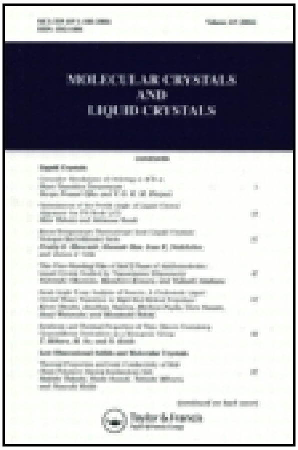

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Characterization of Poly(3-Methylthiophene) Films by IR, Elemental Analysis, Thermogravimetry and Mass Spectrometry

W. Kobel [a] , H. Kiess [a] , M. Egli [a] & R. Keller [a]
[a] Laboratories RCA Ltd., Badenerstrasse 569 CH-8048, Zurich, Switzerland

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CHARACTERIZATION OF POLY(3-METHYLTHIOPHENE) FILMS BY IR, ELEMENTAL ANALYSIS, THERMOGRAVIMETRY AND MASS SPECTROMETRY

W. KOBEL, H. KIESS, M. EGLI and R. KELLER
Laboratories RCA Ltd., Badenerstrasse 569
CH-8048 Zürich, Switzerland

Abstract Poly(3-methylthiophene) films prepared electrochemically with propylene carbonate as solvent contain 21.5% and 16.5% propylene carbonate in the oxidized and reduced state, respectively. The thermally activated release of the solvent and of the dopant BF_4^- are studied by thermogravimetry and mass spectrometry. The activation energies for the release of BF_4^- and of propylene carbonate are both found to be about 1 eV.

INTRODUCTION

Poly (thiophene) films can be grown electrochemically from an electrolyte medium consisting of a solvent, $(Bu)_4NBF_4$ and the monomer. Solvents which have been used are THF, CH_2Cl_2, CH_3CN and propylene carbonate[1, 2]. Our observation was that the best film quality is achieved if the films are prepared with propylene carbonate (PC) as solvent, however at the expense of PC being incorporated in the films. In this paper we want to give quantitative accounts of the amount of solvent and dopant found in electrochemically reduced and oxidized poly(3-methylthiophene) films (PMT), of the thermally activated release of the solvent and dopant BF_4^-, and finally of the thermal stability of PMT itself.

EXPERIMENTAL

Poly(3-methylthiophene) films were prepared in a propylene carbonate /tetrabutylammonium tetrafluoroborate supporting electrolyte as described in our previous paper[3]. As prepared the films have a smooth surface and, if sufficiently thin, appear blue in transmission indicating that the films were oxidized (with BF_4^- incorporated). The reduced films (i.e. without BF_4^-) appear red. Depending on the type of investigation the films were either grown on Si, Pt or on Au. Since PMT adheres only slighly to Pt, free standing films were prepared by peeling the PMT off the Pt substrate.

The samples were characterized by IR-measurements and by elemental (F, S, C, H, N) analysis. Mass spectrometric measurements up to 250°C (or in special cases up to 520°C) were performed on films of $\sim 2\ \mu m$ thickness and an area of $\sim 1\ cm^2$ with a UTI quadrupole mass spectrometer which was operated with a HP 150 personal computer. The programs have been developed in house. The sample temperature was raised linearly with time and the mass spectrum between 10 and 122 amu taken in intervals of 3°C to 5°C depending on the temperature range covered.

Thermal gravimetric analyses were performed in an inert gas atmosphere at heating rates ranging from 1°C/min to 4°C/min on a Mettler TA 2000.

RESULTS

IR-Results

IR-measurements of electrochemically reduced films (see Fig. 1a) reveal substantial amounts of incorporated propylene carbonate solvent irrespective of whether the

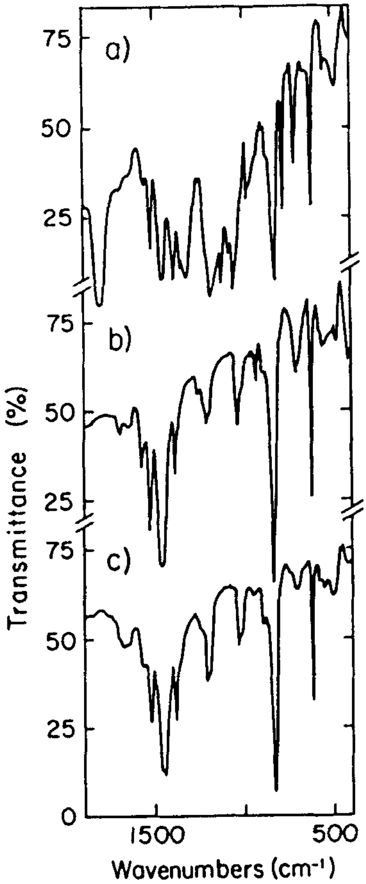

Figure 1a. IR-transmission spectrum of an electrochemically reduced poly(3-methylthiophene) film.

Figure 1b. IR-transmission spectrum of the same film after annealing. Absorption lines assignable to propylene carbonate disappeared, in particular also the strongest line at 1800 cm^{-1}.

Figure 1c. IR-spectrum of oxidized film after annealing. This spectrum is essentially identical with the spectrum shown in 1b.

films were investigated immediately after preparation or whether they had been stored in vacuum (10^{-5} - 10^{-6} Torr) for several days. Only by annealing at elevated temperature ($\gtrsim$ 180°C) for $\gtrsim$ 4 hours in vacuum the lines assignable to propylene carbonate disappear (Fig. 1b). Though propylene carbonate is present in oxidized films (see TGM, MS and elemental analysis) absorption lines due to propylene carbonate could not be detected in oxidized films, a fact which can be attributed to the strong electronic absorption of these highly conducting films ($\sigma \approx 2\times10^4$ S/m) masking the absorption of incorporated solvent. After annealing at 180°C for 4 hours the IR-spectrum of an oxidized film (Fig. 1c) is identical with that of an electrochemically reduced and annealed film (compare with Fig. 1b). Obviously the BF_4^- is lost from PMT films simultaneously with the solvent during the annealing procedure. To gain more quantitative information on the release of solvent and dopant, both oxidized and electrochemically reduced PMT films were investigated by thermal gravimetric analysis and by mass spectrometry.

TGM-Measurements

Electrochemically reduced films exhibit a relative weight loss of about 16% which takes place over the temperature range between 80°C and 250°C. A further weight loss of about 37% is observed between 300°C and 800°C. Measurements on oxidized films indicate the films to lose weight in two not very well resolved steps between 80°C and 250°C of $\Delta m/m \approx 22\%$ and $\Delta m/m \approx 14\%$, respectively. The weight loss between 300°C and 800°C involves $\Delta m/m \approx 30\%$.

Chemical Analyses

Elemental analyses of unannealed as well as of samples which had been heated at constant rate to 230°C are given in Table I. Based on the assumption that only 3-methylthiophene, tetrafluoroborate and propylene carbonate is contained in the samples, the weight percentages of BF_4^- and of propylene carbonate of any PMT film can be calculated from the experimentally determined F and S content. According to elemental analytical data an electrochemically reduced film contains about 16.5% of propylene carbonate which is in fair agreement with the weight loss of 16% observed by thermal gravimetry.

Though not detectable by IR measurements, a reduced film obtained by heating an oxidized film at a constant rate of 2°C/min from 20°C to 230°C still contains 2.8% propylene carbonate. It is interesting to note that the fluorine content is below 0.2% (i.e. below the detection level of the chemical analysis) indicating a complete release of the BF_4^- in contrast to that of the solvent. Since no fluorine is detected in these films it is evident that no reaction of fluorine with PMT occurred during the release of BF_4^-.

Based on the chemical analyses the oxidized films contain 21.5% propylene carbonate and 13.5% BF_4^-. These values are again in fair agreement with the data from thermogravimetry. However, there are deviations of C and H by 2.6% and 0.25% from the expected values in the case of oxidized films, a difference which we cannot account for within our assumptions.

Mass Spectrometry

By mass spectrometric measurements the species released from the films become separable. For oxidized films

TABLE I

a) oxidized PMT

	S	F	C	H	BF_4^-	PC
experiment:	21.1-22.2%	11.6-11.9%	48.2%	4.3%		
expectation:	21.65%	11.75%	50.74%	4.0%	13.4%	21.7%

b) reduced PMT

	S	F	C	H	BF_4^-	PC
experiment:	27.8%	0.2%	59.9%	4.53%		
expectation:	27.8%	0	59.9%	4.48%	0	16.6%

c) oxidized PMT, heated at constant rate up to 230°C

	S	F	C	H	BF_4^-	PC
experiment	31.9%	0.2%	61.93%	4.11%		
expectation:	31.9%	0	61.79%	4.27%	0	4.3%

d) reduced PMT, heated at constant rate up to 230°C

	S	F	C	H	BF_4^-	PC
experiment:	32.4%	0.2%	62.07%	4.26%		
expectation:	32.4%	0%	62.02%	4.24%	0	2.83%

characteristic and significant changes were observed between 80° and 250°C and for amus of m/e = 10, 11, 19, 48, 49, 67, 68. The amus can be assigned to B (10, 11) F (19), BF_2 (48, 49) and BF_3 (67, 68) since the isotope ratio $^{10}B : ^{11}B = 0.25$ was confirmed in all B related amus. In addition the amus 102, 87, 86, 59, 58, 57, 15 and 13 show the same temperature dependence and can be related to propylene carbonate. An unambiguous assignment is certainly possible for amu = 102 and amu = 87, representing the propylene carbonate molecule ion M^+ and $(M - CH_3)^+$.

Characteristic increases of the signal with temperature were found above 250°C for amus 33, 34, 15 and 13. We believe that these masses are due to the decomposition products of the poly(3-methylthiophene) itself. We assign them to SH (33), SH_2 (34) and to the split-off methyl group CH_3 (15) and CH (13).

Electrochemically reduced films show in the temperature range up to 250°C only species related to the release of propylene carbonate. Any masses related to BF_4^- are missing. By comparison with oxidized films we would expect that less than 0.1% BF_4^- should be left in these reduced films. This estimate is in agreement with the elemental analyses of reduced films.

Experimental data for the amus 49 (BF_2), 87 ($M-CH_3$) and 33 (SH) are plotted logarithmically vs. 1/T in Fig. 2. At low temperatures an activation energy of 0.8 - 1.1 eV (depending on the age of the film) is found for the release of BF_4^- whereas above 130°C the curve levels off and remains nearly temperature independent between 180°C and 240°C. The release of propylene carbonate is activated with ~1 eV and shows a wide temperature independent range extending from about 80°C to 200°C. The activation energy for the release of (SH) between 250°C and 520°C is about 0.9 eV.

DISCUSSION

We propose the release of BF_4^- occurs according to the

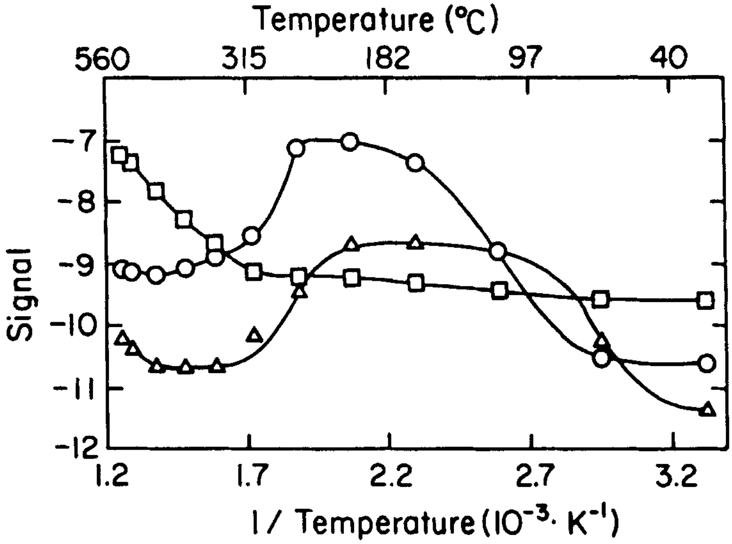

Figure 2. Signals obtained for amus representative for BF_4^- (BF_2 : 49) ○ , for propylene carbonate (|M-CH_3| : 87) △ , and for polythiophene (SH : 33) □ are plotted vs. reciprocal temperature. The ordinate represents the signal of the mass spectrometer on a logarithmic scale.

following reaction scheme:

$$2BF_4^- + PMT^{2+} \longrightarrow 2BF_3 + F_2 + PMT$$

This reaction implies a transfer of the negative charge from BF_4^- to PMT^+, a decomposition of BF_4^- into BF_3 and F_2 without further reaction of fluorine with PMT (which is evidenced by chemical analysis and IR measurements). A similar reaction pathway has been proposed for the depletion of BF_4^- anions from polypyrrole films[4]. The activation energy we measure is determined by the rate limiting step which might involve diffusion and desorption additionally to the aforementioned reaction steps. However, if the relevant dopant species would be BF_3^- [5], then only a charge transfer with a subsequent diffusion and desorption process of BF_3 would be expected. A more detailed analysis of the release rate vs. 1/T curves will be given elsewhere.

Since we observe in the mass spectrum the mass of the complete propylene carbonate molecules the release of the solvent will be determined by the diffusion of the molecules to the polymer surface and by the desorption from there into the gas phase. The plateau of the rate of loss vs. 1/T curve reflects a distribution of activation energies for these processes. The activation energies must be widely spread, the lowest activation energy being about 1.0 eV.

The activation energy of 0.9 eV observed for (SH) is difficult to assess. We cannot decide from our measurements whether these fragments are due to decomposition of the polymer or by desorption of monomers or dimers incorporated into the films during preparation. Measurements going up to 800°C should clarify this point.

CONCLUSIONS

Poly(3-methylthiophene) electrochemically prepared in propylene carbonate as solvent contains in the oxidized and reduced state 21.7% and 16.6% propylene carbonate, respectively. The solvent is remarkably stably incorporated in the films and cannot be removed unless the film is heated to 230°C. Oxidized films with BF_4^- as dopant lose the dopant during the heating process, the activation energy being 0.8 - 1.1 eV. The poly(3-methylthiophene) itself is stable up to about 300°C.

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