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Adsorption of Macromolecules onto Conducting Polymers##)

Summary — This paper reports on the study of adsorption of PMMA, a conventional homopolymer, and DNA onto some conducting polypyrroles (PPys) using a variety of techniques. PMMA adsorption was monitored using X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (ToFSIMS). XPS and ToFSIMS permit to determine the surface composition of PPy surfaces following PMMA adsorption from various solvents, at different concentrations and on three variously doped PPys. Both techniques show that acid-base interactions are important and may govern PMMA adsorption. In addition to these spectroscopies we have used inverse gas chromatography (IGC) to monitor the surface thermodynamic properties of the coated PPy powders and found a solvent effect on the morphology of PMMA coatings. An attempt to check if the same phenomenon is observed on flat surfaces was performed using atomic force microscopy (AFM). In the case of the adsorption of DNA (polyanionic macromolecule) onto PPy (positively charged polymer chains) using the depletion method in combination with UV spectroscopy, we found that adsorption is one to two orders of magnitude higher than that of conventional polymers onto classical filters. The pH effect was found to be of limited influence on the adsorption isotherms contrary to the effect of PPy dopant which was found to be the major factor governing DNA adsorption.

Inherently conducting polymers (ICPs) constitute a novel class of materials [1—4] which find various applications such as: primers in the paint technology and corrosion control [5]; thermoplastics welding [6]; conducting textiles [7]; conducting polymer blends [8]; composites [9]; liquid [10], ionic [11] and thin layer [12] chromatography; and biosensors [13].

In ICPs the electrical current flows *via* the conjugated polymer chains in contrast with conductor-filled conventional polymers where the electrical current flows *via* the filler particles. ICPs can be synthesized either chemically or electromechanically and switched from the oxidized conducting form to the reduced insulating form with a conductivity change of several orders of magnitude ($\sim 10^{-10}$—10^{2} S/cm).

Polypyrrole (PPy), polythiophene (PT) and polyaniline (PANI) are the most important ICPs and their chemical structures are displayed in Fig. 1. In the conducting state, the polymer chains of these ICPs are oxidized and thus bear positive charges which are counterbalanced by anions called "dopants". These dopants are incorporated in the polymer bulk during the oxidative polymerization of the monomer or when the ICP is switched

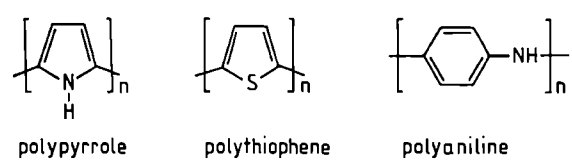

Fig. 1. Chemical structure of some selected inherently conducting polymers

from the reduced insulating state to the oxidized conducting state. The nature and the concentration of the dopants strongly affect the physicochemical and mechanical properties as well as conductivity and long term stability of ICPs [14].

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The major problems encountered with ICPs are their long term stability and processability. A tremendeous progress has been achieved by the polymer community to overcome these problems by synthesizing soluble precursors [15], copolymers [16] and sterically-stabilised colloidal dispersion of ICPs [17]. Advances in processability and long term stability were obtained at the expenses of electrical conductivity but nevertheless resulted in commercial applications of ICPs since 1989 and covering the fields of *e.g.* antistatics, radar absorbers and conductive adhesives 18. In such applications there is a need for a medium conductivity in the 10^{-3}—10^{-4} Scm^{-1} range.

Since ICPs may have applications such as composites and conducting textiles the study of their surface thermodynamic and adhesion properties is of particular importance. Two traditional methods are very well established for the determination of the surface thermodynamic properties of polymers surfaces: contact angle measurements in the case of flat surfaces [19] and inverse gas chromatography (IGC) in the case of powders and fibres [20]. Whilst application of the former technique to flat ICP surfaces is incipient [21, 22], the latter has been extensively used by the Paris group to investigate the properties of PPy powders [23—29], PANI [29], PPy/PMMA interface [30, 31], and PPy-silica nanocomposites [32]. We used IGC to interrogate the susceptibility of PPys and related materials to undergo dispersive and acid-base intermolecular interactions. These are of relevance to adhesion and wetting properties of materials. This study of the adsorption of molecules onto ICP surfaces led us to the more applied field of macromolecule adsorption [33—35].

The aim of the present work is to review some of our recent achievements in macromolecule adsorption onto ICPs. We have chosen a series of conducting PPy powders doped with various couteranions. We have selected PMMA, a conventional insulating homopolymer, and DNA, a biological macromolecule, as the adsorbates. In the case of PMMA we used XPS and ToFSIMS to evaluate the surface composition of PMMA-coated PPys and determine adsorption isotherms. We were mainly interested in the effects of the casting solvent, the temperature and the substrate nature. These adsorption experiments led to very thin coatings and it was very desirable to determine whether or not these coatings were continous and uniform. IGC is a unique tool in characterizing surface properties of absorbates and thus we used it in this regard. To check out our hypotheses drawn from IGC studies of PMMA-coated PPys, we have used AFM in the case of electrochemically synthesized flat PPys coated with PMMA cast from various solvents. In the case of DNA, our preliminary studies were concerned with the effect of pH and PPy dopant on adsorption isotherms. Experiments were conducted using UV spectroscopy in order to monitor DNA depletion from the solutions and determine adsorption isotherms.

RESULTS AND DISCUSSION

I. ADSORPTION OF PMMA

I. A. X-ray Photoelectron Spectroscopy

PPy powders were sieved to 100 m and added to PMMA solutions. The suspensions were stirred for one hour, then filtered and the black PMMA-coated PPy powders were collected, dried overnight and transferred in the ultrahigh vacuum of the XPS equipment for surface analysis. We have investigated four parameters governing polymer adsorption: the casting solvent, the initial PMMA concentration, the temperature and the substrate. The substrate nature depends on the nature of the counteranion incorporated into the polymer.

I. A. 1. Solvent effect

In order to check Fowkes' theory of acid-base interaction in polymer adsorption [36—38], we have used neutral, acidic and basic solvents. The acid-base properties of the solvents were characterized by the Gutmann's donor and acceptor numbers (DN and AN) [39]. DN and AN are scales of basicity and acidity, respectively.

We have monitored the surface composition of coated PPyCl surfaces by recording C_{1s}, O_{1s}, N_{1s} and Cl_{2p} photoelectron signals and Cl_{LMM} Auger electron peak. Using (i) approximations on the escape depths of C_{1s} and N_{1s} photoelectrons emitted from the coated particle surfaces, (ii) the following stoichiometric formulas for PMMA $C_5H_8O_2$, and for PPyCl $C_4H_3N_1O_{0.2}Cl_{0.3}$, and (iii) neglecting the possible surface hydrocarbon contamination of the coated particles we have obtained the following relative proportion of PMMA (% PMMA) at the surface of PMMA-coated PPyCl particles reported in table 1:

Table 1. RELATIVE PROPORTION OF PMMA AT THE SURFACE OF PMMA-COATED PPyCL SURFACES AS A FUNCTION OF THE ACID-BASE CHARACTERISTICS OF THE CASTING SOLVENTS (DN values were reported by Gutmann [39]. AN values were corrected for van der Waals interactions by Riddle and Fowkes [40])

Solvent	THF	DXN	TOL	CTC	DCE	DCM	TCM
DN (kcal/mol)	20	14.8	0	0	0	0	0
AN (ppm)	1.9	0	0	2.3	6.4	13.5	18.7
% PMMA	4.9	11.4	30.0	47.0	16.3	13.3	10.8

Fig. 2 shows the variation of % PMMA with the acid-base characteristics of the casting solvents [41]. The plot is triangle-shaped as in the original study of adsorption of PMMA on silica by Fowkes and Mostafa [36] using the depletion method. The highest amounts of PMMA adsorb from the (quasi)neutral solvents TOL and CTC. As PMMA is a Lewis base [27, 38] and PPyCl is a predominantly acidic polymer [24, 25, 27] the right hand side of Fig. 2 shows a competition between solubility

in acidic solvents (good solvents) and adsorption of PMMA onto PPyCl, and the left hand side of the figure shows a competitive adsorption between the basic solvents (THF and DXN) and the polymer. As a complementary ToFSIMS study, we have checked for the lowest PMMA deposit (4% from THF) that the latter was indeed adsorbed by monitoring mass peaks characteristic of PMMA *e.g.* at m/z= 55^- ($C_3H_3O^-$) and 85^- ($CH_2C(CH_3)COO^-$).

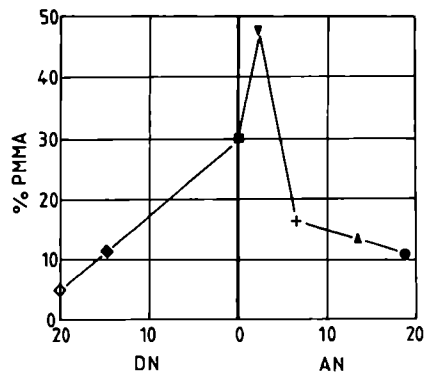

Fig. 2. XPS evaluation of % PMMA at the surface of PPyCl as a function of the acid-base characteristics of the solvents. The plot has the shape of the "Fowkes' triangle". DN are in kcal/mol and AN in ppm. (reproduced from [29], Synthetic Metals ***66*** *(1994) pp 225—233, by permission of Elsevier Science S. A., Lausanne, Switzerland):* □ *— THF,* ◆ *— DXN,* ■ *— TOL,* ▼ *— CTC, + — DCE,* ▲ *— DCM,* • *— TCM*

We determined the average thickness of PMMA coatings using the Cl_{2p}/Cl_{LMM} intensity ratio for both bare and coated PPyCl powders. This ratio varies with the overlayer thickness because Cl_{2p} and Cl_{LMM} have significantly differing mean free paths (λ) and thus have different escape depths (*d*) since *d* ~3 λ [42]. The average coating thicknesses which we have determined are reported in Table 2 together with the amount of adsorbed

T a b l e 2. THICKNESS AND MASS OF PMMA OVERLAYERS (from [41])

Solvent	THF	DXN	TOL	CTC	DCE	DCM	TCM
Thickness (Å)	2	3	7	9	5	5	4
Adsorption (mg/m^2)	0.25	0.39	0.88	1.13	0.63	0.63	0.5

PMMA (in mg/m^2) estimated using the coating thickness and density of PMMA, and the specific surface area 3.3 m^2/g by BET (Brunauer, Emmett, Teller) measurements and weight of PPyCl [41].

Obviously, the PMMA coating thickness obtained in THF is very small and must be an average value for coated and uncoated areas of PPyCl particle surface. Thus, it is likely that only a PMMA submonolayer adsorbs onto PPyCl from THF. This actually parallels the IGC findings on the surface energy of PMMA-coated PPyCl surfaces reported below. The adsorbed PMMA per unit area of PPyCl and estimated from XPS results is of the same order of magnitude generally observed for homopolymers [33].

I. A. 2. Adsorption isotherms

Adsorption isotherm is a very useful piece of information for understanding the polymer-substrate interactions. Adsorption of PMMA on various substrates such as silica, iron and cellulose in various solvents was reviewed by Robb [34]. As far as we are concerned we have investigated the effect of temperature and substrates. Solvent effect has also been studied and the direct isotherms were found to confirm the solvent effect in section I. A. 1. and will not be reported here.

I. A. 2. a. Temperature effect

This effect has been investigated in CTC since this solvent leads to the highest adsorption rate of PMMA. Experiments were conducted at 25 and 40°C. Direct and Langmuir isotherms are shown in Fig. 3. The direct isotherm (Fig. 3a) relates % PMMA to the initial PMMA concentration. Although real isotherms relate the adsorbed amount to the equilibrium concentrations, we have

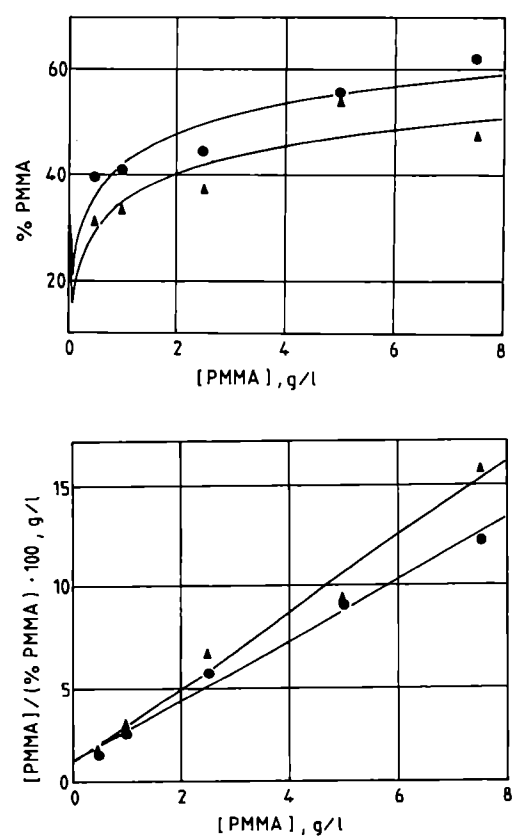

Fig. 3. Adsorption isotherms of PMMA onto PPyCl at 25 and 40°C. (a): direct isotherms relating % PMMA to PMMA initial concentration, (b): Langmuir plots showing a linear correlation [PMMA]/(% PMMA) vs. [PMMA], the initial PMMA concentration: ▲ *— 25°C,* • *— 40°C*

rather used the initial concentrations since they were large enough for the depletion to be significantly detected. Fig. 3a shows that a relatively stronger adsorption occurs at higher temperature. Although contradictory to the expectations from adsorption phenomena, this result is in agreement with studies of other polymer — substrate systems [33]. However, it should be borne in mind that the adsorption of a polymer differs from that of a molecule and that the overall heat of adsorption has at least three contributions [33]. Given that, entropic effects seem thus to be very important in PMMA adsorption onto PPyCl. Fig. 3b displays a plot of % PMMA *vs.* initial PMMA concentration. Linearity is an indication that the isotherms are of the Langmuir type and thus the surface adsorption sites are of equal strength for PMMA.

I. A. 2. b. Substrate effect

During investigations of the adsorption of polymers onto conducting polymers our final goal was to check of the effect of the substrate nature on the adsorption of the polymer. The nature of the substrate has been changed by synthesizing polypyrrole using various oxidizing agents of pyrrole. We have focused on iron III salts. In the present work we report the data of PMMA adsorption onto PPyCl and HSO_3^- doped PPy (PPyH-SO_4). Fig. 4 shows the direct isotherm and demonstrates

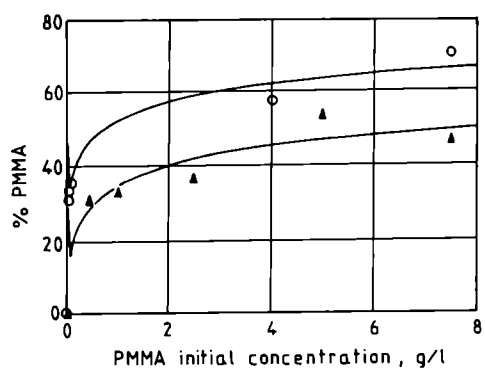

Fig. 4. Langmuir adsorption isotherms of PMMA onto PPyH-SO_4 and PPyCl: ▲ — PPyCl, ○ — PPyHSO$_4$.

that the substrate nature induced by the dopant species is not only important in the adsorption of molecules [24, 26], but also in polymer adsorption. We used CTC, a non competing solvent, to cast PMMA onto PPyCl and PPyHSO$_4$. Fig. 4 brings a strong evidence for the effect of acid-base interactions between the adsorbent (predominantly acidic) and the adsorbate (predominantly basic) on PMMA adsorption. Although speculative at this stage (the experiments were conducted with two substrates only), it is likely that because PPyHSO$_4$ is more acidic than PPyCl as judged from IGC data [26, 27] PMMA adsorbs more favourably onto the former substrate.

I. B. Time of Flight Secondary Ion Mass Spectroscopy (ToFSIMS)

ToFSIMS is an extremely surface-sensitive technique that provides chemical information from a depth of 1 nm only when it is operated in the static mode [42, 43]. We used ToFSIMS as an analytical method complementary to XPS (analysis depth in the 5—10 nm range) to investigate solvent and dopant effects on the PMMA adsorption onto PPys. It is to note that ToFSIMS has several apparent advantages over XPS, not least its superior surface specificity but also molecular specificity and a much better detection limit [43]. In the case of PPy — PMMA interaction, the diagnostic ions chosen were m/z = 31^- (CH_3O^-) for PMMA [44] and m/z = 26^- (CN^-) for PPys [45]. Following a published procedure [44] used to determine the surface composition of copolymers, we have monitored the amount of adsorbed PMMA onto PPys by calculating the I_{31} / (I_{31} + I_{31}) ratio, where [31] and [26] correspond to the diagnostic ions mentioned above, and I is the integrated peak area. We were mainly interested in determining adsorption isotherms, and these were constructed by plotting $I_{31}/(I_{31} + I_{26})$ *vs.* PMMA initial concentration.

I. B. 1. Solvent effect

This effect was studied at constant concentration of adsorbate for comparison of ToFSIMS with XPS results and for various initial concentrations in order to construct adsorption isotherms.

I. B. 1. a. Fowkes' Triangle

For comparison of ToFSIMS results with the results reported above (I.A.1.), we have chosen three solvents: THF, TOL and TCM; basic, neutral and acidic, respectively. Fig. 5 ToFSIMS signals are for uncoated and PMMA-coated PPy in THF. The technique is extremely sensitive with comparison to XPS: this is demonstrated by the PMMA characteristic features and centred at m/z = 55^- and 85^- in the case of PMMA adsorption from THF. However for technical reasons [46] we rather used the mass peak centred at 31^- to quantitatively monitor PMMA adsorption. Fig. 6 shows the variation of $I_{31}/(I_{31} + I_{26})$ *vs.* the Gutmann's numbers of the solvents. Adsorption of PMMA increases on going from a basic to a neutral solvent, then decreases from the latter to the acidic solvent TCM. The plot is triangle-shaped as that reported above in section I.A.1. The relative proportion of PMMA determined by ToFSIMS is however slightly higher than that determined *via* XPS since the latter is less surface sensitive than the former. Nevertheless, ToFSIMS results parallel those obtained by XPS and it was then very desirable to correlate the results of both techniques. This is shown in Fig. 7 which displays plots of $I_{31}/(I_{31} + I_{26})$ and $I_{26}/(I_{31} + I_{26})$ ratios *vs.* % PMMA determined by XPS. The ToFSIMS ratios indicate adsorption of PMMA and attenuation of PPy signals, respectively. Fig. 7 could be used as a calibration method

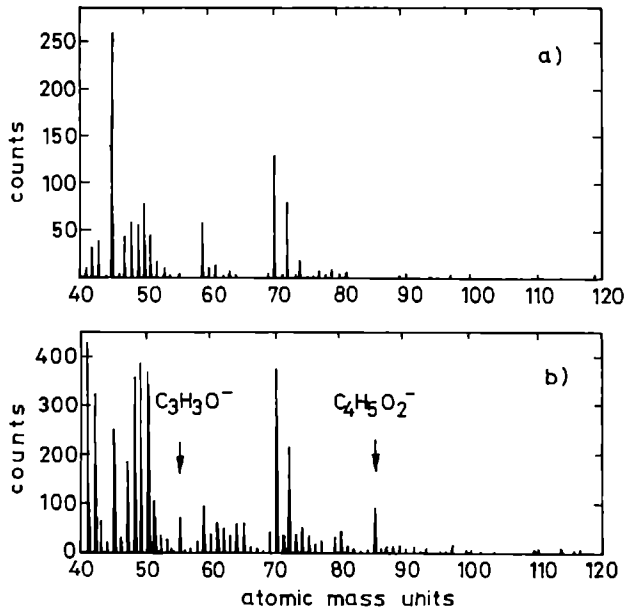

Fig. 5. ToFSIMS spectra of (a) bare PPyCl powder, and (b) PMMA-coated PPyCl in THF. Mass peaks at 70, 72 and 74 are characteristic of Cl_2^- from PPyCl and those centred at 55 and 85 in (b) are characteristic features from PMMA

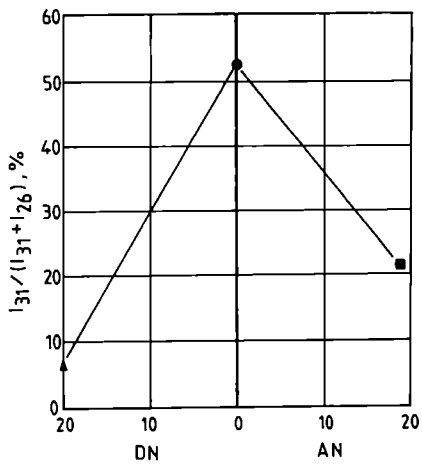

Fig. 6. Adsorption of PMMA onto PPyCl by ToFSIMS. $I_{31}/(I_{26} + I_{31})$ vs. the acid-base characteristics of the casting solvents is a triangle-shaped plot that indicates maximum adsorption of PMMA from the neutral solvent: ▲ — THF, • — TOL, ■ — CH_3Cl_3

for ToFSIMS in studying the PPy—PMMA interface in the initial stage of polymer adsorption.

I. B. 1. b. Adsorption isotherms [46]

Fig. 8 shows negative ion mass spectra of bare PPyH-SO_4 (Fig. 8a) and PMMA-coated $PPyHSO_4$ in TCM (Figs. 8b—8c) and CTC (Fig. 8d). CH_3O^- peak centred at m/z = 31$^-$ is detected following PMMA adsorption. The relative C_3HO^- peak area increases with the initial PMMA concentration (Figs. 8b—8c) and is also very dependent on the solvent nature (Figs. 8c—8d). Fig. 9 displays adsorption isotherms of PMMA onto $PPyHSO_4$ from TCM and CTC. Both isotherms are of the Langmuir type

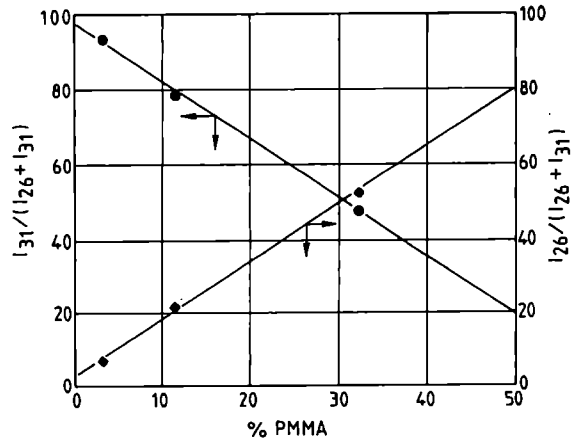

Fig. 7. Plots of $I_{31}/(I_{26} + I_{31})$ determined by ToFSIMS vs. % PMMA determined by XPS. Increasing % PMMA correspond to THF, TCM and TOL, respectively

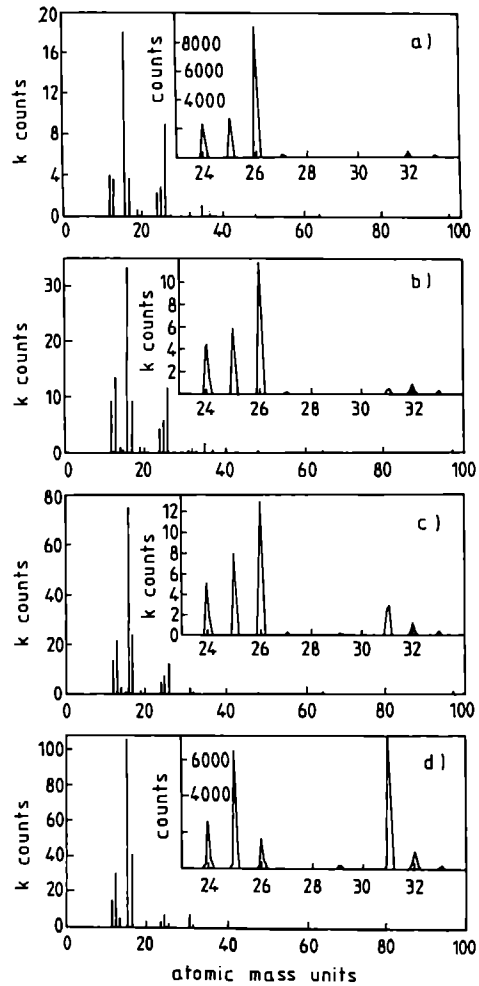

Fig. 8. ToFSIMS spectra of $PPyHSO_4$ (a) and PMMA-coated $PPyHSO_4$ (b—d) in the negative ion mode. The initial concentration of PMMA was 0.5 (b) and 7.5 (c) in $CHCl_3$, and 7.5 g/l in CCl_4 (d)

and clearly PMMA adsorption is more favourable from CTC than from TCM [41], in agreement with XPS results [41]. It is to note that whilst the isotherm in TCM has a rounded shoulder, that obtained in CTC consists of two lines, an initial sharply rising part followed by a

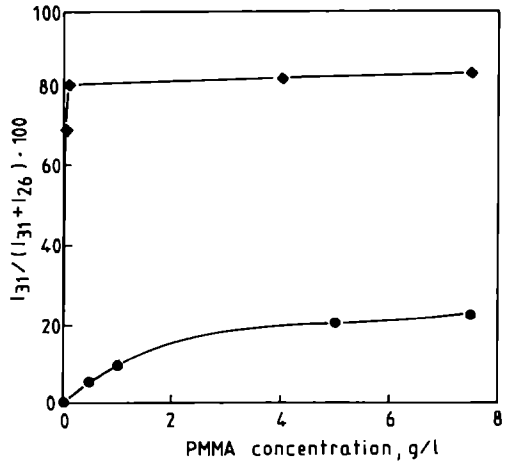

Fig. 9. ToFSIMS adsorption isotherms of PMMA onto PPyHSO4 from CHCl3 and CCl4: • — CHCl3, ◆ — CCl4

plateau, an indication that PMMA strongly binds to $PPyHSO_4$. These isotherms by ToFSIMS were interpreted in terms of acid-base interactions as the driving forces for PMMA adsorption onto PPy [46].

I. B. 2. Substrate effect

The experiments were conducted using CTC as a non-competing neutral solvent to achieve maximum adsorption. Unfortunately, the substrate effect (Fig. 10) does not fully agree with XPS results since ToFSIMS shows overlapping of the isotherms for the three PPys considered [30]. This is perhaps due to the fact that ToFSIMS

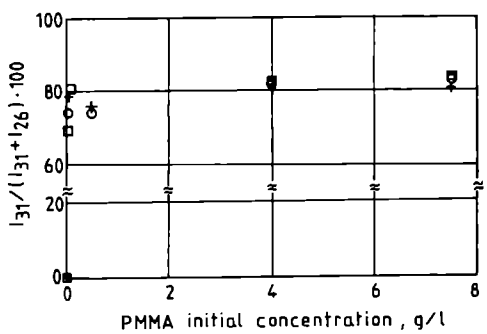

Fig. 10. ToFSIMS adsorption isotherms of PMMA onto PPyCl, PPyNO3 and PPyHSO4: ◡ — PPyHSO4, ○ — PPyCl, + — PPyNO3

is very surface specific: since PMMA readily forms at least 1 nm thick overlayer (from CTC) on the three substrates, there is no subtle difference that can be detected with this technique, whereas XPS probes more buried surfaces so that in this case it can yield chemical informations from deeper layers.

I. C. Inverse Gas Chromatography

XPS and ToFSIMS are useful for determining the surface chemical compositions of coated PPys but not the coating morphologies. In regard to this, we have used IGC 30, 31, a technique that is very popular for the characterization of polymers, mineral fillers and fibres.

The term inverse means that the stationary phase is the main object of investigation rather than the mobile phase. IGC is a very surface sensitive technique based on the measurement of the retention time of molecular probes adsorbed on the surface of the material under test (the packing material) [20]. Retention time data treatment will lead to the evaluation of surface thermodynamic properties of the materials under test. Of relevance to the present case, PMMA and PPyCl have diametrically opposite thermodynamic properties: PPyCl is a high surface energy material and predominantly acidic 27, 31, whereas PMMA is a low surface energy polymer and behaves as a predominantly basic species [37, 38, 47, 48]. Therefore the higher is the surface energy and the specific interactions of a given surface, the longer is the retention of the probes. For PMMA, PPyCl and PMMA-coated PPyCl powders (section I.A.1.) we have determined both London dispersive and Lewis acid-base properties. The former properties were described by γ_S^d, the dispersive contribution to the surface free energy and the latter by acid-base constants K_D (basicity) and K_A (acidity). We have evaluated γ_S^d according to the method of Dorris and Gray [49], and K_D and K_A using the approach of Saint Flour and Papirer [50]. In this paper we rely on K_D/K_A ratio which describes an overall basicity of the PMMA-coated powders. On PMMA adsorption, γ_S^d and K_D/K_A are expected to decrease and increase, respectively. Indeed the reference dispersive and acid-base constants are:

Figures 11 and 12 show the dependence of γ_S^d and K_D/K_A on % PMMA, respectively. Fig. 11 indicates that for the minimum adsorption of PMMA (4% in THF, *cf.* I.A.1.) there is a sharp decrease of γ_S^d from 144 to ~70 mJ/m^2. This is a striking example demonstrating the surface specificity of IGC. In Fig. 11, DXN and DCM lead to γ_S^d values that do not fit the linear plot. The

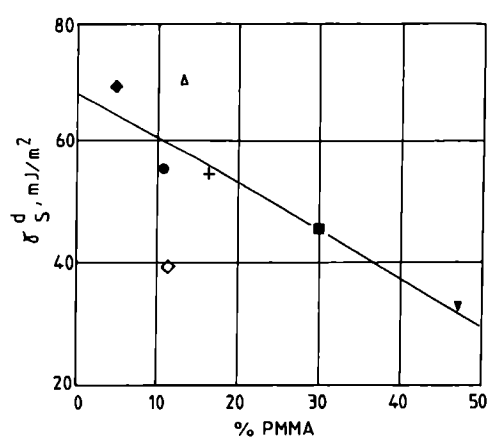

Fig. 11. Effect of the relative proportion of PMMA on the dispersive contribution to the surface free energy of the coated PPy powders: ◆ — THF, ◡ — DXN, ■ — TOL, ▼ — CTC, + — DCE, △ — DCM, • — TCM

former is 39.2 mJ/m^2 and matching that of PMMA (38.8 mJ/m^2, ref. [48]) and the latter is much higher (70.4 mJ/m^2) and comparable to that obtained using THF as a casting solvent. The γ_S^d values corresponding to PMMA-coated PPyCls prepared in DXN and DCM differ by 31 mJ/m^2 although these powders have comparable % PMMA (11.4 and 13.3 %, respectively).

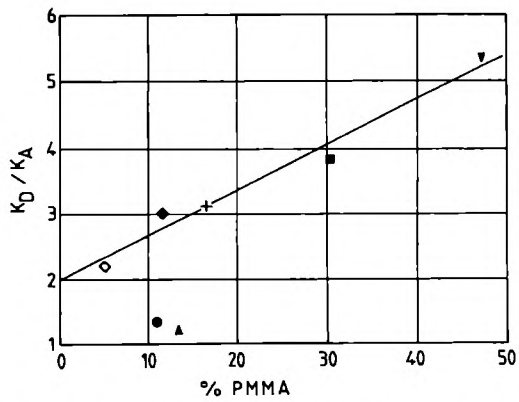

Fig. 12. Variation of the overall basicity K_D/K_A vs. the relative proportion of PMMA for the PMMA-coated PPy powders. The materials corresponding to DCM and TCM do not fit the linear plot: □— THF, ◆ — DXN, ■ — TOL, ▼— CTC, + — DCE, ▲ — DCM, • — TCM.

In Fig. 12, a linear plot is generated if the casting solvents DCM and TCM (good solvents) are excluded. For approximately the same % PMMA, DXN (poor solvent) yields an intermediate K_D/K_A ratio, whereas DCM and TCM lead to low K_D/K_A ratios matching that of PPyCl (1.3).

Figures 11 and 12 show that the non-competitive solvent CTC leads to the lowest value of γ_S^d and the highest value of K_D/K_A, both are comparable to the reference values reported in Table 3 for PMMA. Clearly a solvent effect is demonstrated by IGC and we suggest that for a given minimum of PMMA adsorption, poor solvents (*e.g.* DXN) lead to homogeneous coatings whereas good solvents lead to inhomogeneous coatings most probably

T a b l e 3. DISPERSIVE AND ACID-BASE CHARACTERISTICS OF PPyCL AND PMMA

	γ_S^d (mJ/m^2)	K_D/K_A
PPyCl	144	1.3
PMMA	38.3	5.5

caused by the solubility—adsorption equilibrium competition discussed above. At the present time we can not confirm this with THF (poor solvent) because it leads to a % PMMA that is very low for forming a coating monolayer, but nevertheless high enough to obtain a sharp decrease in γ_S^d from 144 to ~70 mJ/m^2. The solvent effect can be schematically described by Figure 13 which shows possible morphologies of PMMA coatings of PPy cast from a good and a bad solvent.

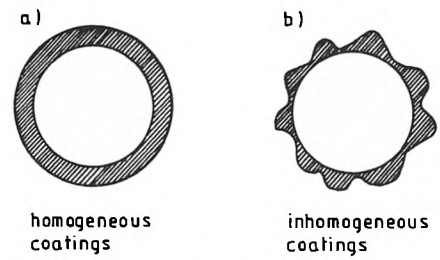

Fig. 13. Schematic representation of homogeneous and inhomogeneous PMMA coatings of PPy particle surfaces. Poor (a) but not good (b) solvents lead to homogeneous coatings

I. D. Atomic Force Microscopy

In order to check the hypothesis drawn from IGC results on the effect of solvent power on coating morphology, we have prepared thin PMMA films (~5 nm) by solvent casting on electrochemically synthesized tosylate-doped PPy(PPyTos) flat surfaces. AFM is able to image surfaces at the nanometre or micrometre scales and obtain a measure of the surface roughness. Fig. 14 shows AFM images of bare PPyTos and PMMA-coated PPyTos from THF and TCM. Fig. 14 qualitatively shows

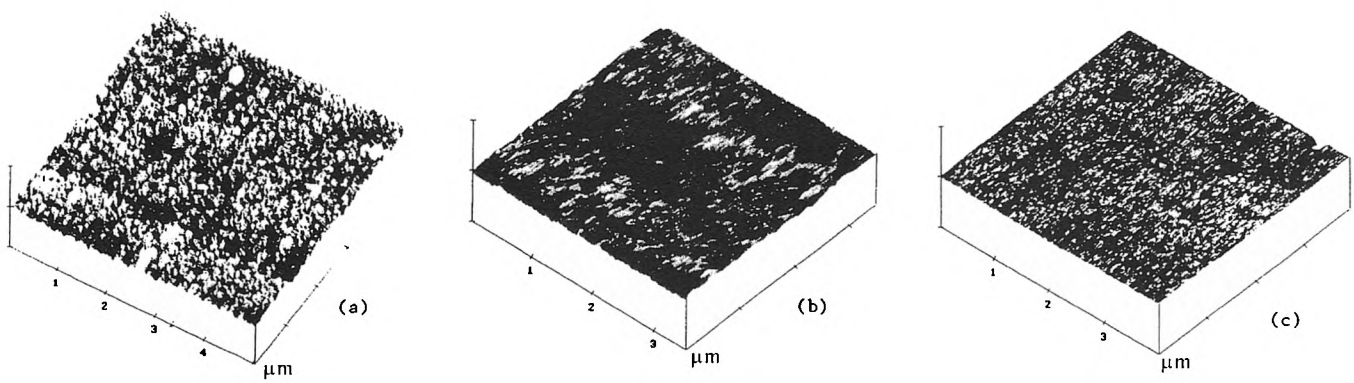

Fig. 14. AFM images of PPyTos flat surface before (a) and following PMMA deposition from THF (b) and $CHCl_3$ (c). x: 1 mm/division and z: 100nm/division

that the roughness decreases in the order PPyTos > PMMA-coated PPy from THF > PMMA-coated PPy from TCM. The latter is particularly smooth although the amount of PMMA cast from THF is identical to that cast from TCM. Morphological information could be gained from the determination of R_a, the average surface roughness, which was found to equal 3.2, 1.7 and 0.4 nm for PPy, PMMA-coated PPy from THF and PMMA-coated PPy from TCM, respectively. The solvent effect on R_a can be understood as follows: THF is a bad solvent and is expected to lead to homogeneous coating which is contrary to the TCM (good solvent). Therefore, PMMA cast from THF fits the surface roughness of PPy. In the case of TCM, a competition between the substrate and the solvent for PMMA interaction prevents the latter from the formation of a homogeneous coating and thus leads to a film which does not properly fit the surface roughness. In the case of thinner PMMA coatings (*ca.* 2 nm) this solvent effect is enhanced since R_a for PPyTos and PMMA-coated PPyTos in THF is practically the same [30]. Solvent effect on PMMA film formation is schematically illustrated in Figure 15.

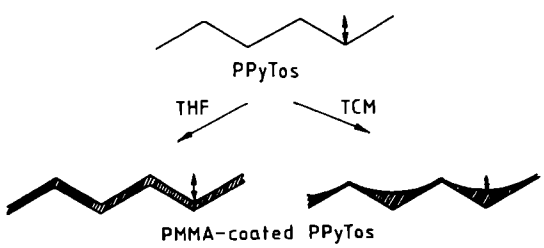

Fig. 15. Schematic modification of PPy surface roughness (indicated by double-headed arrows) following PMMA casting from a good and a poor solvent

II. ADSORPTION OF DNA

Conductivity, electromechanical activity, high intrinsic black coloration, chromatographic capability and ease of electrochemical and chemical syntheses of PPy are attracting physicochemical properties of relevance to biological applications such as biosensors, diagnostic assays, and separation of a range of nucleotides [13, 51—55]. Whilst PPys have been widely used for protein immobilization, the study of PPy — DNA binding is still limited. Livache *et al.* [54] for example prepared a DNA matrix *via* an electrochemically directed copolymerization of pyrrole and oligonucleotides with pendant pyrrole group. In the case of reversible PPy — DNA interaction, Minehan *et al.* [55] investigated the kinetics of DNA adsorption onto tosylate-doped PPy(PPyTos) flat surfaces. In the present review, we deal with preliminary results of the equilibrium aspects of calf thymus DNA adsorption onto a series of PPy powders. We were interested in the effects of pH and substrate nature. The substrates were PPyCl, $PPyHSO_4$ and $PPyNO_3$; and the purpose was to construct adsorption isotherms (in miligram of DNA adsorbed per gram of substrate) for comparison of their adsorptive capabilities. The solutions were buffered using sodium phosphate. pH was varied in the 6.2—7.8 range whereas the ionic force was maintained at 0.1 M for all experiments reported here. DNA was ultrasonically cleaved and the resulting fragment length was in the range of 150—250 nm as evaluated by AFM. We previously established that the adsorption kinetics of DNA onto PPyCl powder is diffusion-limited in agreement with published data using PPyTos film [55].

II. A. pH effect

Fig. 16 displays the pH effect on the DNA adsorption onto PPyCl powder. We note that the plateau of the various isotherms levels off at ~9 mg/g with a variation

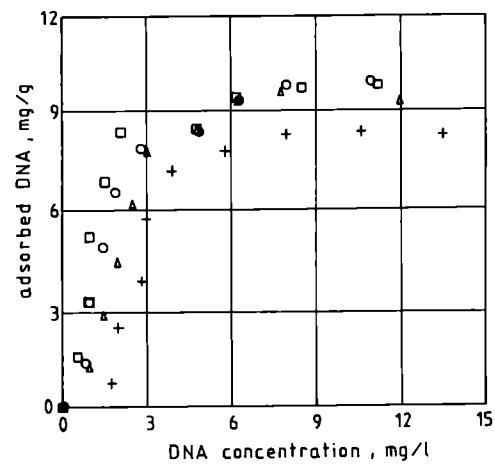

Fig. 16. pH effect on the DNA adsorption onto PPyCl powder at 25°C. Ionic force: 0.1 M: □ — pH 6.2, ○ — pH 7.0, Δ — pH 7.3, + — pH 7.8

that does not exceed 20 %. Of particular interest is the rising part of the isotherms as a function of increasing pH:

(i) the initial edge is obtained for relatively higher DNA concentration,

(ii) the slope of the initial edge is less sharp.

Therefore, DNA adsorbs more favourably at low pH. Experiments at pH 5—6 and 8—9 are underway in order to interpret the pH effect fully.

II. B. Substrate effect

We have tackled with this effect at pH 7 and ionic force of 0.1 M. Fig. 17 displays direct adsorption isotherms of DNA onto PPyCl, $PPyHSO_4$ and $PPyNO_3$. The influence of the dopant is drastic contrary to that of the pH. Indeed, it is shown that the plateau values are *ca.* 9, 5 and 3 mg/g for PPyCl, $PPyNO_3$ and $PPyHSO_4$, respectively. These quantities are 3 to 9 times larger

than those obtained with PMMA (I.A.1.) and can even be two orders of magnitude higher than those frequently obtained for conventional polymer adsorption onto classical mineral substrates [33], but significantly lower than the adsorptions of human serum albumin and human gamma globulin (11 and 33 mg/g, respectively) onto PPy latexes [53].

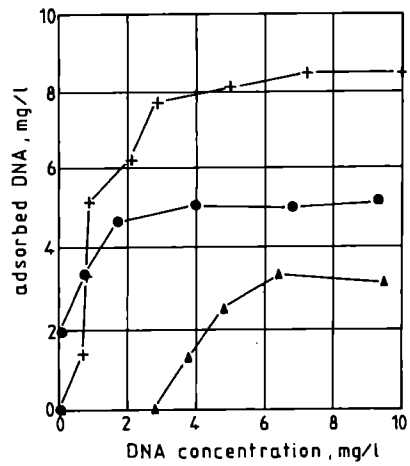

Fig. 17. DNA adsorption onto PPyCl, PPyNO and PPyHSO at 25°C and for pH 7 and ionic force 0.1 M: ▲ — PPyHSO4, • — PPyNO3, + — PPyCl

Inspection of Fig. 17 shows that the isotherms have differing shapes: whilst the isotherm obtained with PPy-NO_3 is of the Langmuir type — which is an indication that the surface sites are of equal strength — those of $PPyHSO_3$ and PPyCl are sigmoid. This shape can be explained by the existence of lateral interactions between the adsorption sites, that is to say that DNA binding at one site modifies the affinity of other sites [35, 56].

This study is an important if not essential step for understanding the DNA — ICP interactions and is pertinent in developing novel applications of ICPs in the field of biotechnology, especially those of relevance to separation methods of biological macromolecules using finely divided ICP-based materials [51, 57].

CONCLUSIONS

In this review paper we have dealt with the adsorption of macromolecules onto conducting polymers. The substrates were finely divided polypyrroles (PPys) and the adsorbates PMMA and DNA. We have reached the following points:

— Acid-base interactions constitute a driving force in PMMA adsorption onto PPys as judged by XPS and ToFSIMS, two complementary surface analytical techniques of differing depth analysis.

— PMMA adsorption isotherms determined by XPS and ToFSIMS were found to be of the Langmuir type for the initial stages of the adsorption process. Adsorption isotherms highlighted solvent, temperature and substrate effects. Indeed, PMMA adsorption is more favourable from a neutral solvent, at 40 rather than 25°C, and onto most acidic substrate.

— Surface chemical compositions of PMMA-coated PPy were reflected in the surface energy of these materials as determined by IGC. Surface thermodynamic properties were helpful in "mapping" the coating morphology of PMMA which is homogeneous when cast from poor but not from good solvents.

— We characterized PMMA films solvent cast onto flat PPy surfaces by AFM and found that poor (THF) but not good (chloroform) solvents lead to continuous films that fit PPy surface roughness. This is in line with IGC findings on coated powders.

— We have for the first time determined adsorption isotherms of DNA onto PPy powders using the depletion method in combination with UV spectroscopy and found that the adsorption kinetics of DNA onto PPy is diffusion-limited as reported elsewhere [55].

— The pH in the 6.2—7.8 range was of limited effect on the maximum amount of adsorbed DNA but nevertheless helpful in understanding the physicochemical aspects of DNA—PPy interaction.

— The PPy dopant effect is the major parameter that influences the DNA adsorption. The maximum amount of adsorbed DNA was in the range of 3—10 mg/g (larger than PMMA adsorption). Moreover, the isotherms have differing shapes which is an indication that depending on the dopant, PPy surface offers to DNA fragments either homogeneous or heterogeneous adsorption sites.

ABBREVIATIONS

THF: tetrahydrofuran	CTC: carbon tetrachloride
DXN: 1,4-dioxane	DCE: 1,2-dichloroethane
TOL: toluene	DCM: dichloromethane
	TCM: chloroform

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