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New Advances on the Characterisation of Polymer Surfaces by HREELS

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Summary: Self assembled monolayers (SAMs) of thiols functionalised with oligothiophene functions were used as models for polymer surfaces. Thienyl functionalisation simulates the surface region and demonstrates that the analysed depth is of the order of 10 Å. Spectra of polystyrene (PS) films were recorded and show that impact mechanism dominates, which corroborates the high sensitivity of HREELS applied to polymer surfaces. Different orientation of phenyl groups is unravel for PS films deposited on platinum and silicon substrates, which is here related to a different conformation of the PS chains in the surface region of the film. To illustrate the state of the art of HREELS applied to organic films, spectra were recorded with old and new generation spectrometers.

Introduction

Due to the constant increasing number of applications, polymer film surfaces and interfaces are the subject of a greater than ever interest nowadays. Their employment is mainly dependent on the chemical nature, on the orientation of the outermost molecular groups of the films and on the conformation of the chains at the surface. To all intents and purposes, these groups determine the physical and chemical properties of the surface, for instance the reactivity or the surface energy. They can also confer certain specific properties to the polymer surfaces such as adhesion or anti-adhesion capability, wetting or dewetting behaviour, friction or sliding characteristics, specific electronic features or even molecular recognition ability. Particularly, in polymer blends, surface properties can be tailored by the segregation of one of the components to the air interface. Polymeric films can also constitute chemical barriers to protect the substrate from exterior agents responsible for

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instance by material corrosion. Another much demanded attribute is the field of sensors using molecular recognition, which greatly depends on the nature and specific reactivity of the outermost chemical groups exposed at the surface of the organic film. In all these applications, as the concentration of species in the bulk and at the surface can be very different, new modern techniques for surface analysis are more and more demanded to identify them, namely those constituting the molecular surface.

In spite of the high degree of sophistication of the many surface tools existing nowadays, only very few are well suited to detail the chemical features in the polymer surfaces. Actually, the requirements of this analysis are very severe implying:

- surface sensitivity;
- composition analysis of the extreme surface;
- orientation detectivity;
- non destructive technique.

High Resolution Electron Energy Loss Spectroscopy (HREELS), a highly surface sensitive electron induced vibrational spectroscopy can respond to all these requirements. In fact, this spectroscopy using electrons as probes, has lately enlarged its domain of applications to the analysis of molecular films and more particularly that of polymer surfaces. It has been largely applied to the study of monolayers or submonolayers of adsorbates on metal and semiconductor substrates. The use of HREELS in organic films lays on the sensitivity of this technique to the outermost groups of the film with a mean depth of analysis of some Ångstroms[1] and on the possibility to provide information about the orientation of molecular groups at the surface of the film. Moreover, spectral domain can be extended to electronic excitations without changing source or detector systems and electronic excitations can be investigated. In opposition, photon induced vibrational spectroscopy as Infrared absorption or Raman scattering are sensitive to the film bulk but not appropriate to the analysis of the film surface.

In an HREELS experiment, a beam of low energy monoenergetic electrons (energy E_i below 10 eV) interacts with the surface region of the sample. During the interaction, vibrational modes of the sample can be excited and the backscattered electrons lose the corresponding amount of energy. Therefore, the analysis of the backscattered electron can give the spectrum corresponding to the vibrational spectrum of the surface. Other excitations as electronic transitions can also be produced, however in this work only those concerned with the vibrational part of the spectrum are analysed.

The potentialities of HREELS spectroscopy derive notably from the different mechanisms involved in the interaction between the electron and the molecules or the molecular groups present in the surface region. One can distinguish three main mechanisms:

- dipolar mechanism - is the electrostatic interaction between the electron and the dipoles present at the surface. This is a long-range interaction with typical distances of some tens of Angstroms. This interaction is also characterised by small deviations of the electrons from their initial paths, which leads in the case of smooth surfaces to an electron backscattering inside very narrow angular lobes. After the substrate reflection, electrons are then backscattered around the specular direction. Moreover, as the energy transferred in a vibrational excitation is much lower than the incident energy, very low momentum amounts are transferred to the sample. This makes the selection rules of dipolar mechanism very similar to those operative in infrared spectroscopy and more particularly, to those of RAIRS (reflection-absorption infrared spectroscopy). Scattering cross sections are large because the slow electrons spend a long time within the range of the interaction and decrease with the energy of the incident electron.[2]
- Impact mechanism - is, in opposition, a short-range interaction of the incident electrons with those of the valence orbitals within distances typically of the order of 1 Å. One must, then, consider the penetration of the electron beam into the film and therefore only backscattered electrons from the extreme surface will be observed as those from inner scattering centres involve multiple losses. Consequently, impact mechanism

enables the analysis of the outermost chemical functions of the film. This short-range interaction also leads to large deviation from the initial paths and weakly angle dependent cross sections. In this case, differential cross sections increase with the energy of the incident electrons.[3] IR inactive modes may be observed.

Resonance mechanism is a particular case of with the formation of transient negative ion states, as those observed in gas phase. Differential cross sections are peaked functions of the incident energy.

HREELS was applied for the first time in 1986 to the study of polymer surfaces.[4] Other studies on polymer and organic film surfaces followed, namely those concerning component segregation in blends[5], end chain surface enrichment[6], metallisation of polymers, describing an interface formation of a polymer-substrate interface[7] or analysing plasma treated polymer surfaces.[8]

One of the aims of the present work, is to give a state of the art of HREELS as a technique of analysis of polymers illustrating its potentialities though a molecular model with surface-bulk contrast and some surface spectra of common samples of polystyrene (PS).

One of the limitations of the application of HREELS to organic films and particularly to polymers, concerns its poor energy resolution. In fact, in electron optics the space charge of the electron beam needs to be taken into account. It has been known for some time that the space charge in electron selectors and associated optics is the limiting factor of resolution. New developments of HREELS spectrometers conducting to "ultimate" resolution are now available.[9] Recently, a new spectrometer design was developed. Here, the dimensions of the different elements requiring trajectory calculations, as the energy selectors and the electron optics, were optimised with the inclusion of the space charge. The final result of such optimisation gives now a high count rate in the inelastic processes, which exceeds by several orders of magnitude that of the earlier instruments. This opens a new age in the study of surfaces and namely those of polymers.

One must admit that characterisation and control of polymer surfaces is not obvious. In fact, polymer surfaces are very difficult to be controlled and modified in a systematic way. To know, for instance, the depth of the analysed region, a contrast between the bulk and the surface is needed to interpret the spectral features. It is however possible to use molecular models, which can replicate polymer surfaces. Organised monolayers with characteristic extremities may be used as models to simulate the polymer surface region. The use of monolayers is a conceptual strategy for a model of a polymer surface, as a good contrast can be created replicating the surface and the bulk region of a polymer. For these models, the depth of analysis or the surface region thickness can be compared with the length of the functionalized end-groups. Self assembled monolayers (SAMs) are good candidates as polymer surface models as they meet the following ideal requirements:[10] (a) highly smooth supporting substrates, (b) complete coverage of the substrate surface by the film (c) wide variability of selection of the outer surface functionality, (d) flexibility in control of surface density and (e) capability to control the surface population of chain folds and chain ends. SAMs process refers specifically to a monolayer that is spontaneously formed during the contact of a solution with the substrate. Molecules must contain at least a functional group capable of spontaneous chemisorption on the surface. Because of this specific chemical reaction between the function and the surface, further adsorption can be avoided as only one molecule occupies the surface site. This is the case of thiols on metal surfaces such as gold or platinum. More specifically functionalised thiols containing a characteristic chemical group in the extremity opposite to that of thiol, are well-suited molecules for this purpose. These molecules have a general formula: $Y - (CH_2)_n - SH$, where Y is the functional group. Thiols spontaneous adsorb on the metal sites with the liberation of hydrogen. On the other hand, the chemical nature of the function in the other extremity, determines the properties of the surface as far as the molecules are well organised on the surface.

For instance, we studied the formation and the characterisation of SAMs of $4TC_{12}H_{24}SH$ (T is the thienyl group) by different techniques such as reflection-absorption infrared spectroscopy (RAIRS), electrochemistry, contact angle, X-ray diffractometry and HREELS.[11] The conclusions of this study show that molecules rapidly graft onto the surface during the first seconds of the interaction with the solution. Then, they slowly assemble through the intermolecular forces always in contact with the solution. For longer periods, as 12 hours, thienyl groups stand in a well-ordered array slightly tilted with respect to the perpendicular. The adsorption leads to a close packed monolayer where oligothiophene groups plaster the surface of the film. In contrast, the alkyl chains exhibit a weak organisation due to several defaults. These molecular layers possess a good surface-bulk contrast and can be used strategically to simulate the polymer surface.

With the goal to create polymer surface models, in this work, a $3TC_6H_{12}SH$ molecule possessing a terthiophene group separate by an aliphatic chain spacer of six carbons from the thiol group was used. SAMs were then formed on gold substrates. The functionalisation thickness depends on the number of thienyl groups in the surface region. In this case, 3T has a molecular length around 11 Å and an aliphatic spacer of ca. 8 Å. For this work, we used a similar SAMs formed from $3TC_6H_{12}SH$ on gold substrates.

As an example of real polymer surfaces, HREELS spectra of PS spectra were revisited[12] and recorded now with new generation spectrometers. They were compared with those obtained by infrared and Raman spectroscopy. This work shows now that more than the double of the bands can be resolved. They can also be easily assigned to those existing in infrared and Raman scattering spectroscopy.

Experiments

Samples

Self-Assembled Monolayers (SAMs): Gold substrates were supplied by Metallhandel Schröer GmbH and flame annealed to obtain Au (111) terraces, after washed with dichloromethane in a ultrasonic bath, rinsed with ultrapure water and dried in an argon flux. STM as well as x-ray diffraction study on such substrates allows observing that the annealing with the hydrogen flame forms terraces (111) of approximately 80 $Å^2$. That implies a roughness of surface superior to the roughness awaited for gold evaporated on mica, more commonly used.

After flamed, gold substrates are cooled under an argon flux then, dipped in a 1 mM solution of $3T(CH_2)_6SH$ in pure dichloromethane for a period of 12 hours and then rinsed thrice in pure dichloromethane in an ultrasonic bath for 2 min. After this treatment, samples were rinsed with ultrapure water and dried under an argon flux. To avoid surface contamination, samples were transferred under an argon environment and introduced in the HREELS UHV chamber under nitrogen flux.

Polymer films: Low dispersity PS (Mw≈8000) was used. Films were cast on platinum substrates 100 nm thick sputtered onto glass substrates. Film casting was performed by dipping the substrates into a 0.5 g l^{-1} solution of pure PS in CCl_4 (spectroscopic grade) and allowing the solvent to evaporate. Film thickness was estimated to be around 5 nm from elastic recoil diffusion analysis (ERDA) measurements.[13]

Apparatus

HREELS vibrational spectra were recorded using both an ELS22 Leybold Heraeus spectrometer and a LK Technologies ELS 3000 (new generation) spectrometer under 10^{-10} Torr at room temperature. The electron primary energy, E_p, was varied from 0.5 to 5 eV. Sweeping steps are of 4.6 cm^{-1}. Incident and analysis directions are measured relative to the normal of the sample surface. Specular geometry was chosen having incident and analysis angles of 60^{o}. The experimental resolution of ELS22, taken, as *fwhm* of the elastic peak, was better than 10 meV. Best experimental resolution achieved with the ELS 3000 on the sample taken as the fwhm of the elastic peak was of 2.55 meV (20.4 cm^{-1}). Samples were irradiated for several days without charging effects being noticed during the spectra recording.

Infrared spectra of thick films of PS deposited on silicon wafers were recorded using a FTIRS Magna-IR Nicolet 850 equipped with a MCT detector. Spectral domain extends from 650 to 4000 cm^{-1} and resolution is of 4 cm^{-1}. Raman spectra of PS powder were recorded employing a XY-Dilor fitted with a CCD detector cooled by liquid nitrogen with a resolution better than 2 cm^{-1}.

Results and discussion

SAMs as a Model of Polymer Surface

Fig. 1 shows the comparison of two spectra of a SAMs of $3TC_6H_{12}SH$ on gold recorded with an old generation spectrometer having a resolution of 60 cm^{-1} and a new generation one with a resolution of 20 cm^{-1}. The position of most important energy losses are inscribed in the figure and assigned in Table 1 from comparison with values found in the literature for similar molecules.

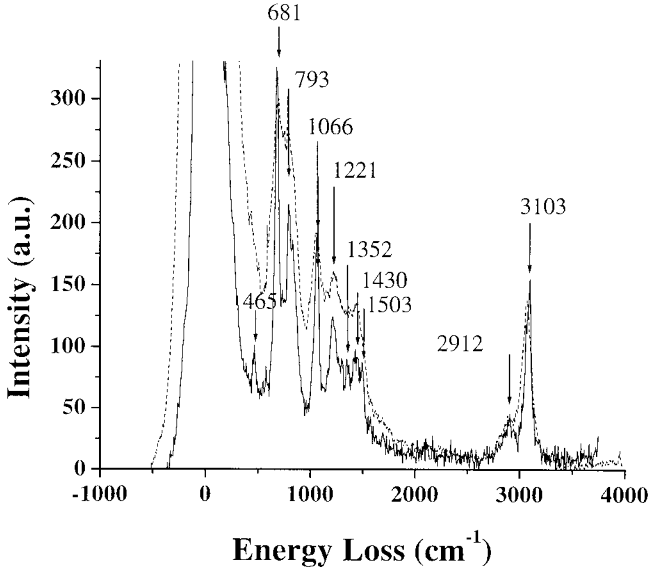

Fig.1 Comparison of HREELS spectra of a $3TC_6H_{12}SH$ SAMs deposited on evaporated gold recorded with 60 cm^{-1} (dots) and 20 cm^{-1} (line) resolution of ELS22 and ELS3000, respectively. Spectra were recorded using incident electrons of 5 eV and a 60° specular geometry.

One can clearly remark that the resolution improvement results in the increase of the number of bands detected. More than the double of the number of bands unravelled with low resolution spectrometer, are now nicely resolved. They are assigned in Table I by comparison with similar molecules[14].

TABLE I

Assignments of the main peaks appearing in the HREELS spectra of a SAMs of $3TC_6H_{12}SH$ deposited on evaporated gold[14]

IR (cm^{-1})	RAMAN (cm^{-1})	HREELS (cm^{-1})	ASSIGNMENTS
453	453	462	ν_{21} ring deformation
565	566	573	ν_{11} ring deformation
687	683	683	ω_2 C_α-H out-of-plane deformation
793	801	793	ω_3 C_β-H out-of-plane deformation
834	826	839	ω_2 C_β-H out-of-plane deformation + CS stretching
1066	1080	1073	ν_6 C_α-H bending + C_β–C_β stretching
1216	1216	1223	ν_3.C_α–C_α inter-ring stretching
1285	-	1298	ν_3 C_α–C_β, symmetric stretching"
1378	1372	1369	ν_3 C_β–C_β, intra-ring sym. stretching
1449	1423	1449	ν_2 C_α=C_β, symmetric stretching
1503	1506	1503	ν_1 C_α=C_β, asymmetric stretching
2850		-	$\nu_s(CH_2)$ aliphatic chain
2920		2912	$\nu_a(CH_2)$ aliphatic chain
3073	3086	3078	ν_0 C_β-H, stretching
3105	3097	3103	ν_0 C_α-H, stretching

Observing the whole spectral domain presented in Fig.1, one concludes that the peaks assigned to the thienyl group dominate the spectrum. Alkyl chain modes are practically absent excluding a weak wide band centred around 2910 cm^{-1} assigned to a sum of the symmetric and asymmetric CH stretching modes of the alkyl chain. Other modes corresponding to chain methylene groups, particularly those around 1420 and 720 cm^{-1} are not sufficiently intense to be noticed.

Another remarkable point is that the bands corresponding to the CH_α can be also resolved from those corresponding to CH_β, particularly the stretching modes of CH_α and CH_β can be separated. However, we have now to determine the electron interaction mechanism, responsible for the different losses before to analyse in more detail the HREELS spectra

Energy Loss Mechanism

As it is referred above, the analysis of the dependence of differential cross sections on the energy of the incident electrons allows us to determine the nature of losses mechanisms.

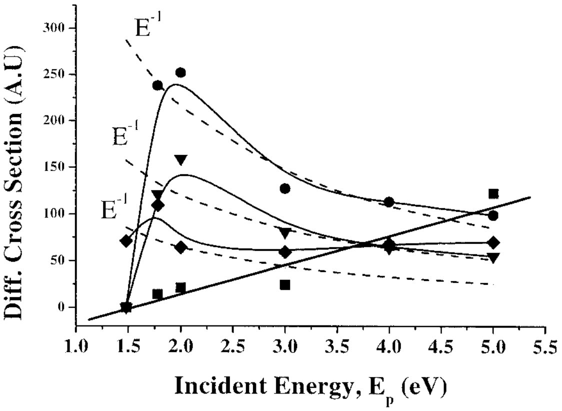

Fig.2 Differential cross sections of CH out-of-plane deformation 683.cm^{-1} (●) and 792 cm^{-1} (▼), CH bending 1070 cm^{-1} (◆) and CH stretching 3102 cm^{-1} (■) are represented versus the incident electron energy, E_p. The stretching curve is fitted linearly whereas other curves are fitted with an E_p^{-1} functions.

Fig. 2 shows the evolution of differential cross section (proportional to the ratio between the intensity of the inelastic event and that of the elastic peak) versus the incident energy E_p. The mechanism characters associated to energy losses appearing in the spectrum are the following: those corresponding to the excitation of CH out-of-plane deformations, located at 683 and 792 cm^{-1}, are governed by dipolar interactions, whereas that of CH stretching modes has a strong impact character. The presence of the later should indicate that thienyl groups are located closely to the outermost surface .

The energy loss assigned to CH_α bending located around 1070 cm^{-1} seems to have a hybrid behaviour in between dipolar and impact meaning showing that both mechanisms or different vibrational modes are involved. It is well-known that the impact mechanism is responsible for the excitation of CH_2 stretching modes[11, 15].

Spectra Analysis

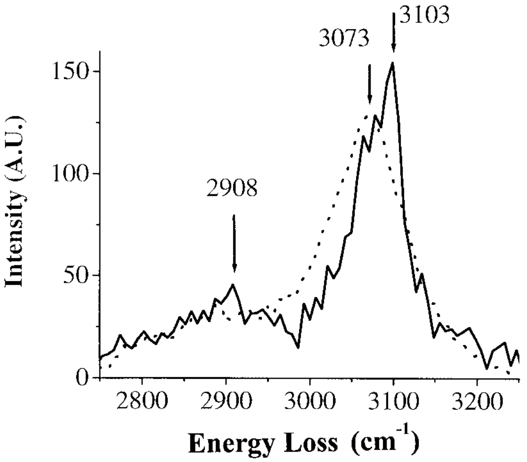

Fig.3 Detail of the stretching CH region of spectra presented in Fig. 1.

Thus the stretching region within 2800-3100 cm^{-1} contains only losses ruled out by impact interactions. The larger intensity of energy losses associated to thienyl groups relatively to those of the aliphatic CH indicate clearly that the extreme surface of the SAMs is mostly occupied by thienyl groups revealing a good organisation of the monolayer functionalities. The main conclusion of using this model for a polymer surface is that the analysed depth is of the same order of magnitude as the length of the 3T functionality. Taking into account that 3T molecular length is ca. 11 Å, the analysed depth must be also of the order of 10 Å for energy losses deriving from impact mechanisms. This value should recover other molecular films including polymers. Another remarkable point is that the bands corresponding to the CH_α can be also resolved from those corresponding to CH_β. In particular, stretching modes of CH_α and CH_β, assigned by Garnier et al[14] could be separated. For instance, the loss assigned to CH_α bonds 3103 cm^{-1} (see Fig. 3) is more intense than that located at 3075 cm^{-1}, in spite of CH_β being six times more numerous than CH_α . According to the impact mechanism rule, CH_α is located on the top of the grafted molecules and therefore constitutes the outermost bond of the organised film. This also indirectly shows that the long axis of the 3T moieties is slightly tilted towards the surface normal. However, this tilt must exist since the aromatic out-of-plane losses ω(CH) ruled out by dipolar interactions are present in the spectra.

Polymer Surfaces

To illustrate the state of the art of HREELS spectroscopy applied to polymer surfaces, two spectra of PS films 10 nm thick are presented in fig. 4, where two different generation spectrometers were used with resolutions of 13 meV (104 cm^{-1}) and 2.55 meV (20.4 cm^{-1}), respectively. In spite of the resolution being different, peak positions roughly agree with those obtained with similar films dipped on silicon substrates.

The improvement of HREELS resolution inherent to the new spectrometers enables now the observation of about twenty peaks in contrast to the limited number of peaks formerly recorded. New generation spectrometers enable now to easily distinguish energy losses corresponding to the excitation of the different out-of-plane deformation modes around 700 cm^{-1} and separate the contributions of the CH stretching vibrations of the aliphatic and aromatic groups.

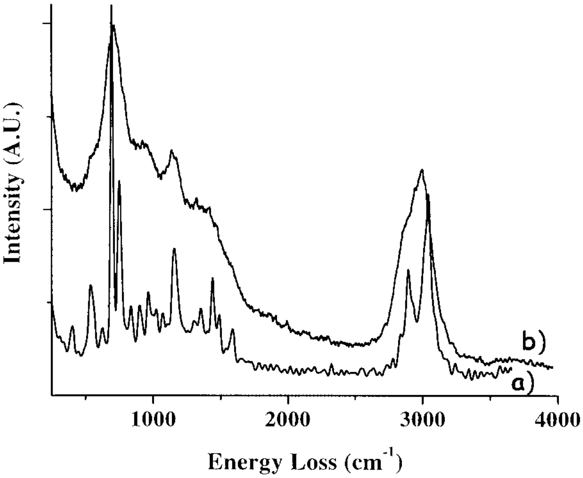

Fig.4 Comparison of two HREELS spectra (E_p= 4eV and angles of incidence and analysis of 60°) recorde with different resolutions:

a) 2.55 meV (20.4 cm^{-1})

b) 13 meV (104 cm^{-1}).

One can also easily remark that HREELS spectra contain energy losses corresponding to infrared and Raman peaks. In fact, these bands can be straightforwardly assigned by comparison with those obtained using infrared transmission (PS film deposited on silicon) and Raman scattering spectroscopy (powder), as it is shown in Fig. 5.

The assignment of the different losses to the different vibration modes is now quite straightforward. Table II establishes a comparison of the band intensity of excitation of the different vibrational modes of PS in infrared, Raman and HREELS spectroscopy[16].

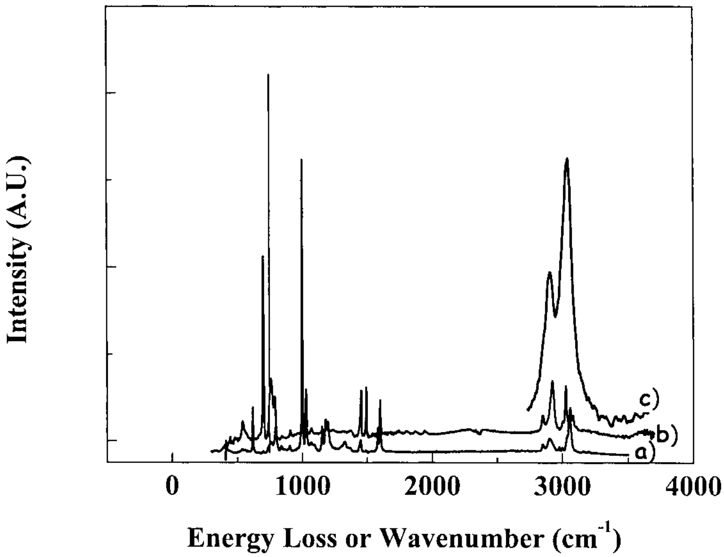

Fig.5 Comparison of PS spectra:

a) Raman spectrum of the powder;

b) Infrared transmission spectrum of a thick film deposited on a silicon wafer;

c) HREELS spectrum recorded using E_p= 6 eV and angles of incidence and analysis of 60°.

The analysis of the intensity of the different features arising in HREELS spectra vs Ep, the energy of the incident electrons shows a dominating impact mechanism. This also confirms the surface specificity of the analysis, which, as it was demonstrated above, is associated to an analysis depth estimated to be of the order of 10 Å.

TABLE II

Comparison of the intensities of different modes of PS in Infrared, Raman and HREELS spectroscopy[16]

Main vibrational modes	Frequency, cm^{-1}	IR	Raman	HREELS
Ring Vibrations				
CH out-of-plane	410	W		S
CH out-of-plane	545	S		S
CH out-of-plane	705	VVS		VS
CH out-of-plane	760	VS		VS
CC chain rocking	990	-	VVS	VS
CH_2 Ring in Plane	1027		S	W
CH_2 Chain	1170		VS	VS
CH2 wagging	1345		S	S
CH_2 chain bending	1460	VS	S	S
CC Ring stretching	1590	VS	-	W
CH Ring Stretching	3050	S	VS	VVS
Chain Vibrations				
CH_2 rocking	725	VS		VS
CCC Chain	1157		S	VS
CH_2 sym. stretching	2850	VS	S	VS
CH_2 asym. stretching	2906	VS	S	VS

However, comparing HREELS spectra of polystyrene films with the same thickness magnitude deposited on platinum and on silicon, a notorious divergence occurs in which respects the mechanism responsible for the excitation of the CH out-of-plane deformation around 680 cm^{-1}. In fact, the analysis of the differential cross section of this peak shows a clear dipolar behaviour in PS deposited on silicon, in PS films deposited on platinum, it has a clear impact behaviour, as it is shown in Fig. 6.

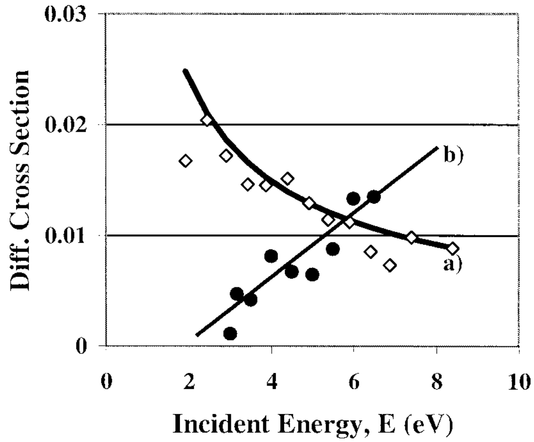

Fig.6 Differential cross sections of the energy loss peak centred at 683 cm^{-1} for a PS films deposited on:

a) silicon substrates and fitted with E^{-1};

b) platinum substrates linearly fitted.

Considering the selection rules for dipole mechanism, one should conclude for a favoured orientation of phenyl groups parallel to the silicon substrate in opposition to that of films on platinum substrates, where phenyl groups are perpendicular to the substrate. This observation could be due to substrate effects, since the thickness of films are of the same order of magnitude. Similar conformational effects in polystyrene films on silicon and on a metallic substrate (gold) have been observed using broadbandwidth vibrationnally-resonant sum frequency generation[17]. This work is still under investigation now.

Conclusion

HREELS spectra of models of polymer surfaces and real polymer samples were recorded using new generation spectrometers. Resolution improvement enables the access to a higher number of peaks, which can be now straightforwardly assigned. The electron-interaction mechanisms also become easier to identify. Using SAMs as molecular models for polymer surfaces, analysis depths were estimated to be of the order of 10 Å. Spectra of surfaces of polystyrene films show a higher number of bands, which were assigned to infrared and Raman active modes. Preferential orientation effects were found, which are likely associated to a different chain conformation induced by the substrate.

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