weight loss process to the pristine PPA. In the temperature range

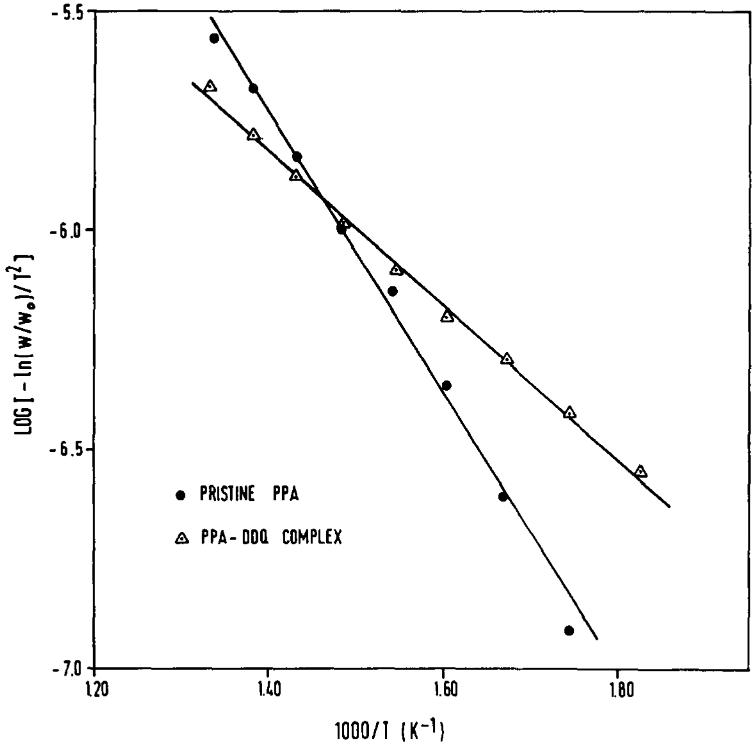

Fig. 3. Plot of first-order reaction using the method of Coats and Redfern [17].

450–520 °C, the weight of sample left in air is higher than in N_2. The mechanisms by which O_2 increases the stability of the pristine PPA residue are probably also applicable to the PPA–acceptor complexes at these temperatures. However, isothermal TG runs with the PPA–acceptor complexes in pure O_2 at 110–130 °C show insignificant weight gain, unlike the pristine PPA. It is possible that the electron acceptors interfere with the oxidative attack that results in the formation of hydroxyl, ether or other oxygen-containing groups in this temperature range.

The decomposition of PPA is expected to yield a variety of products. However, if the process is assumed to follow first-order kinetics, the apparent activation energy can be obtained from the TG data [17,18]. Figure 3 shows the first-order reaction plot by the method of Coats and Redfern [17] and the activation energy is estimated from the slope. The data show that for the pristine PPA, a straight line can be obtained between 325 and 475 °C and the apparent activation energy is about 16.9 kcal mol^{-1}. This value can be compared with the activation energies ranging from 0.2 to 22.3 kcal mol^{-1} reported for the formation of individual pyrolysis products from polymethylacetylene [15]. These values do not include the initial chain scission activation energy. From Fig. 3, it can be seen that the apparent activation energy for the pyrolysis of PPA–acceptor complexes is lower than for the pristine PPA. This lower value of apparent activation energy is consistent with the postulate that the dopants enhance the pyrolysis mechanisms [15].

In the presence of O_2, a straight line cannot be drawn between 300 and 475 °C. There is a slope change at about 380 and 450 °C which indicates a change in mechanism. Between 300 and 380 °C, the apparent activation energy is 11.7 kcal mol^{-1} compared with 16.9 kcal mol^{-1} in N_2.

Elemental and XPS analysis

Elemental analysis shows that the H : C mole ratio of the PPA samples heated in N_2 and O_2 at 110–130 °C for 1 h is 0.71, compared with 0.75 for an idealized chain of phenylacetylene units. The elemental analyses account for 98.67% of the materials in the N_2 heated sample, compared with 96.1% for the O_2 heated sample. The presence of oxygen in the samples may account for the lack of complete closure. The higher percentage of O_2 in the latter sample is consistent with the TG, XPS and IR absorption results. The similarity between H : C ratios of the samples heated in the absence and in the presence of O_2 at 130 °C suggests that hydrogen is not lost during the formation of oxygen-containing groups at this temperature. However, at higher temperatures the H : C ratio decreases, indicating hydrogen-enriched volatile products and, conversely, a hydrogen-deficient char.

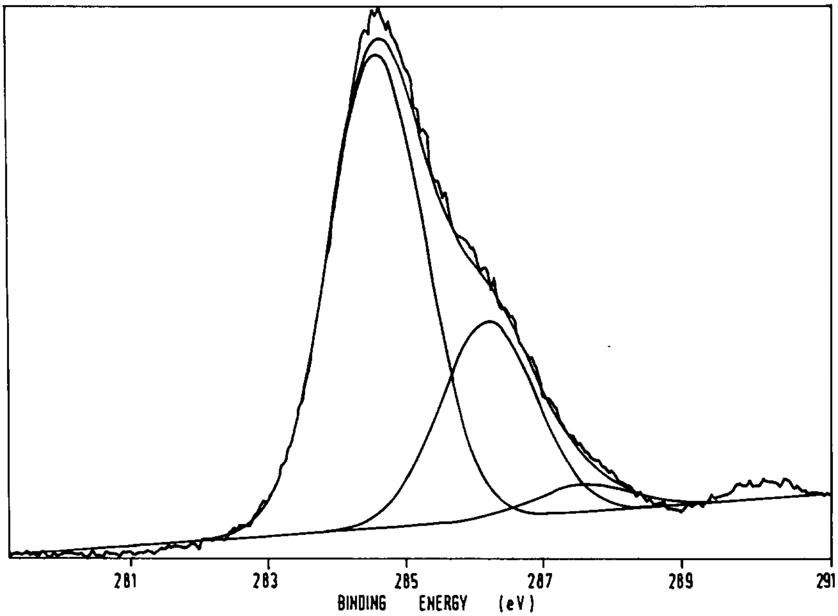

Fig. 4. XPS C 1s core-level spectrum of PPA after heating in O_2 at 110–130 °C for 1 h.

The XPS C 1s core-level spectrum of PPA after heating in O_2 at 110–130 °C for 1 h is shown in Fig. 4. The spectrum is skewed towards the high binding energy side with the main component peak at 284.6 eV attributable to the normal C atoms in the polymer. The spectrum can be deconvoluted into two other major components and a shake-up satellite at the high binding energy tail. The shake-up satellite is consistent with the retention of the aromaticity in the polymer. The peak at 287.6 eV is attributable to the carbonyl group, while the bigger peak at 286.3 eV is probably associated with the C–O structure. Calculations show that the proportion of C–O structures is about seven times that of the C=O group. This would be consistent with the postulate that at 130 °C, the formation of oxygen-containing groups involves primarily addition to the double bond in the chain rather than replacing the hydrogen atoms. The XPS spectrum of the pristine PPA also indicates the presence of C atoms bonded to oxygen but these groups form a significantly smaller fraction of the total C than the sample that has been heated in O_2. The IR absorption spectra also indicate that pristine PPA does not contain substantial amounts of oxygen-containing groups, while the sample which has been heated in O_2 does (see next section).

IR and UV absorption spectroscopy

The IR absorption spectra of the pristine PPA and the heated PPA samples are shown in Fig. 5. The IR absorption spectrum of PPA heated in N_2 at 110–130 °C for 1 h (Fig. 5b) is very similar to that of the pristine PPA (Fig. 5a). After PPA is heated in O_2 at 110–130 °C for 1 h, the IR absorption spectrum (Fig. 5c) shows absorption bands due to the O–H stretch at 3500 cm^{-1} and the C=O stretch at 1730 and 1675 cm^{-1} [13]. The band at 1260 cm^{-1} may be due to C–O and the increased absorption between 1000 and 1300 cm^{-1} could be associated with peroxy groups [16]. This indicates that the PPA reacts with O_2 to form oxygen-containing groups attached to the polymer and may account for the slight weight gain observed in the TG experiments. Figure 5d shows the IR absorption spectrum of the PPA sample after being heated to 450 °C in a 50% O_2–50% N_2 mixture. The absorption bands due to the presence of oxygen-containing groups shown in Fig. 5c are still present in this spectrum. However, the spectrum in Fig. 5d shows a marked decrease in intensity of many absorption bands, notably, the band between 3000 and 3100 cm^{-1} due to the aromatic C–H stretch, the bands at 1445 and 1495 cm^{-1} due to aromatic ring vibrations and the bands between 900 and 1100 cm^{-1}. The two bands at 695 and 755 cm^{-1}, attributable to the C–H out of plane deformation of monosubstituted benzene [19], are still very prominent. This spectrum indicates that after heating the polymer to 450 °C in a 50% O_2–50% N_2 mixture, the aromatic ring is still intact although loss of hydrogen and addition of oxygen have occurred with

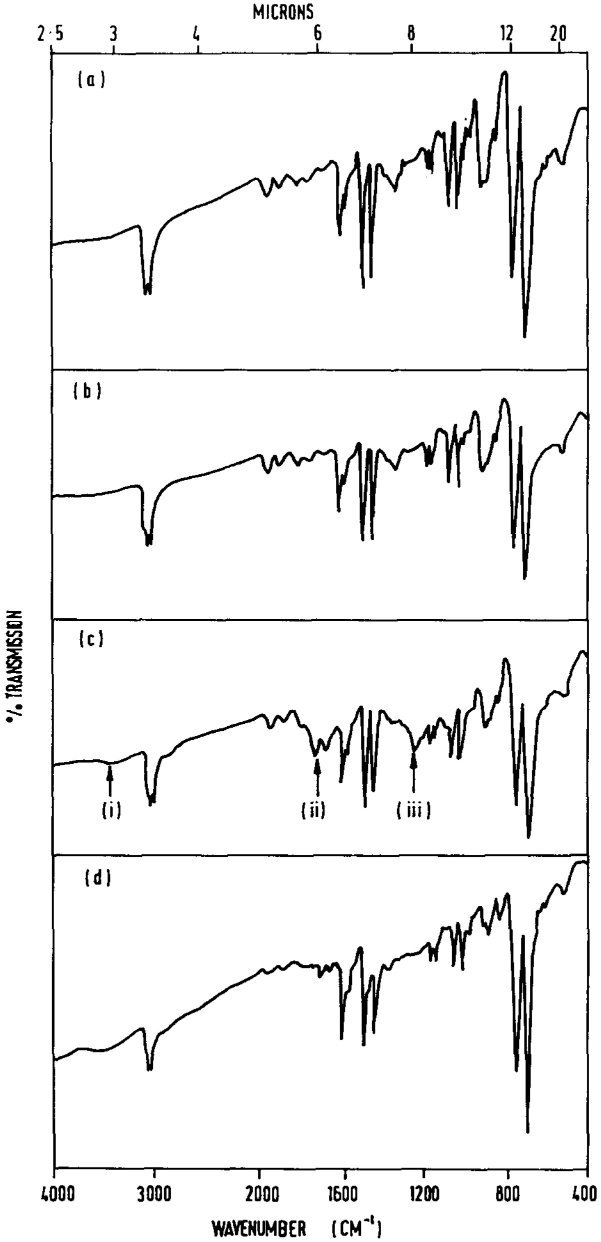

Fig. 5. IR absorption spectra of (a) pristine PPA; (b) PPA after heating in N_2 at 110–130 °C for 1 h; (c) PPA after heating in O_2 at 110–130 °C for 1 h and (d) PPA after heating in 50% O_2–50% N_2 mixture to 450 °C.

possibly the formation of linkages between chains. The XPS C 1s core-level spectrum of this sample shows the presence of the shake-up satellite, thus confirming the aromaticity of the polymer.

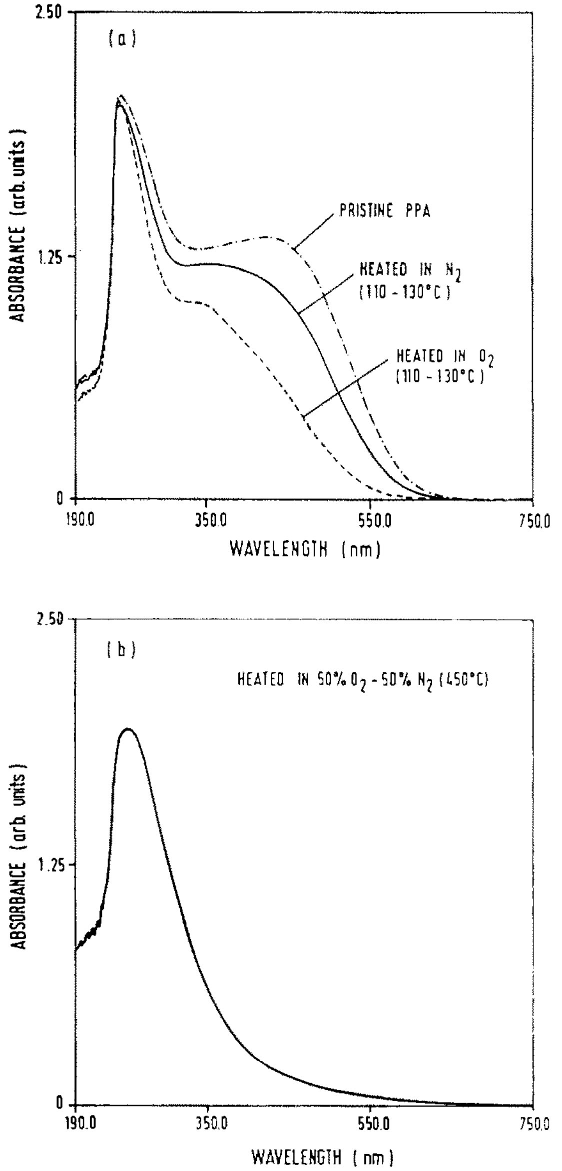

Fig. 6. UV-visible absorption spectra of (a) pristine PPA, PPA after heating in N_2 and O_2 at 110–130 °C for 1 h and (b) PPA after heating to 450 °C in 50% O_2–50% N_2 mixture.

The formation of oxygen-containing compounds in PPA heated in the presence of O_2 is expected to affect the extent of effective conjugation in PPA, which in turn will affect the photoconductive properties of the sample [2]. This is illustrated by the UV-visible absorption spectra in Fig. 6a. For the pristine PPA, the maximum absorption at about 245 nm is due to the phenyl ring substituent, while the absorption shoulder at 330 nm with a second absorption peak at 430 nm is attributed to effective conjugation in the PPA. When PPA is heated in N_2, there is some loss of effective conjugation. A similar loss in effective conjugation has been observed for PPA dissolved in organic solvents and this loss can be retarded with a decrease in temperature [7]. As expected, when oxygen is present, the loss of effective conjugation is accelerated both for solid samples and for PPA dissolved in organic solvents. When the PPA is heated to 450 ° C, the structure of the sample is drastically altered. The sample is only partially soluble in chloroform and the UV-visible absorption spectrum of the solution fraction (Fig. 6b) shows a drastic decrease of the effective conjugation shoulder. A reduction in solubility would be consistent with linkage formation between chains or condensation reactions.

Earlier studies [20,21] showed that heat treatment of low molecular weight PPA (thermally polymerized at 150 ° C) leads to degradation and crosslinking. Among the pyrolysis products were phenylacetylene, styrene and other aromatic hydrocarbons and a loss of solubility of the pyrolysed product was observed. Luminescence spectra [20] revealed that the PPA produced by thermal polymerization at 150 ° C contained conjugated blocks of only 3–4 units, compared with 4–7 units in PPA produced over Ziegler–Natta catalyst. Thermal treatment at 400 ° C was then found to increase the conjugation length of certain fractions separated by elution chromatography on Al_2O_3. In the present work, a loss of effective conjugation is observed when the PPA is heated to 450 ° C (Fig. 6b). However, since O_2 is used in the thermal treatment in the present work, this difference in results may be attributed to the reactions of O_2 with the polymer chain.

CONCLUSION

In this paper we address the differences in the degradation of PPA in the absence and presence of O_2, and the effects of halogen and organic electron acceptors on the degradation process. Pristine PPA readily reacts with O_2 at 130 ° C to form C=O, C–O and O–H groups which results in a weight gain. When PPA is heated, the effective conjugation decreases and the presence of these groups accelerates the process. In the presence of O_2, the loss of volatile products occurs at a lower temperature than in N_2 but in the former case, a plateau is reached at around 450 ° C before a second rapid weight loss step occurs. The slower rate of weight loss at this temperature when O_2 is present may be due to O_2 promoting linkage formation between chains or condensation reactions, thus rendering the residue more stable. Halogen or organic electron acceptor dopants have the effect of interfering with the formation of oxygen-containing groups at low temperatures, and promoting char yield during pyrolysis.

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