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## CHEMICAL PREPARATION AND CHARACTERIZATION OF CONDUCTIVE POLYPYRROLE COMPOSITE THIN FILMS

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### ABSTRACT

Chemically synthesized polypyrrole (PPY) composites with poly-methyl methacrylate (PMMA), using sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) or bromine ( $\text{Br}_2$ ) as the oxidant, have been prepared and studied by thermogravimetry (TG) and x-ray photoelectron spectroscopy (XPS). Results show PMMA/PPY oxidized by persulfate yields the best films. In the case of the PMMA/PPY/bromine composite. XPS results suggest interaction between the bromine dopant and the PMMA substrate. The dopant anion in the persulfate oxidized films is identified to be mainly  $\text{HSO}_4^-$  instead of  $\text{SO}_4^-$ . The bulk concentration of the dopant is about 30% by weight, which is higher than that found at the surface. In addition, the degree of doping as assessed by charged nitrogen by XPS is found to be between 10 and 15%. The air side is rich in the matrix polymer while the oxidized side is rich in PPY. Such films combine good electrical properties with excellent mechanical strength of the matrix polymer. Extensive penetration of the conducting PPY/bromine system into

the PMMA substrate was observed, in marked contrast to previously prepared PMMA/polyaniline laminate films.

## INTRODUCTION

Polypyrrole (PPY) has been much studied as a potential electroactive material for use in the electronics field [1–3]. Appropriate chemical or electrochemical oxidative polymerization of pyrrole in aqueous or non-aqueous medium generally leads to the conductive form holding one unit positive charge for every 3–5 pyrrole rings, with overall neutrality maintained by the incorporated anions [4–6]. PPY produced in this manner usually takes the form of intractable, bulky powders or weak, brittle films with a low level of processibility.

Many methods exist to fabricate conductive PPY in the form of thin, tough films suitable for commercial applications [7–10], the most promising of which is to support PPY with a commodity polymer like polyethylene [10], polymethyl methacrylate (PMMA) [11], polyurethane [12], and paper [13]. Such films combine the good electrical properties of PPY with the mechanical strength and desired characteristics of these polymers. In principle, it is possible to electrochemically deposit PPY on any polymer substrate as a bi-layer thin film if a suitable solvent to swell the supporting polymer can be found. However, this approach suffers the inherent difficulty of obtaining large film areas and high cost. Recently, monolayer thin films of conducting PPY have been fabricated by the Langmuir-Blodgett technique [14].

Morita [11] recently reported a relatively simple chemical route to obtain large PMMA/PPY/persulfate films by oxidizing a pyrrole-PMMA solution over the surface of an aqueous oxidant. Optimization of experimental variables was reported, but with little detailed characterization of these films. In this article we report the results of preliminary investigation into the structure of these systems by bulk techniques including elemental analysis and thermogravimetry, as well as surface techniques like x-ray photoelectron spectroscopy (XPS) and surface conductivity measurements. The reported method of preparation was modified in this work to ensure the fabrication of high quality films. We have recently reported [15] XPS results of laminate thin films comprising PMMA or polystyrene (PS) with electroactive polyaniline (PANI) incorporated with HCl dopant. Significant differences found between the PPY and the PANI systems will be discussed in later sections.

## EXPERIMENTAL

### Chemicals

Pyrrole from Aldrich Chemical Co. was vacuum distilled and kept in the dark before use.  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{Br}_2$ , PMMA ( $M_n = 260,000$ ), and butanone were of reagent grade from BDH and used as received.

### Synthesis of PPY Composite Thin Films

Concurrent polymerization and doping of pyrrole monomer at the interface between PMMA solution and the aqueous layer is affected by the persulfate or bromine initially dissolved in the aqueous phase. Gradual volatilization of the solvent yielded a free-standing composite film for characterization.

Pyrrole (0.20 mL, 2.9 mmol) was mixed with 0.5 mL of 10 wt% PMMA/butanone solution to give a single-phase mixture. This was then carefully introduced onto the surface of the aqueous oxidant containing 0.79 g (3.3 mmol)  $\text{Na}_2\text{S}_2\text{O}_8$  or an equivalent amount of  $\sim 0.17$  mL  $\text{Br}_2$  in 7.5 mL deionized water. The oxidizing solution was initially placed in a Petri dish to a depth of  $\sim 1$  mm and an area of  $\sim 60$  cm<sup>2</sup>. The PMMA/butanone and pyrrole solution was spread over this area, taking care not to mix the layers. Polymerization was allowed to proceed at 27°C for 2 h, after which the formed film was removed, rinsed with deionized water, and dried to constant mass under dynamic vacuum at 50°C.

### Elemental Analysis

The elemental analyses were conducted by the Microanalytical Laboratory using a Perkin-Elmer model 240C C, H, N analyzer. The halogen content was determined by the oxygen flask method.

### Thermal Analysis

Oxidative thermal degradation studies were performed on a Du Pont 9900 thermal analyzer under a dynamic air flow of 75 cm<sup>3</sup>/min at a linear heating rate of 10°C/min from room temperature to 700°C. The samples were run in the form of films of  $\sim 2$  mg weight.

### X-Ray Photoelectron Spectroscopy

The thin films were mounted onto a standard VG holder by double-sided Scotch tape. Core level spectra were obtained on a VG ESCA/SIMSLAB MK II spectrometer using  $MgK_{\alpha}$  radiation, operating on a fixed retardation of 40. The binding energies were referenced to the hydrocarbon component in the C1s envelope, defined at 285.0 eV to compensate for surface charging. Surface atomic stoichiometry ratios were obtained from peak area ratios corrected with appropriate experimentally determined sensitivity factors. Deconvolution of overlapping spectra components were performed on VG software.

### Electrical Conductivity

Conductivity measurements were made by using a four-point probe connected to a Keithley voltmeter constant-current source system. Six measurements were made on each side of the composite film.

## RESULTS AND DISCUSSION

The persulfate oxidized films are opaque black with the air side possessing a smooth glossy appearance of PMMA while the oxidized side has the rich black matt appearance of the PPY. PMMA/PPY/persulfate gives the best composites which are easily obtained as large continuous films. On the other hand, bromine-oxidized films are of poor quality with distinct yellow-brown and black regions. All experiments were performed on the black regions which were judged to have a higher PPY density. The thickness of the composite films is in the order of 60–100  $\mu\text{m}$ .

Considerable morphology differences exist between these PPY composites and the polyaniline composites synthesized earlier [15]. The use of polar butanone as the organic phase apparently allows the oxidizing  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{Br}_2$  to migrate into the organic layer and polymerize pyrrole at the interface as well as inside the PMMA. This is in contrast to the earlier aniline/chloroform system in which aniline was rapidly extracted into the acidic aqueous layer as the soluble anilinium ion; the polymerization was initiated only at the interface with a limited amount of aniline available to give a very thin layer of doped polyaniline.

### Elemental Analysis

Bulk elemental composition of the films is presented in Table 1. Little useful information can be derived because of interfering contributions from all the film components, viz., PPY, PMMA, and traces of residual solvents. However, it is interesting to note that the bulk S/N ratio is  $\sim 0.3$  and the Br/N ratio is 0.6, which will be compared with the surface composition later in this article.

### Thermogravimetry

The TG and DTG curves of PMMA and PMMA/PPY/persulfate composite are shown in Fig. 1. It can be seen that the conducting PPY/persulfate system exerts a small stabilizing effect on PMMA. The temperature of the maximum weight loss has increased from 320 to 375°C, and a decrease in the rate of weight loss compared to that of PMMA (55%/min, not shown in the derivative scale in Fig. 1) is also observed. In the case of the PMMA/PPY/bromine system (see Fig. 2), the weight loss between 100 and 200°C is due to the loss of some of the bromine dopant as previously reported [16]. Of the two composites, the PMMA/PPY/persulfate system is more thermally stable up to 375°C, after which there appeared to be a reversal of stability. In both systems there was zero weight residue at about 600°C, indicating the absence of refractory inorganics. The sub-

TABLE 1. Bulk Elemental Analysis Results for PMMA/PPY/Bromine and PMMA/PPY/Persulfate Composites

Sample	% Composition						Calculated atomic ratio <sup>b</sup>
	C	H	N	Br	S	O <sup>a</sup>	
PMMA/PPY/ persulfate	53.2	5.3	7.9	—	6.2	28.4	C <sub>7.9</sub> H <sub>9.3</sub> N <sub>1.0</sub> O <sub>3.1</sub> S <sub>0.34</sub>
PMMA/PPY/ bromine	49.4	6.0	3.9	13.3	—	27.4	C <sub>14.8</sub> H <sub>21.2</sub> N <sub>1.0</sub> O <sub>2.1</sub> Br <sub>0.6</sub>

<sup>a</sup>Determined by difference.

<sup>b</sup>Normalized to N = 1.0.

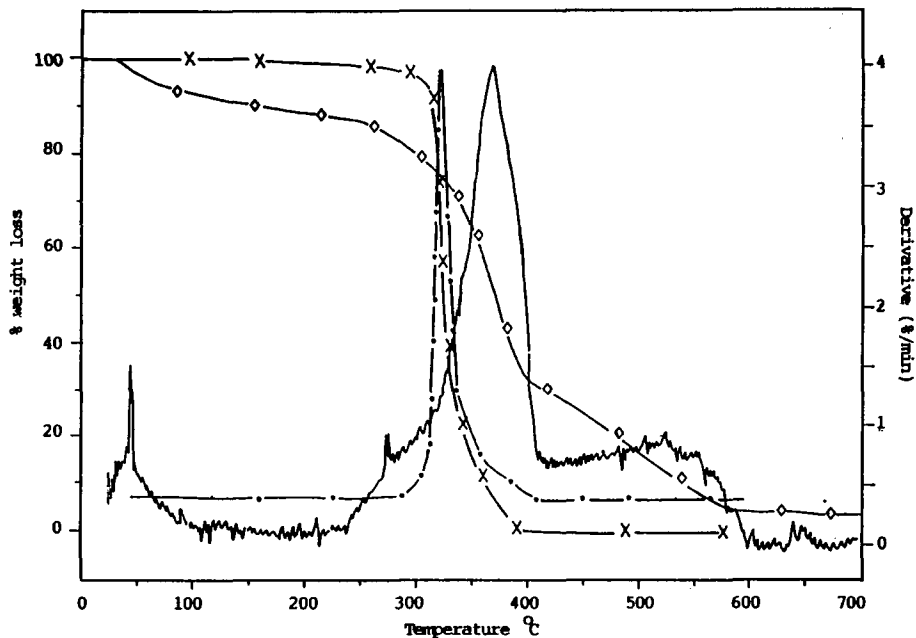


FIG. 1. TG curves of PMMA (×) and PMMA/PPY/persulfate (◇) composite. DTG curves of PMMA (·) and PMMA/PPY/persulfate (—) composite.

stantial increase in the rate of weight change between 500 to 600°C observed in the PMMA/PPY/bromine system suggests the decomposition of a species formed by the interactions of the three components.

### X-Ray Photoelectron Spectroscopy

XPS is a particularly powerful tool to examine the surface composition of films. The use of XPS in the study of conducting polymers has been reported extensively [17–21]. Spectra of interest were fitted to Gaussian component peaks. The position, intensity, and peak width (FWHM) of the main components were unambiguous. The position and intensity of other component peaks were then optimized to give the best fit to the experimental spectrum while maintaining the same FWHM.

Atomic concentration ratios, after correction for the appropriate sensitivity factors, at the surface of the air and oxidized sides are shown in Table 2. The C1s and O1s envelopes of the air and oxidized sides of the PMMA/PPY persulfate composite are shown in Figs. 3 and 4. It can be

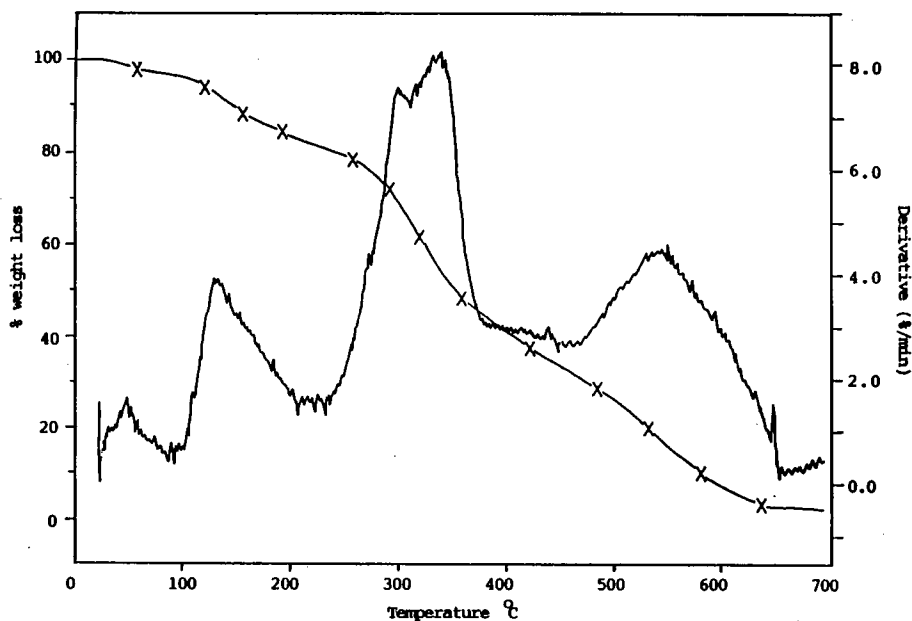


FIG. 2. TG curves (×) and DTG curve (—) of PMMA/PPY/bromine composite.

TABLE 2. Surface Stoichiometries by XPS and Conductivity Results

Sample	Calculated atomic ratio <sup>a</sup>	Conductivity, S/cm
PMMA/PPY/persulfate (air side)	$C_{87}N_{1.0}O_{31}S_{0.0}$	$< 10^{-12}$
PMMA/PPY/persulfate (oxidized side)	$C_{5.2}N_{1.0}O_{0.30}S_{0.16}$	$5.8 \times 10^{-1}$
PMMA/PPY/bromine (air side)	$C_{53}N_{1.0}O_{19.0}Br_{0.09}$	$10^{-4}$
PMMA/PPY/bromine (oxidized side)	$C_{6.0}N_{1.0}O_{0.60}Br_{0.23}$	$0.43 \times 10^2$

<sup>a</sup>Normalized to N = 1.0.



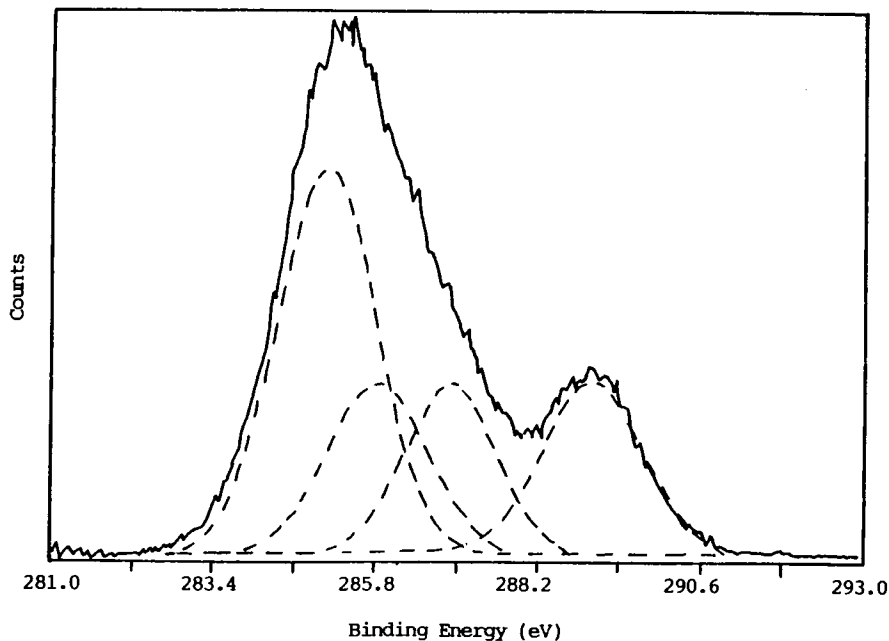


FIG. 3. C1s XPS spectrum of PMMA/PPY/persulfate composite (air side).

seen from Figs. 3 and 4 that the C1s and O1s component peaks (O=C=O at 288.9 eV,  $\text{-OCH}_3$  at 286.8 eV, C=C=O at 285.7 eV, and  $\text{CH}_2$  and C- $\text{CH}_3$  at 285 eV; C-O at 533.7 eV and C=O at 532.2 eV) of the air side are identical to those reported for PMMA [22]. This, together with the very high air side C/N ratios, demonstrates very clearly the predominance of the substrate PMMA polymer on the air side.

In contrast, XPS reveals the total absence of C-O and C=O components for the oxidized side. This, together with the high concentration of nitrogen, indicates that the oxidized side is essentially the doped PPY complex. The slightly high C/N ratio (theoretical = 4.0) may be attributable to hydrocarbon contamination. Curve fitting of the N1s spectrum (Fig. 5) shows the expected presence of two nonequivalent N environments at 400.2 and 401.7 eV. It has been shown that the 401.7 eV component arises from oxidized N heteroatoms bearing a +1 formal charge and that the doping level can be related to the area ratio of this component [23]. The doping level at the surface of the oxidized side for both systems

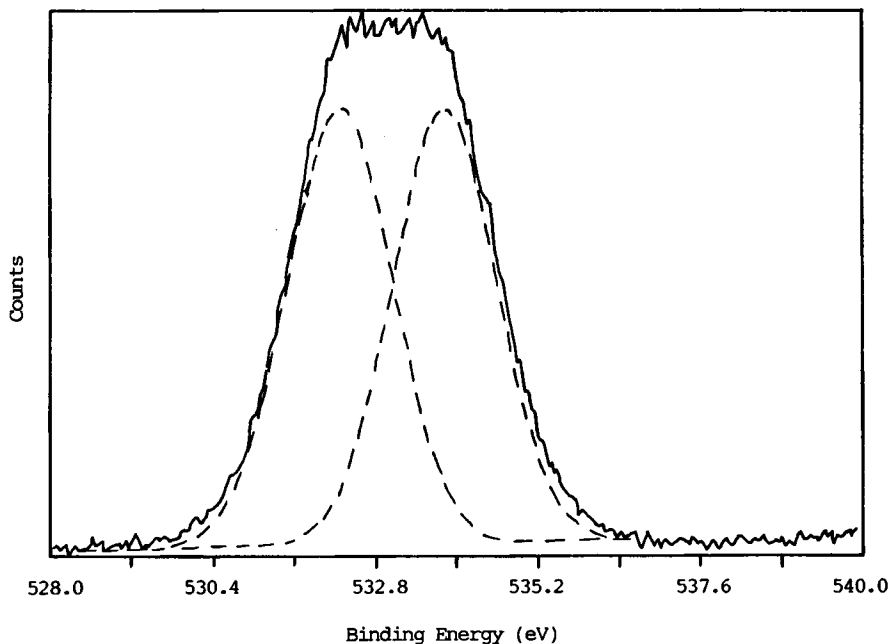


FIG. 4. O1s XPS spectrum of PMMA/PPY/persulfate composite (air side).

is about 10% (see Table 3). This rather low level may be attributed to the migration of the bromine and the bisulfate/sulfate ions into the PMMA substrate with an excess of neutral nitrogen atoms at the surface. This is reflected in the lower conductivity of these films as compared to pure doped PPY powder pellets.

The S2p and Br3d spectra should provide useful information on the nature of the dopant in the two systems. The S2p spectrum shown in Fig. 6 can be fitted with one major component centered at  $\sim 169.1$  eV (91% total area) and a minor component at  $\sim 171$  eV (9% total area). We have assigned the former binding energy (BE) to  $\text{HSO}_4^-$  and the latter to  $\text{SO}_4^{2-}$ . This indicates that the dopant anion is almost entirely the singly-charged bisulfate in the present system. This is consistent with the required amount of charged nitrogens needed to achieve overall neutrality. The presence of  $\text{HSO}_4^-$  in a persulfate oxidized system was reported previously [24].

As for the bromine-doped system, the curve-fitted Br3d envelope of

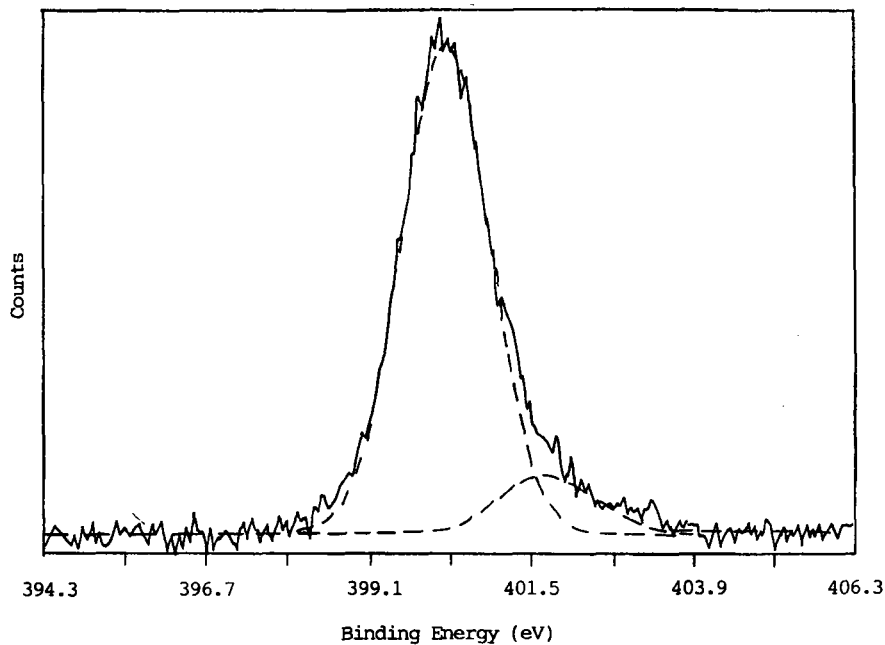


FIG. 5. N1s XPS spectrum of PMMA/PPY/persulfate composite (oxidized side).

TABLE 3. Curve Fitting of the N1s Components of PMMA/PPY/Bromine and PMMA/PPY/Persulfate Composites

Sample	N1s <sup>a</sup>
PMMA/PPY/persulfate (oxidized size)	400.2 eV (90%), 401.7 eV (10%)
PMMA/PPY/bromine (oxidized side)	400.2 eV (85%), 401.7 eV (15%)

<sup>a</sup>Area percentage in parentheses.

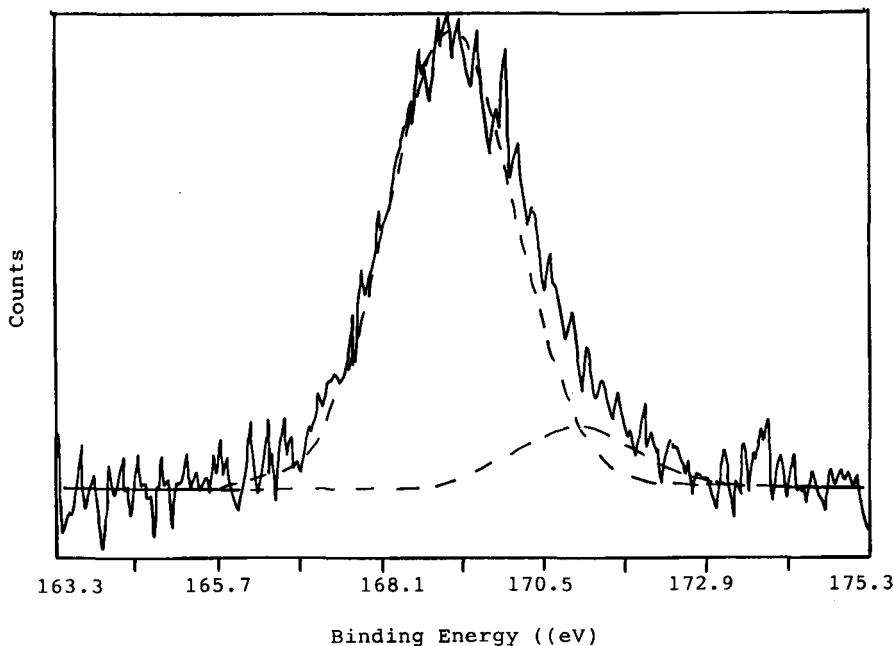


FIG. 6. S2p XPS spectrum of PMMA/PPY/persulfate composite (oxidized side).

PMMA/PPY/bromine (oxidized side) (see Fig. 7) clearly displays two components at  $\sim 68.4$  and  $\sim 71.0$  eV, corresponding to the  $\text{Br}^-$  dopant and the covalent ring-substituted bromine. The  $\text{Br}^-/\text{N}^+$  area ratio corrected with the appropriate sensitivity factor is close to 1.0, in agreement with earlier XPS studies of PPY [25]; the ionic  $\text{Br}^-$  to covalent Br ratio is roughly 1:1 at the surface. The existence of covalent bromine has been confirmed by x-ray diffraction experiments [26]. The presence of bromine on the air side is confirmed by the Br3d spectrum shown in Fig. 8. Interestingly, the covalent bromine component is now greater than the ionic bromine component. A plausible explanation is that during its migration through the PMMA, some of the bromine reacts with the pendant ester group and becomes covalently bonded. It should also be noted that a very small amount of nitrogen is detected, which suggests that the PPY/bromine has come through to the top side of the PMMA.

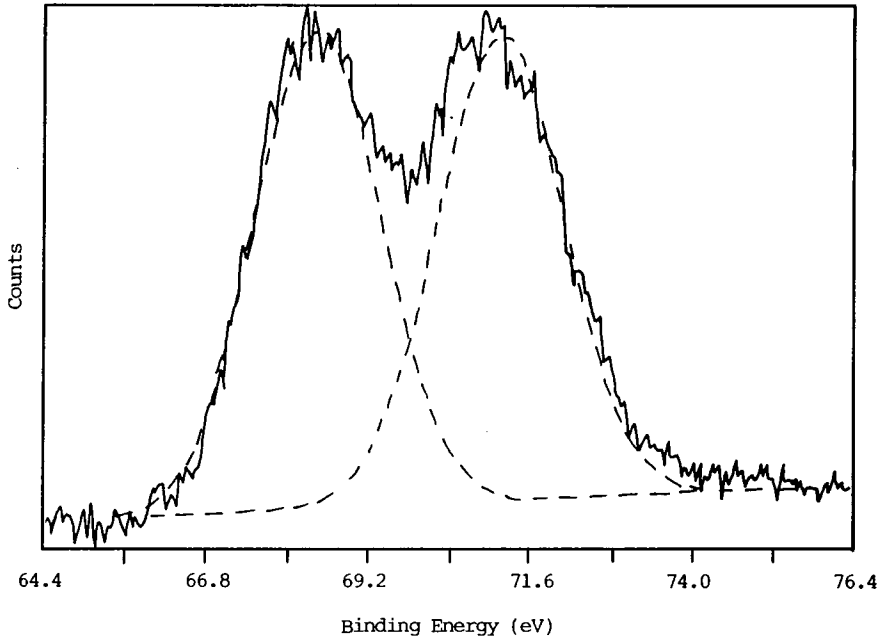


FIG. 7. Br3d XPS spectrum of PMMA/PPY/bromine composite (oxidized side).

## CONCLUSION

Conducting composite thin films of PPY with PMMA have been synthesized by oxidation of a pyrrole-PMMA-butanone solution over an aqueous sodium persulfate or bromine surface. PMMA/PPY/persulfate yields the best films in terms of homogeneity and conductivity. Bromine-doped systems are charge-compensated by  $\text{Br}^-$ , but there is evidence to suggest the predominant counterion in persulfate oxidized films is not  $\text{SO}_4^{2-}$  but  $\text{HSO}_4^-$ . In all cases the bulk doping level is  $\sim 30\%$ , although the surface level is between 10 and 15%. XPS also reveals the oxidized side is composed essentially of doped PPY while the air side is rich in the matrix polymer. 50% of the halogen incorporated in  $\text{Br}_2$  oxidized films is ring-substituted. Thermal analysis and XPS results strongly suggest that the PPY/bromine species is distributed intimately in the PMMA matrix to facilitate interaction between the dopant and the PMMA.

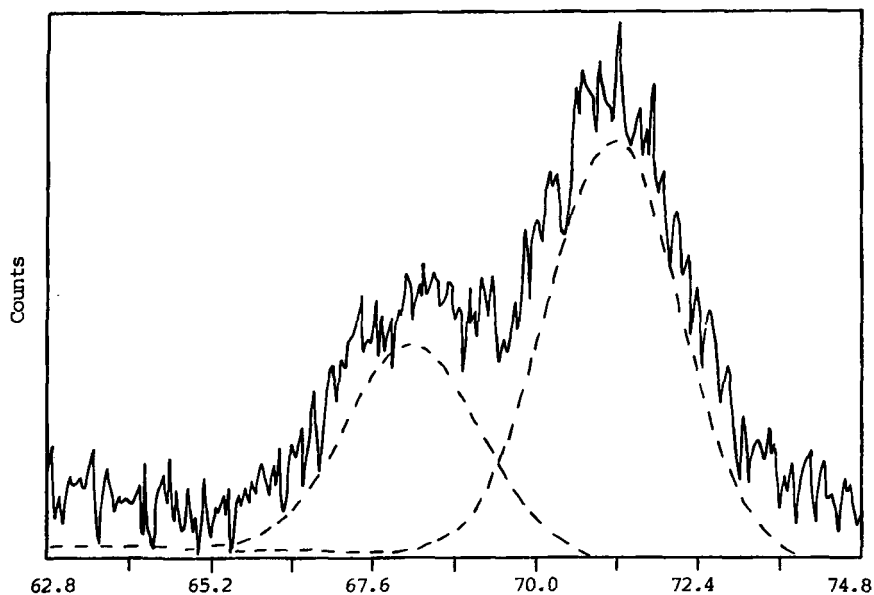


FIG. 8. Br3d XPS spectrum of PMMA/PPY/bromine composite (air side). The abscissa is the binding energy (eV).

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