

Thermal Decomposition Kinetics of Iodine-Doped Polyacetylene in Vacuum

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Synopsis

The thermal stability of iodine-doped polyacetylene films, $(\text{CHI}_y)_x$, has been studied by means of electrical conductivity measurements, measurements on weight loss, and mass spectrometric analysis of desorbing species. When heated between room temperature and 125°C in vacuum, these films proved to be of poor thermal stability, being unstable at temperatures above 20°C. During the thermal treatments, molecular iodine desorbs from the films, resulting in an appreciable dopant weight loss with accompanying decrease in the electrical conductivity. The decomposition process does not follow simple kinetics.

INTRODUCTION

Polyacetylene, $(\text{CH})_x$, synthesized as freestanding, flexible, thin films according to the techniques developed by Shirakawa et al.^{1,2} has been one of the most investigated polymers during the past few years. Chiang et al.³⁻⁶ showed that these films undergo a dramatic change in their electrical properties when doped with electron acceptors such as the halogens and AsF_5 or with electron donors such as sodium naphthalide in a THF solution. By careful control of the doping reaction, films can be obtained having any desired conductivity ranging from insulators to semiconductors to metals. Thus, it has been shown⁷ that partially oriented AsF_5 -doped $(\text{CH})_x$ films have conductivities in excess of $10^3 \Omega^{-1}\text{cm}^{-1}$, a conductivity increase of more than 12 orders of magnitude compared with undoped *cis*- $(\text{CH})_x$.

A vast majority of the work done so far on $(\text{CH})_x$ and its doped derivatives has been concerned with clarifying the complex transport properties of these films.⁸ Since doped $(\text{CH})_x$ might be of potential use as active components in electrical devices, it is of fundamental importance to have a good knowledge of the thermal stability of these highly conducting films.

Although $(\text{CH})_x$ does not decompose with an observable weight loss at temperatures below 340°C,⁹ recent studies have argued that prolonged heat treatments above 100°C introduces defects in the conjugation of the polymer backbone, thus severely reducing the mechanical and electrical properties of the films.¹⁰ Studies on the thermal decomposition kinetics of AsF_5 -doped polyacetylene,^{11,12} $[\text{CH}(\text{AsF}_5)_y]_x$, showed that heating these films at temperatures

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between room temperature and 130°C under dynamic vacuum conditions ($<10^{-3}$ torr) resulted in a conductivity decrease, the rate of decrease increasing with increasing temperature. This conductivity decrease was shown to be caused by thermal decomposition of the active dopant species, AsF_6^- , into AsF_3 , As, and F_2 . The average activation energy for this decomposition, which was shown to follow first-order kinetics, was found to be 16 kcal/mol as determined by three different experimental techniques.¹¹

In this paper, we wish to report studies made on the thermal decomposition kinetics of another common $(\text{CH})_x$ derivative, namely the one doped with iodine.

EXPERIMENTAL

The $(\text{CH})_x$ films used in this study were prepared according to the techniques of Shirakawa et al.,^{1,2} at -78°C , using the $\text{Ti}(\text{OC}_4\text{H}_9)_4\text{—Al}(\text{C}_2\text{H}_5)_3$ catalyst system in toluene. Exposure of this solution to a 400-torr pressure of highly purified acetylene resulted in polymer formation on the surface of the catalyst solution which was spread on the glass walls of the polymerization reactor. The *cis*- $(\text{CH})_x$ so formed was, after careful washing with pure toluene, converted to the thermodynamically stable *trans*- $(\text{CH})_x$ by heating at 150°C for 30 min. The resulting 0.1 mm thick films had a *trans* content of 95% as determined from their infrared spectra. The films were stored under dry argon prior to use. Care was taken throughout the film preparation to minimize contact with oxygen by using inert atmosphere, Schlenk-tube techniques, and vacuum.

The doping was carried out in vacuum by simply exposing freestanding films of *trans*- $(\text{CH})_x$ to iodine vapor. Iodine vapor pressures of 0.3 torr and 0.03 torr were used to get films of high and low doping levels, respectively. The dopant concentration was determined by weight uptake of a reference sample doped simultaneously.

All conductivity measurements were carried out using the standard four-probe technique. The samples were mounted on Teflon frames. The electrical contacts were made using platinum wires and a low resistance graphite contact cement. The contacts were Ohmic up to 200 mA. Typically, the electrical conductivity measurements were carried out between 100 μA and 5 mA. The mounted samples were placed in a glass vessel which was evacuated. The heating was done by immersing the glass vessel in an oil bath which was held at different temperatures.

The mass spectra of desorbing species were recorded using a mass filter, Model 22PC180 GE Monopol Analyzer, attached to a high vacuum chamber. The samples, typically 1 cm^2 in size, were mounted on a heating stage and placed in the chamber which was subsequently evacuated ($<10^{-8}$ torr). The mass spectra were scanned up to $m/e = 300$, the electron beam energy being 70 eV. The temperature of the samples was monitored using a copper-constantan thermocouple pressed onto the surface of the films.

The weight loss measurements were performed using a Chan RH Automatic Electrobalance. Samples, typically 20 mg in weight, were suspended from a Pt-wire. Pt-wires were also used as counterweights. The whole balance was evacuated ($<10^{-2}$ torr) and an oil bath was placed around the sample tube of the balance. Calibration of the balance was done according to the basic procedures

for this balance. The accuracy of the weight loss measurements was estimated to be $\pm 5 \mu\text{g}$.

All the different experiments were carried out under dynamic vacuum conditions.

RESULTS AND DISCUSSION

Several different experimental techniques have identified iodine to be present as at least three different species in films of $(\text{CHI}_y)_x$. Thus, the I_5^- and I_3^- anions have been identified by use of Raman¹³ and X-ray photoelectron spectroscopy.¹⁴⁻¹⁶

In addition to these two active dopant species, molecular iodine, I_2 , is present in large amounts in films doped to saturation, i.e., in films of composition $(\text{CHI}_{\sim 0.25})_x$. This large excess of I_2 resides preferentially on the surface of the fibrils and is easily removed by vacuum pumping at room temperature. We found it essential in the thermal measurements to start out with a more stable dopant concentration. This was achieved by pumping our saturated samples in vacuum at room temperature overnight, thus obtaining a sample composition $(\text{CHI}_{0.14})_x$. At this composition, although not stable, the dopant concentration changes negligibly during the time used for starting the different experiments. The conductivity at this dopant concentration was $50 \Omega^{-1}\text{cm}^{-1}$.

During the initial heating period, at each temperature, the conductivity increases as previously reported.¹¹ After 2–5 min of heating, the conductivity starts decreasing, the rate of conductivity decrease increasing with increasing temperature. It is important to point out that in these $(\text{CHI}_y)_x$ films the conductivity maximum occurs before the film is thermally in equilibrium with the surrounding oil bath. In fact, we found, using a copper-constantan thermocouple pressed onto the surface of a $(\text{CHI}_{0.14})_x$ film, that it took 10–15 min for the sample to reach the temperature of the surrounding oil bath. The thermalization time increased slightly with increasing temperature. In order to facilitate a comparison, the initial conductivity σ_0 was chosen as the conductivity after 15 min of heating at each temperature.

In Figure 1, we show the relative conductivity σ/σ_0 as a function of time at different temperatures for films of initial composition $(\text{CHI}_{0.14})_x$. These kinetic curves are characterized by an initially fast rate of decrease in σ/σ_0 followed by a gradually slower rate for longer times.

In a separate experiment, the change in σ/σ_0 as a function of time at constant temperature (100°C) for films of different dopant concentrations was studied. Figure 2 shows that at high doping levels ($y = 0.14$ and $y = 0.082$), i.e., in the metallic regime, there is a small difference in the behavior of the curves with nearly a 2 orders of magnitude conductivity decrease in 7 hr. In contrast, at lower doping levels, close to the semiconductor–metal (SM) transition region ($y = 0.02 - 0.01$) and in the semiconductor region, the relative conductivity nearly reaches a steady state value in 7 hr.

In order to explain these features, we refer to Figures 3 and 4, which show the initial electrical conductivity of the $(\text{CHI}_y)_x$ films of Figure 2 as a function of dopant concentration and the change in conductivity of the films during the thermalization time, respectively. We observe from Figure 3 that above the SM-transition region the conductivity is nearly independent of dopant con-

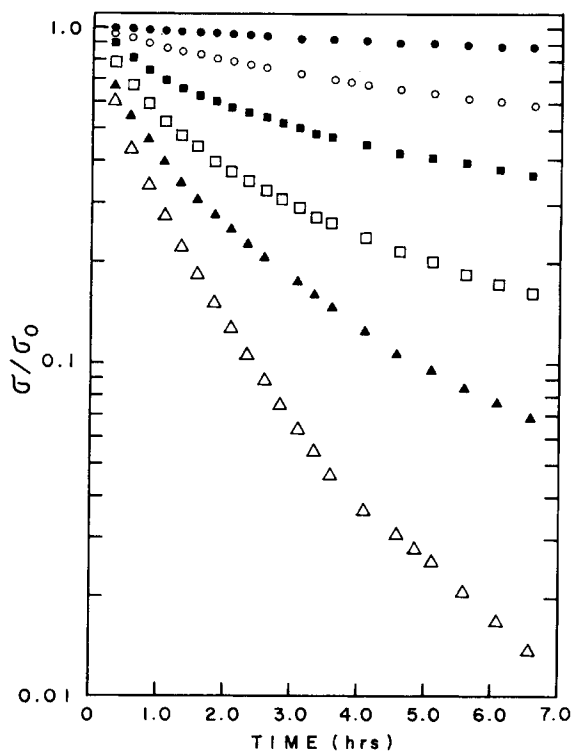


Fig. 1. Decrease in relative conductivity with time at higher temperatures ($^{\circ}\text{C}$) for $(\text{CH}_{10.14})$ films: (●) 21; (○) 50; (●) 60; (□) 80; (▲) 90; (Δ) 100.

centration, consistent with the behavior of the $y = 0.14$ and $y = 0.082$ curves of Figure 2. Once we are below the SM-transition region, however, the conductivity becomes very concentration dependent, so that a small dopant desorption will result in a considerable conductivity decrease. This behavior is clearly seen in Figure 4 for the films initially doped at $y = 0.013$ and $y = 0.0035$. The value of the steady state conductivity of doped films always remained higher than the room temperature conductivity value of the undoped $\text{trans}(\text{CH})_x$ film. We observed at 100°C a steady state value of $\sim 1 \times 10^{-4} \Omega^{-1}\cdot\text{cm}^{-1}$ for films initially doped to $y = 0.013$ and $y = 0.0035$ as compared with the room temperature conductivity value of $1.8 \times 10^{-5} \Omega^{-1}\cdot\text{cm}^{-1}$ for the undoped film. In an attempt to explain this observation, we measured the conductivity of an undoped $\text{trans}(\text{CH})_x$ film at higher temperatures. Table I summarizes these results.

TABLE I
Electrical Conductivity of Undoped $\text{Trans}(\text{CH})_x$ as a Function of Temperature

T ($^{\circ}\text{C}$)	Conductivity ($\Omega^{-1}\cdot\text{cm}^{-1}$)
25	1.8×10^{-5}
40	2.7×10^{-5}
60	3.0×10^{-5}
80	3.8×10^{-5}
100	5.7×10^{-5}
125	8.6×10^{-5}

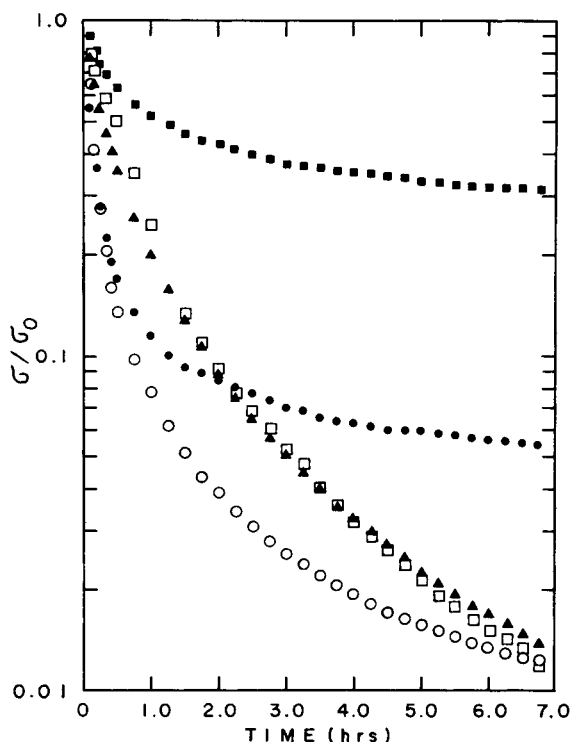


Fig. 2. Decrease in relative conductivity with time for films of different dopant concentrations at constant temperature (100°C). y : (■) 0.0035; (●) 0.013; (○) 0.048; (▲) 0.082; (□) 0.14.

We observe that, although increasing with temperature, the conductivity of undoped $(\text{CH})_x$ does not reach the steady state conductivity value at 100°C . The rapid arrival at steady state observed for the lower dopant concentration curves in Figure 2 should therefore be regarded as describing a state in which there still exist residual dopant species that are not removable at this temperature, rather than describing the undoped state.

In Table II, we give the initial relative peak intensities of desorbing species as observed in the mass spectra of $(\text{CHI}_{0.14})_x$ films when heated at different temperatures. The only fragments observed in addition to the residual gas spectra are those contributed by I_2 and HI . All fragments are observable at room

TABLE II
Relative Initial Peak Intensities of Desorbing Species from $(\text{CHI}_{0.14})_x$ Films at Different Temperatures

$T(^{\circ}\text{C})$	m/e				
	63.5 I_2^{+}	64 HI^{++}	127 I^{+}	128 HI^{+}	254 I_2^{+}
25	42	<1	100	26	16
60	39	<1	100	29	13
80	37	~1	100	31	11
100	33	2	100	35	9
125	30	3	100	42	7

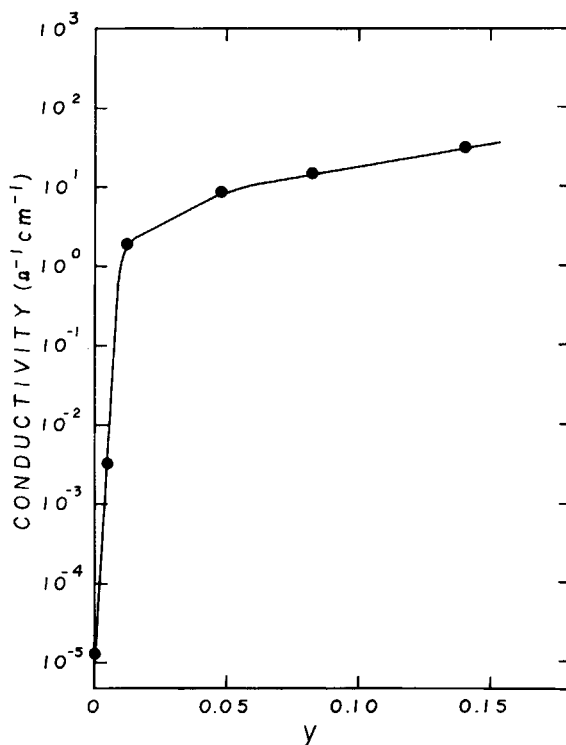


Fig. 3. Electrical conductivity of iodine-doped *trans*-(CH)_x films as a function of dopant concentration.

temperature. The relative peak intensities of all fragments decreases with time although the intensity ratio of HI/I₂ fragments increases with time at each temperature. It is possible that the observed HI is produced by desorbing I₂ reacting with moisture on the sample surface and/or in the surroundings, rather than being produced by partial dehydrogenation of the polymer itself. This is supported by the fact that under identical experimental conditions the mass spectra of gaseous I₂ matched the mass spectra of desorbing species from (CHI_{0.14})_x. We therefore believe that the only species actually desorbing from the doped polymer is gaseous molecular iodine I₂.

Figure 5 shows the ratio of the relative peak intensity I/I₀ for the I₂⁺ fragment at *m/e* = 254, vs. time at higher temperatures. I₀ is the relative peak intensity taken at the time when the sample was thermally stabilized (i.e., at *t* = 15 min). For short times, we observe a rapid decrease in I/I₀. The rate of intensity decrease then slows down and for long heating times tends toward zero, the steady value of the relative intensity decreasing with increasing temperature. We found that these desorption curves do not follow simple kinetics. In order to get an estimation of the activation energy of iodine desorption from the (CHI_{0.14})_x films, we used the method of initial slopes. From the Arrhenius plot in Figure 6 the activation energy was calculated to be 4.7 kcal/mol.

During the weight loss measurements, we observed a considerable iodine desorption during the thermalization period, i.e., during the first 15 min of heating. In Figure 7, we have plotted the iodine concentration of films of initial composition (CHI_{0.14})_x vs. the thermalization time at different temperatures. Thus,

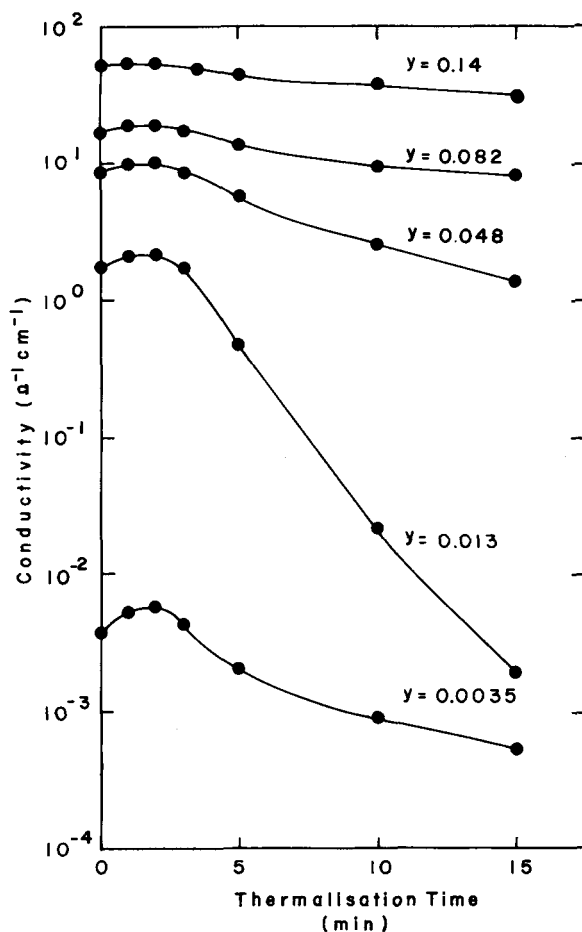


Fig. 4. Change in conductivity of films of different dopant concentration at constant temperature (100°C) during thermalization time.

at 125°C , the dopant concentration γ decreases from 14 to 8 mol % during 15 min. However, since we are in the metallic regime, this large dopant loss results in only a small decrease in the absolute conductivity.

Figure 8 shows the kinetic curves obtained from the weight loss measurements, where the relative dopant concentration $[I_2]/[I_2]_0$ is plotted vs. time at higher temperatures. The value of $[I_2]_0$ is the iodine concentration of the film at $t = 15$ min. The features of the weight loss curves are the same as those found from the mass spectrometric data; an initially fast desorption rate is gradually slowed down for longer heating times. A zero weight loss is reached for long heating times. Using the initial slopes of the kinetic curves in Figure 8, we calculated the activation energy for iodine desorption to be 4.7 kcal/mol, i.e., the same value as found from the mass spectrometric measurements. The corresponding Arrhenius plot is shown in Figure 6. The observed weight loss from films of low dopant concentrations ($\gamma < 0.02$) was too small to be accurately measured with the balance setup used.

In comparing the consistency of the results obtained by the different experimental techniques, we again refer to Figures 3 and 4. In light of the significant

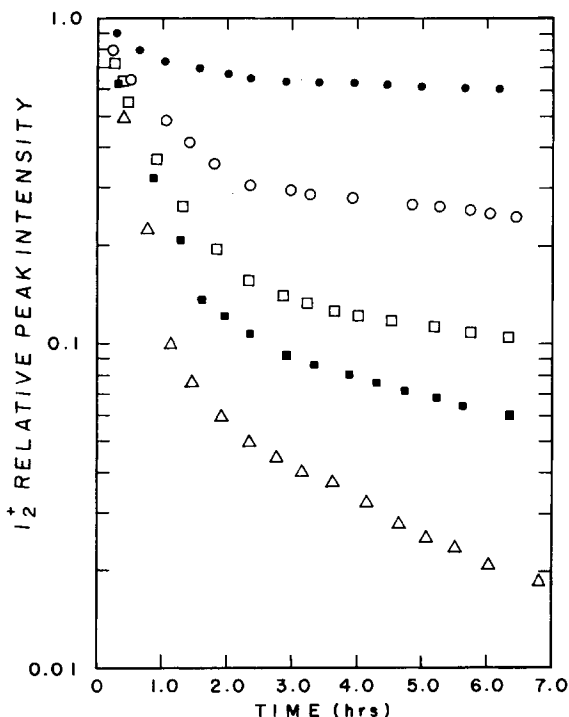


Fig. 5. Decrease in relative peak intensity of I_2^+ ($m/e = 254$) with time at higher temperatures ($^{\circ}\text{C}$): (●) 28; (○) 60; (□) 80; (■) 100; (△) 125.

dopant desorption during the thermalization time, the fact that the conductivity maximum earlier mentioned occurs before the film is thermally stabilized is easily understood. After the films are thermally stabilized, we observe an initially fast dopant desorption accompanied by a slow change in the absolute conductivity, consistent with Figure 3. Due to the temperature range and relatively short heating times used in these experiments, we did not reach the SM transition for our films of initial composition $(\text{CHI}_{0.14})_x$. However, the dopant dependency of the conductivity below the SM transition was confirmed by using films of different dopant concentrations as seen in Figure 4, and by observing a very small dopant weight loss in the lightly doped films. Rolland et al.¹⁷ recently reported similar findings using saturated samples, high temperatures ($80\text{--}180^{\circ}\text{C}$), and longer heating times.

Earlier studies have shown that one of the active dopant species is very sensitive to thermal treatment and to mechanical stress. Thus, X-ray photoelectron spectroscopy studies^{14-16,18} showed that the $I_{3d_{5/2}}$ core level can be deconvoluted into two separate peaks with binding energies of 620.6 and 619.0 eV. These two peaks have been assigned to the I_5^- and the I_3^- species, respectively, after comparing the peak shapes of model substances known to contain these species. It is noted that the higher binding energy peak, i.e., the I_5^- peak, decreases in intensity relative to the lower binding energy peak, i.e., the I_3^- peak, upon thermal treatment of the doped films. Similar observations have been made using Raman spectroscopy¹⁷; the I_5^- peak at 164 cm^{-1} decreases in intensity relative to the I_3^- peak at 107 cm^{-1} when the samples are heated. Rolland et al.¹⁷ recently showed that heating a saturated $(\text{CHI}_y)_x$ film at 110°C for 45 min increases the

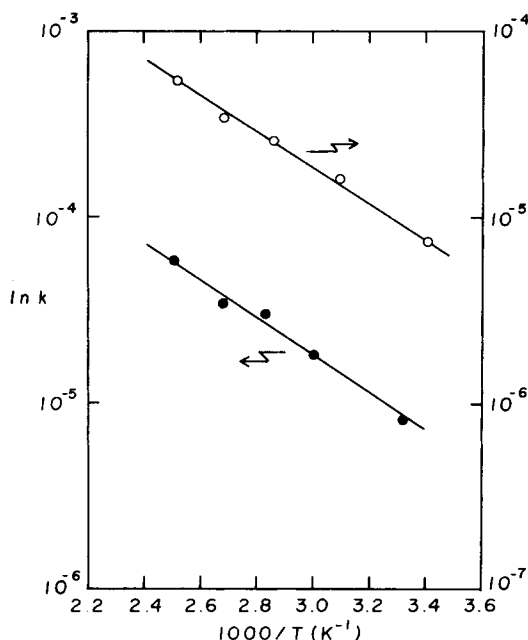


Fig. 6. Initial rate of decrease of relative peak intensity of I_2^+ vs. $1/T$ (●); initial rate of decrease of relative iodine concentration vs. $1/T$ (○).

intensity ratio (I_3^-/I_5^-) from 1.7 to 15. Allen et al.,¹⁹ using mass spectrometric techniques, found that the I_5^- species is present in the films preferentially at high doping levels.

Keeping these observations in mind, we suggest the following possible decomposition mechanism for highly doped $(CHI_y)_x$ films. Initially, iodine is present as the I_2 , I_5^- , and I_3^- species. The initially fast rate of dopant desorption is due to a simultaneous desorption of I_2 residing loosely on the surface of the

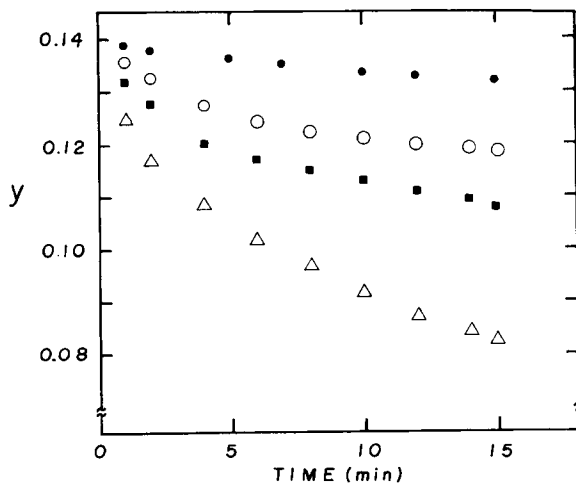


Fig. 7. Decrease in iodine concentration of $(CHI_{0.14})_x$ films during thermalization time. Temp ($^{\circ}C$): (●) 50; (○) 75; (■) 100; (Δ) 125.

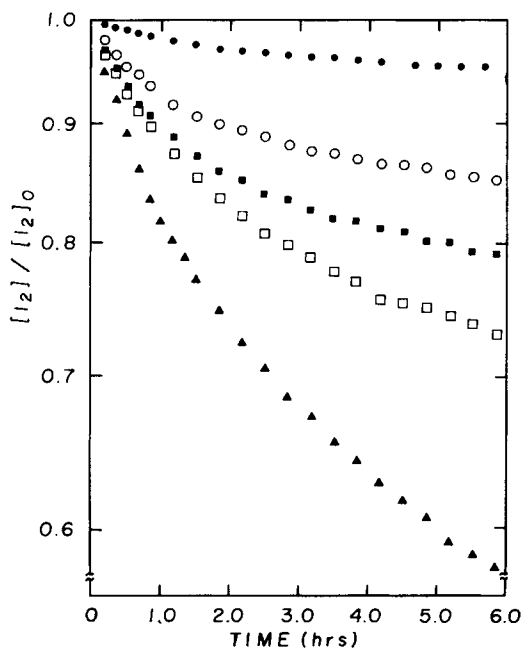


Fig. 8. Decrease in relative iodine concentration with time at higher temperatures ($^{\circ}\text{C}$): (●) 20; (○) 50; (■) 75; (□) 100; (▲) 125.

fibrils and of I_2 produced by the decomposition of the thermally less stable I_5^- into I_3^- and I_2 . This would, for short heating times, lead to a net increase in the concentration of the I_3^- species, which also have been observed by Rolland et al.¹⁷ using Raman spectroscopy. After longer heating times the rate of iodine desorption slows gradually down. This behavior can be viewed as a reduced rate of formation of I_2 , most of the I_5^- species already having been decomposed. At this stage the films are almost entirely doped by the I_3^- species. It is observed that the I_3^- Raman signal, after an initial increase, slowly decreases with time at higher temperatures. One might therefore assume that some of the I_3^- species slowly decompose into I_2 , resulting in the continued small observed dopant weight loss for longer heating times. We observed for one $(\text{CHI}_{0.14})_x$ film heated at 100°C for 36 h that a zero weight loss was reached after 22 h, giving a sample composition of $(\text{CHI}_{0.006})_x$. Thus, small amounts of I_3^- will remain in the polymer even after very long heat treatments at high temperatures, consistent with the observations made from the conductivity measurements.

CONCLUSIONS

In conclusion, we have shown that in contrast to $(\text{CH})_x$ films doped with AsF_5 ^{11,12} and SbF_5 ¹⁷ which are reasonably stable at temperatures up to $50\text{--}80^{\circ}\text{C}$, the $(\text{CHI}_y)_x$ films are stable only below room temperature in vacuum. Our results indicate that I_2 is the only desorbing species from the thermally treated $(\text{CHI}_y)_x$ films. Combining our results with earlier spectroscopic observations, a possible decomposition mechanism for these films is



If the films have been heat treated at temperatures low enough not to introduce defects into the conjugation of the system, the decomposition mechanism should be reversible, since redoping a $(\text{CHI}_y)_x$ film to saturation after short heat treatments makes the I_5^- species reappear.

The activation energies reported in this paper cannot be simply interpreted. Because these activation energies were obtained using the initial slopes of the desorption curves, i.e., at a time when I_5^- species still exist in the films, they might be regarded as composed of contributions from both the decomposition of I_5^- species and from diffusional effects of I_2 prior to desorption.

These studies and others^{11,12,17} indicate that it is necessary to undertake a systematic study of the stability of the numerous dopants used to date to establish the most stable $(\text{CH})_x$ derivative that might be used in practical applications.

The authors wish to thank Professor William J. James for helpful discussions. We also thank Mr. Scott McCullough and Mr. Bruce McCoy for doing some of the conductivity measurements as NSF Undergraduate Research Fellows during the summers of 1980 and 1981, respectively.

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Received February 16, 1982

Accepted November 29, 1982