Photodegradation of poly(*o*-(trimethylsilyl)-phenylacetylene) in solutions

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Poly(*o*-(trimethylsilyl)phenylacetylene), poly(TMSPA) has been found to be highly stable in organic solvents in the absence of light and also in film form under ultra-violet/visible light irradiation. However, when poly(TMSPA) in chlorinated solvents is irradiated with ultra-violet and short-wavelength visible light, the polymer degrades and the rate of degradation is highest in the more highly chlorinated solvents such as $CHCl_3$ and CCl_4. After 2 h irradiation of a 2×10^{-3} M CCl_4 solution the molecular weight of poly(TMSPA) may decrease by almost two orders of magnitude. Ultra-violet/visible absorption spectroscopy suggests the presence of charge-transfer interaction between $CHCl_3$ and CH_2Cl_2 with the poly(TMSPA) after irradiation. X-ray photoelectron spectroscopy results indicate that chlorine is incorporated into the polymer during the degradation process.

(Keywords: photodegradation; poly(*o*-(trimethylsilyl)phenylacetylene); light irradiation; X-ray photoelectron spectroscopy; charge transfer)

INTRODUCTION

Poly(phenylacetylene), PPA, a conjugated polymer, develops significant semiconductivity on doping with organic[1] and inorganic[2,3] electron acceptors. It has also been found that solution-cast films of *trans*-PPA are semiconducting photoconductors when undoped, when doped with certain inorganic and organic electron acceptors and when sensitized with organic dyes[4–7]. We have recently shown that thin films of a Si-containing PPA derivative, poly(*o*-(trimethylsilyl)phenylacetylene), poly(TMSPA), also possess good photoconducting properties, which are different from those of PPA[8].

Earlier investigations into the stability of *trans*-PPA revealed that the PPA samples gradually lose effective conjugation when dissolved in organic solvents[9]. The rate of loss of effective conjugation is affected by the choice of solvents, temperature and solution concentration and is greatly accelerated by ultra-violet/visible (u.v./vis.) light illumination[9]. The introduction of the trimethylsilyl group into PPA has been found to retard the thermal oxidation of the polymer[10]. Similarly, the introduction of a Si-containing group into polyacetylenes greatly enhances the thermal stability[11]. The present study is concerned with the effects of solvents and light illumination on the stability of poly(TMSPA) and how the degradation differs from that of PPA.

EXPERIMENTAL

The monomer, *o*-(trimethylsilyl)phenylacetylene, was prepared by addition of alkali metals at the terminal and *ortho* positions of phenylacetylene, followed by silylation at both positions and then partial desilylation[12]. The polymer, poly(TMSPA), was prepared in toluene at 30°C in the presence of WCl_6–Et_3SiH catalyst, according to the method of Masuda *et al.*[13]. The polymer was recovered by precipitation into methanol. Poly(TMSPA) was dissolved in various solvents and these solutions were either kept in the dark or exposed to irradiation from a 150 W Xe arc lamp (Kratos LH151). Filters with various cut-off wavelengths were also used with the Xe arc lamp. The solvents investigated were tetrahydrofuran (THF), toluene, chlorobenzene, dichloromethane, chloroform and carbon tetrachloride. All the solvents were obtained from Merck (GR grade) with the exception of chlorobenzene, which was obtained from BDH. The effect of temperature on the degradation of poly(TMSPA) in solution was also investigated. At selected time intervals, the u.v./vis. absorption spectra and molecular weight were determined using a Shimadzu UV-260 spectrophotometer and a Waters 150°C gel permeation chromatograph respectively. For selected conditions, the solid was recovered from the solution after solvent evaporation and i.r. absorption spectroscopy (with a Perkin–Elmer model 682 spectrophotometer) and X-ray photoelectron spectroscopy (x.p.s.) were performed. The x.p.s. measurements were carried out on a VG Escalab Mk II spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The 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.

Solid poly(TMSPA) samples (either film or powder) were also subjected to u.v./vis. irradiation and elevated temperatures. The samples were characterized using the techniques mentioned above and the results were compared with those obtained from poly(TMSPA) in solutions.

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RESULTS AND DISCUSSION

Stability in solution in the absence of irradiation

In the absence of illumination, poly(TMSPA) shows a high degree of stability in the six solvents tested. There is no significant change in the u.v./vis. absorption spectra of the solutions even after 72 h at room temperature. In contrast, the u.v./vis. absorption spectra of PPA solutions in the dark show changes that are apparent after 1 h at room temperature. The effects of CCl_4 on the u.v./vis. absorption spectra of PPA and poly(TMSPA) are illustrated in *Figure 1*. The concentrations of both solutions are 2×10^{-4} M. The u.v./vis. absorption spectrum of pristine PPA shows a maximum absorption at ~260 nm, which is attributed to the phenyl substituent, followed by a broad absorption shoulder between 330 and 430 nm. The absorption shoulder is attributed to effective conjugation in PPA and the gradual blue wavelength shift of this shoulder when PPA is dissolved in organic solvents is probably due to the decrease in effective conjugation. It has also been reported that a blue wavelength shift in absorption bands occurs when the chloroform fraction of a chloroform–methanol solution of poly(3-hexylthiophene) is increased[14]. The correlation between the length of conjugated segments and the energies of absorption has been established[15] and the effect observed with poly(3-hexylthiophene) solutions has been interpreted as due to interruption of conjugation due to an increase in conformational defects in good solvents (e.g. chloroform)[14].

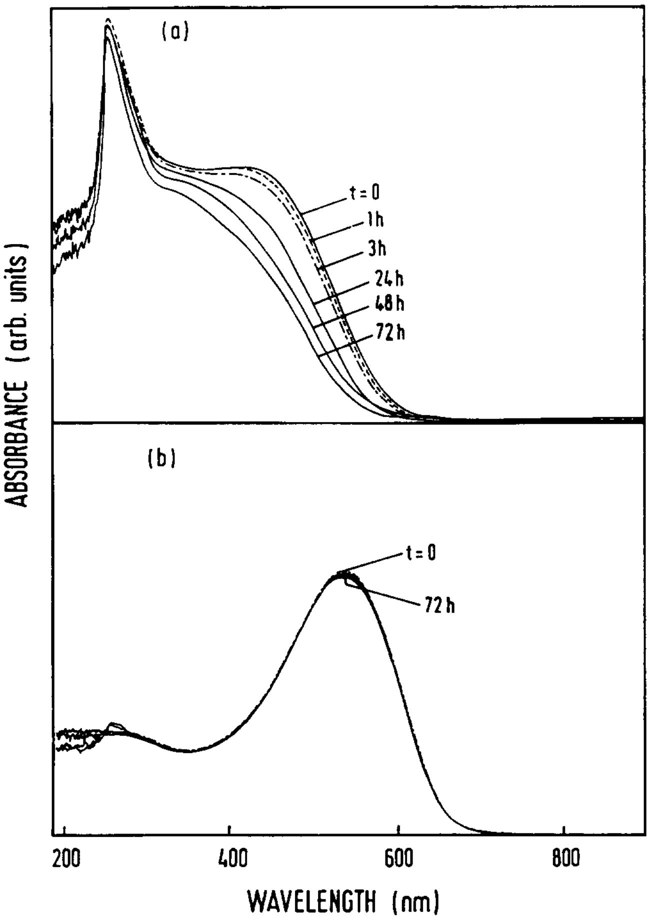

Figure 1 U.v./vis. absorption spectrum of (a) PPA in CCl_4 and (b) poly(TMSPA) in CCl_4. Solutions are not irradiated

The u.v./vis. absorption spectrum of poly(TMSPA) does not exhibit a prominent absorption band due to the phenyl ring (*Figure 1b*). The very broad and prominent absorption band is centred at about 540 nm. The u.v./vis. absorption spectrum suggests the presence of an extended conjugation from the polymer chain into the phenyl ring and this extended conjugation does not appear to be affected by solvents in the absence of light. The u.v./vis. absorption spectra of poly(TMSPA) solutions do not show substantial changes even after the solutions have been refluxed for 1 h. Thermogravimetric experiments with solid poly(TMSPA) in air indicate that there is no weight change until about 275°C. Thus, these results indicate that solid poly(TMSPA) and poly(TMSPA) dissolved in organic solvents are highly stable in the absence of light irradiation.

Effects of solvents under light irradiation

When poly(TMSPA) solutions are exposed to u.v./vis. irradiation, drastic colour changes may be observed depending on the solvent used. With toluene and THF, the poly(TMSPA) solution retains its original purple colour after several hours under irradiation and the u.v./vis. absorption spectrum of the solution shows no significant changes over the period of irradiation. The irradiation of poly(TMSPA) film for 6 h also induces no significant changes in the u.v./vis. absorption spectrum. However, when chlorinated hydrocarbon solvents are used, the u.v./vis. absorption spectrum of the solution after illumination shows a decrease in the intensity of the 540 nm absorption band. This effect in 2×10^{-4} M solutions is illustrated in *Figure 2*. With chlorobenzene as solvent, the u.v./vis. absorption spectrum also shows an increase in the intensity of the phenyl absorption band in the u.v. region (*Figure 2a*). However, for this solvent and CH_2Cl_2 (*Figure 2b*), the decrease in intensity of the 540 nm band is very much slower than when either chloroform or carbon tetrachloride is used (*Figures 2c* and *2d* respectively). When poly(TMSPA) in chloroform is irradiated, the decrease in intensity of the 540 nm band is very rapid in the first 16 min. However after this initial period, the absorbance of this band does not change significantly, but the band shifts to progressively shorter wavelengths. In CCl_4, the blue wavelength shift of the original 540 nm band is accompanied by a decrease in intensity. However, at 3.5 h, this band is no longer discernible and the u.v./vis. spectrum shows only one absorption band at 260 nm with an absorption shoulder extending to ~430 nm, which is similar to that of PPA (*Figure 1a*).

Comparison of the u.v./vis. absorption spectra of poly(TMSPA) film and solutions under light illumination and those of similar solutions kept in the dark indicates that poly(TMSPA) interacts with certain solvents in the presence of light. Experiments with various cut-off filters indicate that light of $\lambda > 460$ nm has no significant effect on the poly(TMSPA) solutions. The lower-wavelength limit is determined by the walls of the glass vessel containing the polymer solution, which prevent the transmission of most of the irradiation below 300 nm. The possibility of the solvent being a source of radicals in polymer degradation has been reported[16]. From degradation experiments with polystyrene and poly(α-methylstyrene), various modes of participation of the solvent have been proposed[17–21]. During γ-irradiation

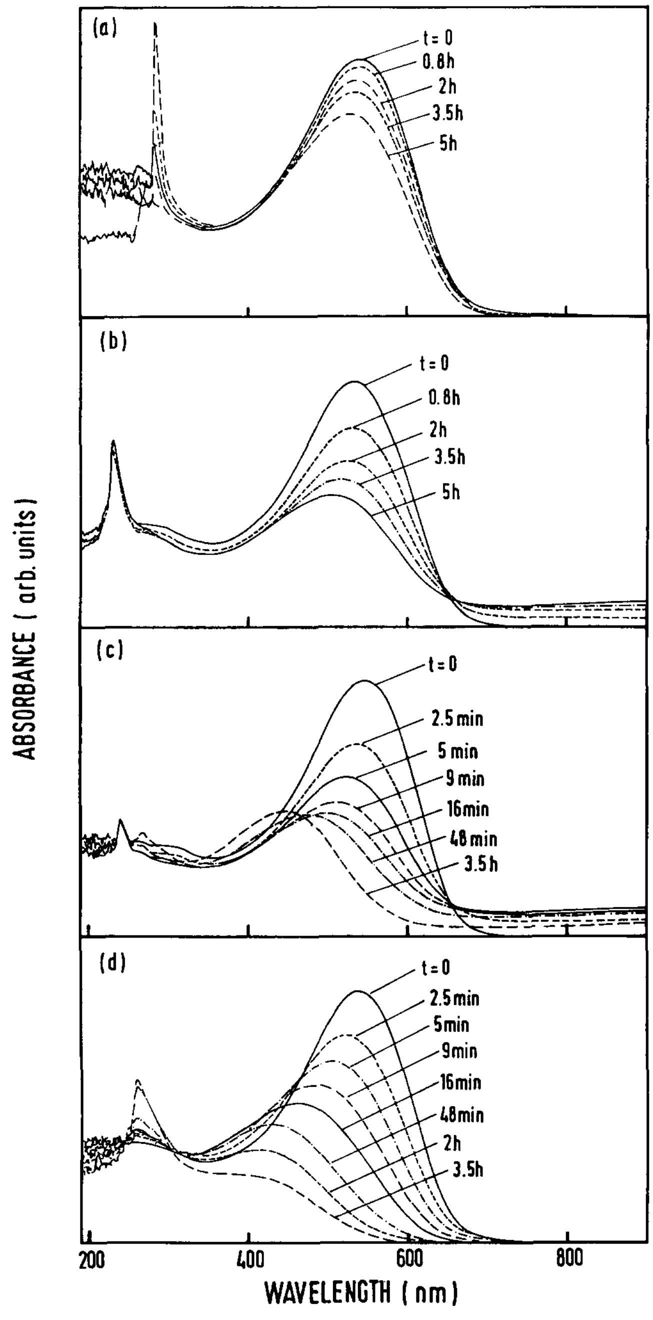

Figure 2 U.v./vis. absorption spectrum of poly(TMSPA) after light irradiation in (a) C_6H_5Cl, (b) CH_2Cl_2, (c) $CHCl_3$ and (d) CCl_4

of polystyrene in chlorinated solvents, Cl radicals are formed, which attack the polymer backbone at random[17]. Photolysis ($\lambda = 265$ nm) of poly(α-methylstyrene) in $CHCl_3$ and CCl_4 suggests that radicals may also be generated from the solvents by energy transfer from the polymer[18]. In the poly(α-methylstyrene)/$CHCl_3$ system, charge-transfer complexes between the excited polymer and solvent may be formed[19]. Other mechanisms proposed for long-wave irradiation (>270 nm) include the formation of molecular complexes between $CHCl_3$ and polystyrene, which decompose into radicals[20], and activation of polystyrene by energy transfer from solvents[21].

The results in the present work suggest that under light irradiation in the wavelength region of 300–460 nm, the Cl group in the solvent participates in the degradation of poly(TMSPA) (for example, comparing toluene and chlorobenzene) and the more highly chlorinated solvents, i.e. $CHCl_3$ and CCl_4, appear to have a more drastic effect on the degradation process. However, the rate of degradation and the interaction of poly(TMSPA) with $CHCl_3$ and CCl_4 are different. In $CHCl_3$, as the intensity of the absorption band of poly(TMSPA) at 540 nm decreases, an absorption tail extending into the near-i.r. region is observed (*Figure 2c*). At a concentration of 2×10^{-4} M, the intensity of the absorption tail increases to a maximum after about 9–16 min of light irradiation and then decreases. At 16 min, the intensity of the main absorption band (now shifted to 510 nm) is about half the pristine value. After 16 min, the intensity of this band does not decrease significantly but the band progressively shifts to lower wavelengths. A similar absorption tail extending into the near-i.r. region is also observed with CH_2Cl_2 as solvent, but not with C_6H_5Cl and CCl_4. As mentioned earlier, the trend in the decrease in intensity of the main absorption band is also different when CCl_4 is used as a solvent instead of $CHCl_3$.

The presence of the absorption tail extending into the near-i.r. region (*Figures 2b* and *2c*) suggests the existence of charge-transfer interaction between poly(TMSPA) and the solvent. An earlier study has shown that poly(TMSPA) undergoes charge-transfer interaction with certain organic electron acceptors[10]. With a strong electron acceptor such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), a prominent absorption tail extending into the i.r. region is observed, but no such absorption tail is observed with tetrachloro-*p*-benzoquinone (*p*-chloranil). In the present work, irrespective of whether a charge-transfer absorption tail is observed, the decrease in the intensity and wavelength of the main absorption band is accompanied by a decrease in molecular weight. This is illustrated in *Figures 3a* and *3b* for poly(TMSPA) in $CHCl_3$ and CCl_4 respectively. In the experiments to determine the effect of light irradiation on molecular weight, the concentration of the solutions used is 10 times higher than that of the solutions used to obtain the results in *Figure 2*. The more concentrated solutions show a slower rate of decrease in the intensity of the main absorption band (*Figure 3*). The molecular weight of the pristine polymer based on gel permeation chromatography with polystyrene calibration is between 10^5 and 10^6. The decrease in molecular weight is much more rapid with CCl_4 as solvent and, after 2 h of irradiation, the molecular weight has decreased by about a factor of 80.

The i.r. absorption spectra of pristine poly(TMSPA) and a degraded sample obtained by evaporating to dryness a poly(TMSPA)/CCl_4 solution after 2 h irradiation are compared in *Figure 4*. The prominent i.r. absorption bands of pristine poly(TMSPA) at 2900–3060 cm^{-1} (C–H stretch), 1250 cm^{-1} (CH_3 deformation of Si–CH_3 group), 1120 cm^{-1} (Si–phenyl group), 835 and 755 cm^{-1} (methyl rocking and Si–C stretch) and 725 cm^{-1} (1,2-disubstituted aromatic rings)[22,23] remain prominent in the spectrum of the degraded sample. However, the spectrum of the degraded sample shows two bands (I and II) that are absent in the spectrum of the pristine sample. Band I at 1690 cm^{-1} is attributed to the C=O group. During irradiation, the polymer may have reacted with O_2 from the air that is present in the glass vessel or dissolved in the solvent. Alternatively, the degraded polymer may react with O_2 in the air during the period of evaporation to dryness. PPA samples obtained from evaporating a $CHCl_3$ solution to dryness

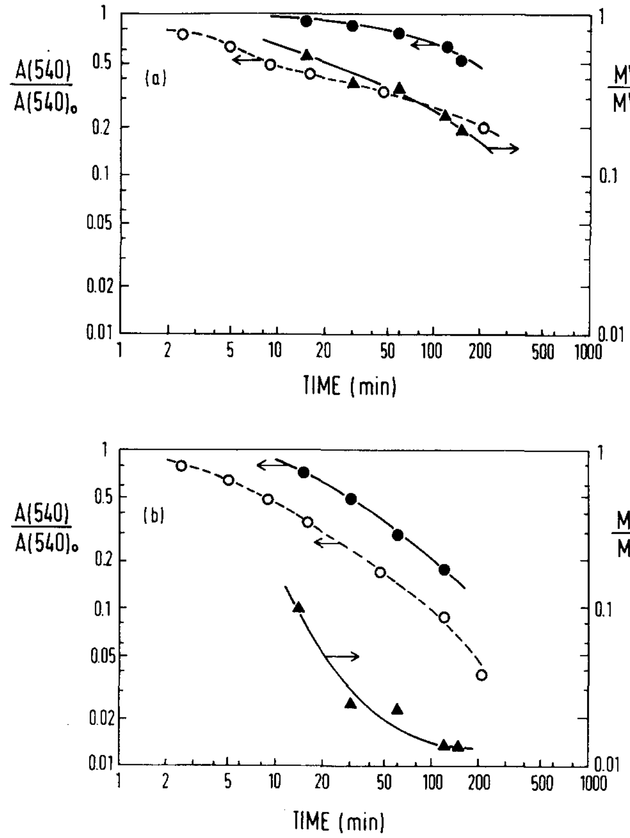

Figure 3 Effects of u.v./vis. irradiation on the absorbance at 540 nm ($A(540)$) and molecular weight (MW) of poly(TMSPA) in (a) $CHCl_3$ and (b) CCl_4. The subscript 0 denotes the values prior to irradiation. Concentrations of poly(TMSPA) solutions are 2×10^{-4} M (open symbols) and 2×10^{-3} M (filled symbols)

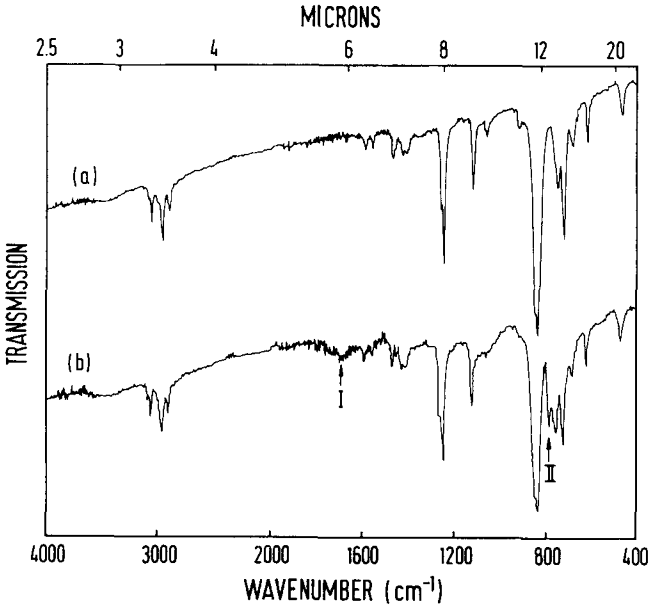

Figure 4 I.r. absorption spectrum of (a) pristine poly(TMSPA) and (b) degraded poly(TMSPA) after 2 h irradiation in CCl_4 solution

in air or O_2 have also been found to react with oxygen to form carbonyl and ether-type structures[9]. Band II at 785 cm^{-1} is in the region of bending of C–H bonds on aromatic rings, and may indicate the presence of trisubstituted aromatic rings[22]. Another possibility is band II is due to C–Cl bonds since it is in the aliphatic C–Cl region[23]. The x.p.s. Cl 2p core-level spectrum of the degraded sample from poly(TMSPA)/CCl_4 solution shows a main peak centred at about 200.5 eV (*Figure 5a*), which corresponds to the Cl $2p_{3/2}$ binding energy of chlorine bonded to C atoms[24], and a much smaller peak component at 199.2 eV. The x.p.s. Cl 2p core-level spectrum of a similar sample from poly(TMSPA)/$CHCl_3$ solution (*Figure 5b*) shows a lower binding energy component that is significantly larger than that in *Figure 5a*. In *Figure 5b*, the lower binding energy component amounts to about 66% of the covalent chlorine component. This lower binding energy component suggests the presence of an electron-rich environment in addition to the neutral covalent chlorine. Since the pristine poly(TMSPA) does not contain chlorine, the chlorine species incorporated in the degraded samples must be from the chlorinated solvents.

The wavelength region between 300 and 460 nm, where the photodegradation of poly(TMSPA) in chlorinated solvents occurs, corresponds to the region where the conjugated backbone of the polymer absorbs. Experiments with solutions of PPA in mesitylene when irradiated with light of $\lambda > 305$ nm indicate that certain π-bonds are broken[25]. In the present work, the polymer in its excited state may react with chlorinated solvents resulting in the generation of radicals. The main chain

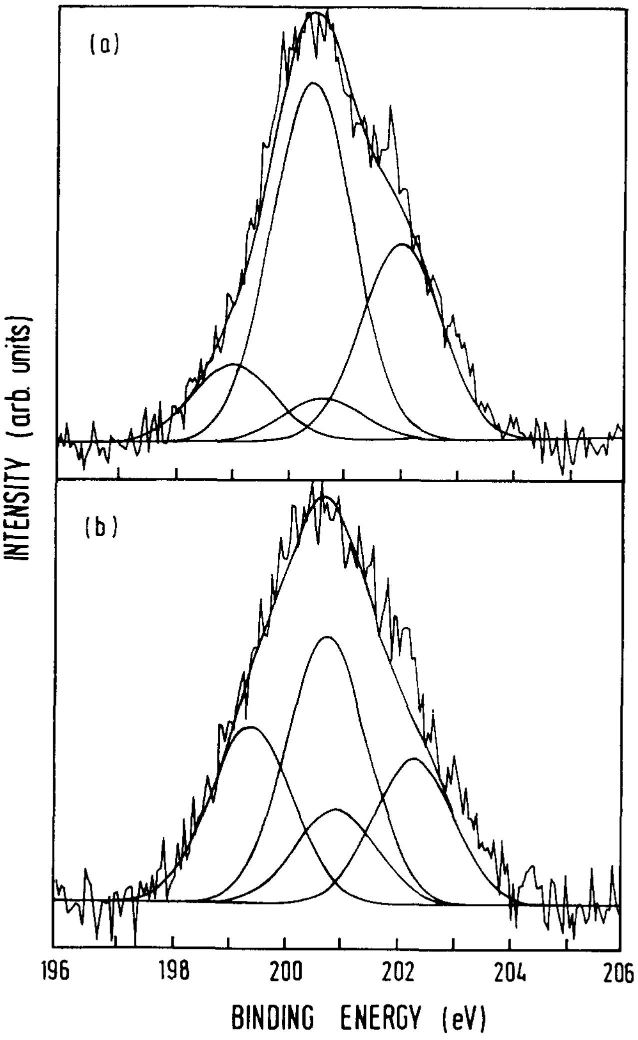

Figure 5 X.p.s. Cl 2p core-level spectra of samples from (a) poly(TMSPA)/CCl_4 solution and (b) poly(TMSPA)/$CHCl_3$ solution, after u.v./vis. irradiation

undergoes scission and chlorine species from the solvent may be incorporated into the polymer through covalent bonding. A portion of the chlorine may also participate in charge transfer with the conjugated π-bonds of the polymer. This would be consistent with the x.p.s. data, which indicate the presence of two chlorine environments. However, since the binding energy separation between the covalent chlorine and the lower binding energy component is 1.3 eV rather than 3 eV expected for ionic chlorine[26], the interaction between the chlorine and the polymer can be considered to involved only partial charge transfer. The x.p.s. data are consistent with the u.v./vis. absorption spectra in *Figure 2*, which show that the charge-transfer interaction between the polymer and chlorine is much more significant when $CHCl_3$ is used. However, the rate of main-chain scission, as indicated by the decrease in molecular weight of the polymer, is much more rapid in CCl_4.

The i.r. spectrum of poly(TMSPA) film after being subjected to irradiation for 6 h shows no difference from that of the pristine poly(TMSPA). The i.r. absorption spectrum and x.p.s. C 1s and Si 2p core-level spectra of a poly(TMSPA) sample after being heated to 270°C in a 50% O_2/50% N_2 mixture are also very similar to that of the pristine sample. No absorption bands due to oxygen groups such as O–H, C=O, C–O or Si–O groups are discernible in the i.r. absorption spectra of the heated sample and the irradiated film.

CONCLUSIONS

The incorporation of a trimethylsilyl group into the phenyl rings of poly(phenylacetylene) has resulted in a photoconducting polymer that is much more stable in organic solvents than PPA. In the absence of light, the loss of effective conjugation observed when PPA is dissolved in organic solvents does not occur with poly(TMSPA) even when the solutions are refluxed at atmospheric pressure for 1 h. However, in the presence of u.v. and short-wavelength visible light, poly(TMSPA) degrades in chlorinated solvents. During the degradation process, there is a decrease in the extent of conjugation and molecular weight. The degraded poly(TMSPA) reacts with chlorine from the solvent and oxygen. In contrast, solid poly(TMSPA) is highly stable to O_2 attack under prolonged periods of u.v./vis. irradiation as well as when subjected to elevated temperatures up to 270°C.

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