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THE POLYMERIZATION AND OXIDATION OF PYRROLE BY HALOGENS IN ORGANIC SOLVENTS

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ABSTRACT

Simultaneous chemical polymerization and oxidation of pyrrole have been initiated by a halogenic electron acceptor, bromine or iodine, in various organic solvents. The polypyrrole (PPY)-halogen charge transfer (CT) complexes obtained from polymerization in acetonitrile are of particular interest. Both the PPY-I_2 and PPY-Br_2 CT complexes are granular in nature and have an electrical conductivity in the order of 1 to 10 ohm^{-1} cm^{-1}. Both complexes show remarkable stability in the atmosphere and in the presence of moisture. The PPY-I_2 and PPY-Br_2 CT complexes in the form of thin, coarse films have also been synthesized on a SnO_2 electrode by electrochemical polymerization in acetonitrile. The physicochemical properties of the PPY-I_2 and PPY-Br_2 CT complexes prepared by the chemical methods are characterized by means of UV-visible and IR absorption spectroscopy, thermal and chemical analysis, and electrical conductivity and density measurements.

INTRODUCTION

Electrically conductive conjugated polymers have been under intensive investigation in recent years [1, 2]. Most of the attention has been centered on three main classes of polymers: polyacetylene and its derivatives, polyphenylene and its derivatives, and poly(heterocyclic) polymers and cations [3]. Indeed, conducting polymers have emerged as a new class of electrical/electronic materials [4]. The interest in polyacetylenes arises mainly from their exceptional electrical properties when oxidized (doped) with an electron acceptor, such as iodine or arsenic pentafluoride [5]. Unfortunately, the electrical properties of doped polyacetylenes are not stable in ambient air [6], as is common for some other doped polymers with conjugated backbones.

The heterocyclic polymers are usually prepared by electrochemical polymerization in the form of highly conducting poly(heterocyclic) cations [7-9]. In particular, highly conductive polypyrrole (PPY) cations, such as PPY-BF_4, obtained by such a method in appropriate electrolytes have been extensively studied [10-13]. In contrast to chemically oxidized polymeric systems, PPY cations retain their conductivity when exposed to ambient conduction for long periods of time [11, 14]. Recently, polypyrrole systems have been investigated for their potential applications as electrode materials [15], and in Schottky diodes [16], photovoltaic cells [17], detectors [18], etc. The availability of stable conductive PPY in film form made by electrochemical polymerization has encouraged us to search for a chemical method of preparation.

PPY has been synthesized chemically in the presence of an acid or peroxide initiator [19,20]. However, such methods of preparation have resulted mainly in insulating PPY films with room-temperature conductivity typically of the order of 10^{-11} ohm^{-1} cm^{-1} [19, 21]. Moreover, such films are not completely stable in air even at room temperature [19]. These initially insulating films can be oxidized (doped) with bromine or iodine to achieve stable conductivity of the order of 10^{-5} ohm^{-1} cm^{-1} [19]. In this report we describe a relatively simple and novel method for the simultaneous polymerization and oxidation of pyrrole in organic solvents and in the presence of a halogen, such as Br_2 or I_2. The resulting PPY-I_2 and PPY-Br_2 charge transfer (CT) complexes are much more conductive and are relatively stable in ambient air. The physicochemical properties of these polymeric complexes are characterized by UV-visible and IR absorption spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), chemical analysis, electrical conductivity, and density measurements.

EXPERIMENTAL

Polymer Synthesis and Oxidation (Doping)

The pyrrole monomer used for the present study was obtained from Merck (Reagent Grade) and was purified by cold vacuum distillation before use. All solvents were of reagent grade and were used as received. Well-cleaned glassware was used, but no attempt was made to remove moisture/grease films or trace impurities. All polymerization work was carried out under a nitrogen atmosphere, unless specified otherwise. However, no special effort was made to exclude trace oxygen, and all samples were exposed to the atmosphere after removal from the reaction mixture.

The PPY-I_2 CT complex was synthesized in acetonitrile as follows. Solid iodine (1.5 g) (sublimed, Aldrich Chemical Co.) was dissolved in about 125 mL of acetonitrile. Pyrrole (1.5 mL) was then introduced into the acetonitrile solution with vigorous stirring. The color of the solution changed almost instantaneously from the original purple color of iodine to dark green, which is characteristic of the CT complex formation. The reaction mixture was stirred continuously for about 6-8 h. Black powdery precipitate began to appear in the solution mixture during stirring. The UV-visible absorption spectra of the acetonitrile solution alone showed an enhanced absorption in the entire visible region and extending into the near-IR region. This readily suggests the presence of soluble low-molecular-weight polymeric complex in the reaction mixture. The black precipitate was removed by filtration and rinsed thoroughly with copious amounts of acetonitrile, carbon tetrachloride, and methanol (in that order). The washing procedure was repeated until no unreacted monomer or acceptor could be detected in the methanol wash by UV-visible absorption spectroscopy. The black powdery material was subsequently dried by pumping in a rotary vacuum evaporator at 10^{-2} torr for at least 6 h. The yield was about 20-30%. The synthesis procedures were repeated in other solvents, such as chloroform and methanol. However, only traces of solid precipitate were obtained for reaction carried out in methanol.

The PPY-Br_2 CT complex was synthesized in acetonitrile by the procedure described above for the PPY-I_2 complex. In this case, about 0.6 mL of Br_2 (BDH Chemical, Reagent Grade) was used instead. Again, a black granular precipitate was obtained in the reaction mixture and was subjected to the same washing sequence as the PPY-I_2 complex. The yield was about 50-60%.

Attempts were also made to polymerize pyrrole electrochemically in acetonitrile solution according to the method of Diaz et al. [11]. However, the inorganic supporting electrolyte was replaced by either I_2 or Br_2 in the present experiment. The polymeric complex was synthesized at a constant positive potential on a SnO_2-coated glass slide (NESA) against a Pt counterelectrode. The film so deposited on the SnO_2 electrode was granular in appearance. As the film grew thicker, the polymer dropped off into the solution as a powdery precipitate. UV-visible absorption measurements indicated that the film was basically that of oxidized PPY (see below). Since I_2 or Br_2 alone in acetonitrile can also initiate the chemical polymerization and oxidation of pyrrole, as described above, we cannot at this stage differentiate between the polymers obtained from the two processes. Thus, the electrochemical polymerization was not studied further, and only the polymers obtained from the simultaneous chemical polymerization and oxidation in organic solvents will be characterized.

Polymer Characterization

The UV-visible absorption spectra were measured using a Shimadzu UV-260 spectrophotometer equipped with microprocessor. The spectrophotometer has a ceiling wavelength limit of 900 nm. The IR absorption spectra were measured on a Perkin-Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr pellets. DSC scans were performed on a Perkin-Elmer Model DSC-2C calorimeter, with a heating/cooling rate of 10°C/min under a constant flow of nitrogen. TGA scans were carried out using a Netzsch simultaneous TG-DTA apparatus, Model STA 409, at a heating rate of 10°C/min in nitrogen. The chemical compositions of the polymeric complexes were determined by elemental analysis. Electrical conductivities were measured by using both the standard four-probe and two-probe techniques. For electrical conductivity measurements, the polymer samples were pressed into thin circular disks of about 0.05-0.1 cm in thickness and 1.2 cm in diameter in a stainless steel press at a pressure of about 300 kg/cm^2. Densities of the polymeric complexes at 25°C were determined by the flotation method in an ethanol/tetrabromoethane mixture. The density of the solution mixture was measured using a PAAR calculating digital density meter, Model DMA 46.

RESULTS AND DISCUSSION

UV-Visible and Infrared Absorption Spectra

All the polymeric complexes obtained by the present chemical synthesis and oxidation have a granular morphology, although the films obtained at the initial stage of the electrochemical polymerization appeared to be somewhat uniform. Figure 1 shows the UV-visible absorption spectra of the black PPY-I_2 and PPY-Br_2 films deposited on the SnO_2-coated glass slide during the electrochemical polymerization. Since chemical oxidation and polymerization take place simultaneously in the electrolyte solution, the films deposited during electrochemical oxidation may have been blended to some extent with the PPY complex from the chemical polymerization. The UV-

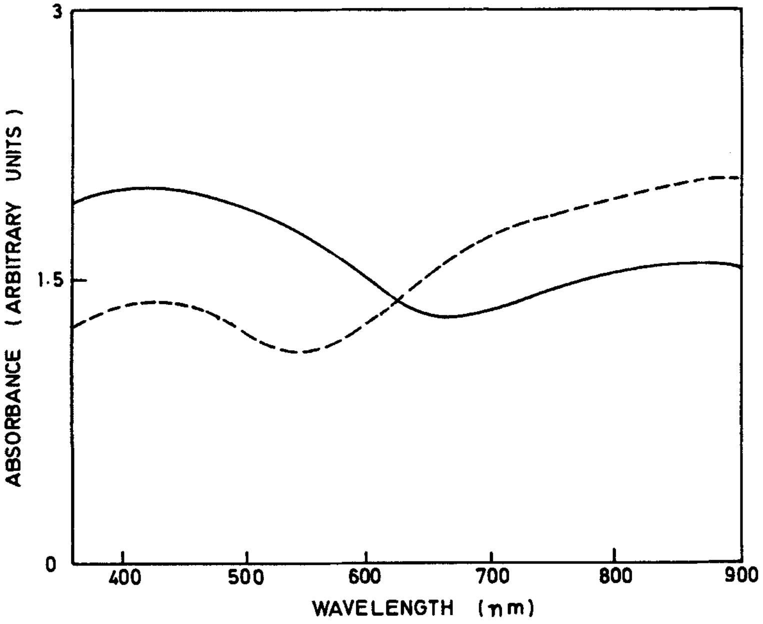

FIG. 1. UV-visible absorption spectra of the PPY-I_2 (—) and PPY-Br_2 (- -) CT complexes synthesized in acetonitrile.

visible absorption spectra of both the PPY-I_2 and PPY-Br_2 CT complexes reveal two relatively broad bands: one band centers at about 420 nm and is characteristic of polypyrrole [21, 22]; the other intense broad band, which appears in the red and extends well into the near-IR region, probably results from the CT interaction between the polymer and the halogenic electron acceptor, since undoped PPY does not have any appreciable absorption in the near-IR region [21]. The observed CT band in the red and near-IR is consistent with the absorption data reported by Kanazawa et al. [23] for oxidized PPY. These authors attributed the broad band peak near 1.0 eV to the conduction electrons.

The IR absorption spectra for the PPY-I_2 and PPY-Br_2 complexes synthesized chemically in acetonitrile solutions (Figs. 2a and 2b) show a featureless decrease in absorption from 4000 to 1700 cm^{-1}. This long absorption tail has been assigned to be the tail of the absorption peak located in the near-IR for oxidized PPY [3, 23]. The respective NH and CH stretching mode absorptions at about 3300-3500 cm^{-1} and 3000 cm^{-1} are obscured

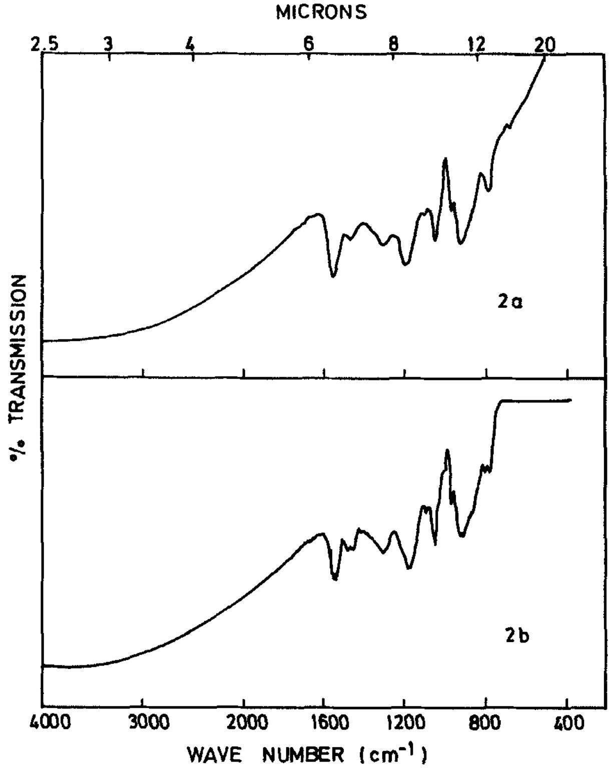

FIG. 2. Infrared absorption spectra of (a) PPY-I_2 complex and (b) PPY-Br_2 complex prepared in acetonitrile.

by the long absorption tail. However, the absorption spectra of both complexes below 1700 cm^{-1} are dominated by the pyrrole moiety. The bands at about 1540, 1300, 1170, 1030, and 900 cm^{-1} are all characteristic of PPY [3, 23]. Comparison of the absorption spectra between PPY-I_2 and PPY-Br_2 reveals minor differences in the relative absorbance of the respective PPY bands. This is probably due to the difference in the degree of CT interaction between the polymer and the halogen in the two complexes.

Chemical Compositions and Electrical Conductivity

Results of the elemental analysis of the PPY-halogen CT complexes prepared in acetonitrile solutions and their respective room temperature elec-

TABLE 1. Chemical Composition and Electrical Conductivity of the PPY-I_2 and PPY-Br_2 CT Complexes

Polymerization			
System	Medium	Chemical composition (normalized to C = 4.0)	Conductivity σ (ohm^{-1} cm^{-1}), 27°C
PPY-I_2	CH_3CN, 27°C	$C_{4.0}H_{3.0}N_{0.93}O_{0.69}(I_2)_{0.23}$	2
PPY-Br_2	CH_3CN, 27°C	$C_{4.0}H_{2.7}N_{1.0}O_{0.63}(Br_2)_{0.24}$	5

trical conductivities are summarized in Table 1. The elemental analysis data indicate that the present CT complexes are primarily polymerized pyrrole units plus the halogen.

For the PPY-I_2 CT complex, the stable, optimum stoichiometric composition corresponds to a ratio of about four pyrrole units to one molecule of iodine. The iodine content can be increased by further exposure of the sample to iodine vapor. However, no significant increase in electrical conductivity was observed, and the sample lost its excess iodine gradually upon returning to ambient air. The exact nature of the halogen anions remains to be determined by Raman spectroscopy, but near-UV absorption spectra measurements suggest the presence of triiodide species. In the case of the PPY-Br_2 CT complex prepared in acetonitrile solution, the conductivity is slightly higher than that of the corresponding PPY-I_2 CT complex. The stable, optimum stoichiometric composition for the present PPY-Br_2 CT complex also corresponds to a pyrrole:Br_2 ratio of about 4:1. Our recent results on the bromine-induced polymerization of pyrrole in aqueous media [24] indicate that a higher Br_2 content can be incorporated into the pyrrole polymer. However, no increase in electrical conductivity was observed, and the results of elemental analysis indicated that the composition of the polymeric complex varies with the method of preparation. Furthermore, electrophilic substitution of halogens on the pyrrole ring may not have occurred to a significant extent in both complexes. This is suggested by the simultaneous presence of a substantial effective conjugation length in both complexes, as indicated by the spectroscopic data, and a C:H:N mole ratio close to the theoretical value for a perfectly linear chain of disubstituted pyrrole rings (see below).

The oxygen contents of both polymeric complexes were determined by difference. They are somewhat lower than that of the PPY produced by the chemical oxidation of pyrrole [19]. However, the presence of oxygen in the present PPY-I_2 and PPY-Br_2 complexes readily suggests that both samples may have been doped to some extent by oxygen, as in the case of neutral and oxidized PPY films obtained by electrochemical polymerization [22]. Interaction of electrochemically oxidized PPY film with oxygen can result in a significant enhancement of the UV-visible absorption spectra but has virtually no effect on its electrical conductivity [22]. Polymerization of pyrrole by chemical oxidation always results in the presence of a substantial amount of pyrrolidinone carbonyl structure [19, 20, 26], which gives rise to an IR absorption band at about 1700 cm^{-1} [19]. However, this carbonyl absorption band is not observed (Fig. 2) in the IR spectra of the present PPY-I_2 and PPY-Br_2 CT complexes synthesized in acetonitrile under a nitrogen atmosphere. The C:H:N mole ratios in the PPY-I_2 and PPY-Br_2 CT complexes are rather close

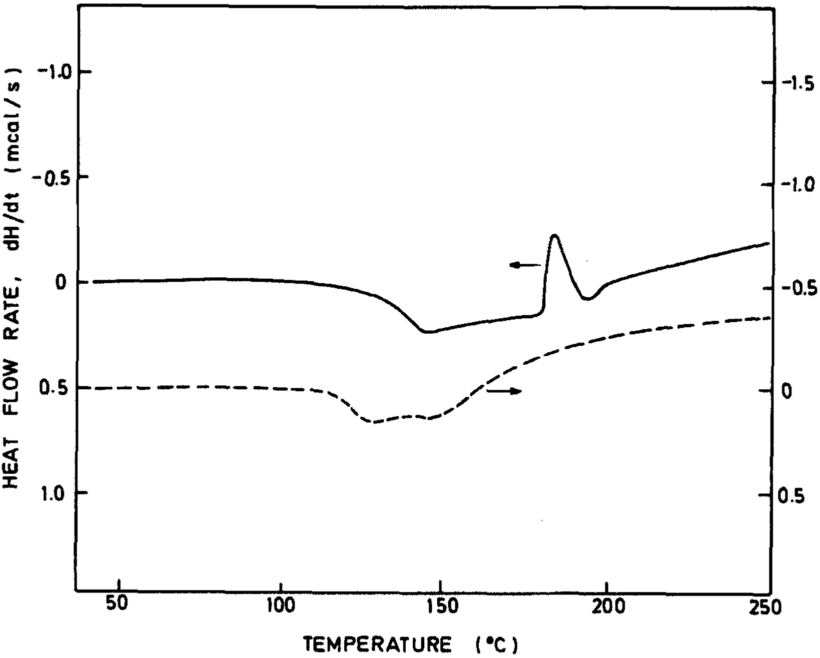

FIG. 3. DSC scans of the PPY-I_2 (—) and the PPY-Br_2 (– –) complexes prepared in acetonitrile.

to the theoretical value of 4:3:1 for a perfectly linear chain of disubstituted pyrrole rings [11]. The slight deficiency in H in the present PPY-Br_2 complex suggests the simultaneous presence of α and β linkages for some of the pyrrole units in this complex, probably as a result of crosslinking or chain branching. The simultaneous presence of α,α' coupling and β coupling of the pyrrole moiety has been reported for the products of some chemical oxidation reactions [25, 26]. Furthermore, based on the observation that the H mole ratios in the present complexes are equal to or less than 3, we are tempted to conclude that both PPY-I_2 and PPY-Br_2 may not contain any significant amount of pyrrolidine units and/or partially saturated units although the presence of these has been suggested for the chemically [19] and electrochemically [22] synthesized PPY.

We wish to emphasize that both the PPY-I_2 and PPY-Br_2 CT complexes synthesized in acetonitrile are stable in the atmosphere. The electrical conductivity of both complexes shows only a weak temperature dependence near and below room temperature in four-probe conductivity measurements. However, treatment of either CT complex with concentrated NH_4OH solution for prolonged periods of time returns the polymer to an insulating state. The treatment also results in a distinctly blue-shifted absorption spectrum, suggesting a decrease in the effective conjugated length of the polymer. This may readily arise from the reaction of some PPY cationic sites with ammonia species to produce interruptions in the conjugation length of the polymer chain.

The flotation densities of the PPY-I_2 and PPY-Br_2 CT complexes synthesized by the present CT polymerization technique in acetonitrile were determined to be 1.89 and 1.75 g/cm^3, respectively.

Effect of Solvents

Attempts were also made to prepare the PPY-I_2 CT complexes in other organic solvents. For reactions carried out in chloroform solution, the IR absorption spectra of the black precipitate still retain most of the characteristic features of oxidized PPY. However, the intensity of the absorption tail between 4000 and 1700 cm^{-1} is much reduced and a new absorption band appears at about 1400 cm^{-1}. Furthermore, the electrical conductivity of this complex is almost five orders of magnitude lower than that of the PPY-I_2 complex prepared in acetonitrile. For reactions carried out in methanol, only traces of black precipitate were obtained. The IR absorption spectra of the precipitate show an even more substantial deviation from that of oxidized PPY. The electrical conductivity of this material is characteristic of that of an insulator. These results are consistent with the observations that the composition of the chemically oxidized pyrrole varies substantially with the method of preparation and the reaction medium [19, 20, 25]. It appears that chemical oxidation and polymerization of pyrrole by halogens are facilitated by the presence of aprotic solvents, as in the case of electrochemical oxidation and polymerization [11].

Thermal Properties

The DSC scans of the PPY-I_2 and PPY-Br_2 CT complexes are shown in Fig. 3. The scan for the PPY-I_2 CT complex shows a broad exothermic peak centered at about 145°C and a relatively sharp endothermic peak at about 183°C. It is interesting to note that the peak at about 183°C not only coincides with the vaporization temperature of iodine (184°C), but also corresponds to the onset of major weight loss for the PPY-I_2 CT complex (see TGA data below). Thus, the endothermic process at 183°C may be associated with the physical vaporization or removal of I_2 from the complex. The nature of the exothermic reaction between about 120 and 170°C is not clear at this stage, but is probably associated with the further oxidation and/or crosslinking of PPY by the halogen, since this exothermic process is not associated with any noticeable weight loss or decomposition reaction (see TGA data). The arguments for the nature of the two thermal processes are further supported by the fact that in the second heating, after the sample is allowed to cool from 250°C to room temperature, the scan becomes featureless, consistent with the irreversible nature of the proposed reactions. The thermal behavior of the PPY-Br_2 CT complex differs somewhat from that of the PPY-I_2 CT complex. The DSC scan is featureless at the vaporization temperature of bromine (59°C), but shows a major exothermic reaction between 120 and 160°C. This exothermic process is irreversible and is not observed on a second scan. The peak temperature of this reaction at around 140°C also corresponds to the onset of major weight loss in TGA (see below). Thus, this exothermic process may be associated with the thermal decomposition reaction of the PPY-Br_2 complex.

The thermogravimetric scans in nitrogen of the PPY-I_2 and PPY-Br_2 CT complexes synthesized in acetonitrile are shown in Fig. 4. Both complexes retain more than half of their original weight when heated to a temperature as high as 750°C. The PPY-I_2 complex is stable to heating up to slightly above the boiling point of iodine (184°C) when it begins to lose weight gradually. Similar thermal stability at temperatures below 184°C is observed for scans carried out in air, except that the complex loses almost all of its weight at 750°C. Similarly, the PPY-Br_2 CT complex is thermally stable up to the decomposition temperature of about 140°C. In both cases the weight loss is associated with a loss in electrical conductivity. In comparison, oxidized PPY films obtained from electrochemical polymerization lose 7-10% of their weight when heated between room temperature and 250°C. Above this temperature, the weight loss becomes more rapid [10].

CONCLUSIONS

A relatively simple and novel method for the simultaneous chemical polymerization and oxidation of pyrrole by halogens in appropriate solvents has been described. Due to the ionic nature of this process, the degree of CT interaction is dictated to a large extent by the solvent medium used. In fact, almost no polymerization was observed for reactions carried out in protic solvents, such as methanol. The PPY-halogen CT complexes prepared

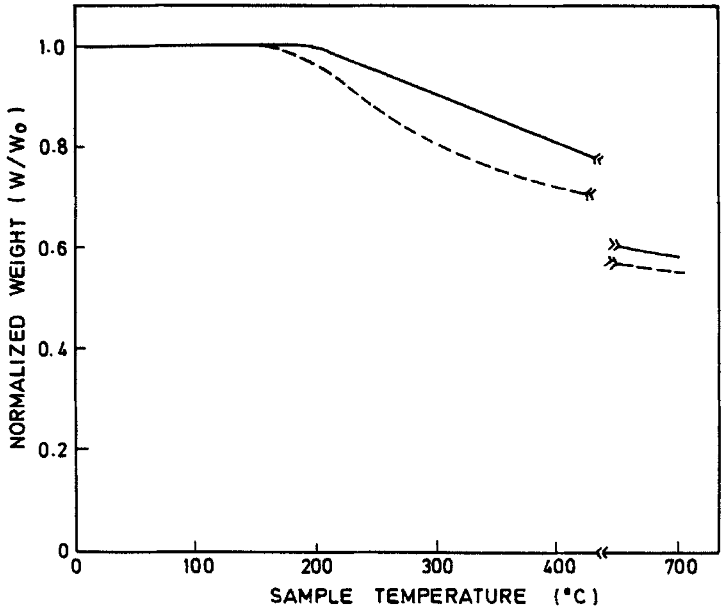

FIG. 4. TGA scans of the PPY-I_2 (—) and the PPY-Br_2 (- -) complexes prepared in acetonitrile.

in acetonitrile are granular in nature and show good thermal stability. Both complexes exhibit electrical conductivities of the order of 10^0 to 10^1 ohm^{-1} cm^{-1} and are remarkably stable in the atmosphere. Recently, stable PPY-I_2 and PPY-Br_2 complexes with conductivities as high as 30-40 ohm^{-1} cm^{-1} have also been synthesized at temperatures below room temperature. The detailed electrical and electronic properties of the PPY-I_2 and PPY-Br_2 complexes are currently being investigated in our laboratory.

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