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Electron-Induced Vibrational Spectroscopy. A New and Unique Tool To Unravel the Molecular Structure of Polymer Surfaces

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Among the surface-sensitive spectroscopies used to characterize clean and surface-modified polymers, one technique has rather recently emerged as a very promising complementary tool. High-resolution electron energy loss spectroscopy, or electron-induced vibrational spectroscopy, has potentially all the attributes of the well-known optical (infrared and Raman) spectroscopies; it clearly adds to X-ray photoelectron spectroscopy the possibility to go beyond surface elemental and chemical analysis and to unravel the molecular structure of an extremely thin surface layer of a polymer. This ultrahigh vacuum spectroscopy is shown here to gather information from the last 25 Å or so of the polymer surface, as deduced from the analysis of sandwich layers of normal and perdeuterated PMMA Langmuir-Blodgett films. Four case studies of molecular-type information are presented, illustrating (1) the preferential surface segregation of CH₃ chain ends on a crystalline polyethylene, (2) selective surface segregation and dynamics of deuterated material in mixtures of normal and deuterated polystyrenes, (3) tacticity induced molecular orientation of PMMA's and polystyrene, and (4) metalization induced molecular reorientation on the surface of polyimide films.

Introduction

Nowadays, synthesis of new polymers is more and more application oriented. With the increasingly important role held by the polymer—original or purposely modified—surfaces, e.g. in bi- or multilayered or composite materials, it is understandable that new spectroscopies are being searched for to complete the arsenal of existing techniques. Infrared and Raman spectroscopies are probably the most routinely used methods to study polymer materials. With resolution comparable to natural linewidths, they are unbeatable to fingerprint polymers (and impurities), to study conformation, tacticity, or crystallinity of the materials; however these easy to use optical spectroscopies are per se bulk sensitive in their normal experimental setups. On the contrary, electron- and ion-induced spectroscopies are known to be surface sensitive; the attributes of X-ray photoelectron spectroscopy (XPS) and secondary ion mass Spectrometry (SIMS) are now well established (they will be summarized here), but still do not yet extend all the IR capabilities to polymer surfaces.

HREELS (high-resolution electron energy loss spectroscopy) took about 20 years to be applied from adsorption studies to polymer surfaces.¹ This electron-induced vibrational spectroscopy has been—and still is—extremely useful in elucidating chemical reactions and reaction sites of adsorbed molecules on surfaces. Electron-induced vibrational fingerprints from polymer surfaces appeared only 5 years ago, because it is difficult to collect spectra from insulating materials, and interpretation of rather

poorly resolved spectra of very complex molecules is not straightforward. Nevertheless, it has been very exciting and rewarding to launch a fundamental research program on the possibilities and drawbacks of what might become a new powerful experimental tool to study polymer surfaces. This is still a long term project, but in the meantime, some key questions have already addressed, if not yet solved; let us mention a few reports on the initial concerns of HREELS,² on the quantitative aspects of the spectroscopy,³ and on its application to study polymer-metal interactions⁴ and a recent comparison between the HREELS and SIMS/ISS techniques.⁵

This paper will largely refer to those data, going rapidly through the preliminaries, and focusing on one aspect of HREELS applied to polymer surfaces that appears as its most promising quality: the possibility to unravel the molecular structure of the extreme surface, i.e. to go beyond a chemical analysis and learn about the polymer chain configuration and the relative orientation of chemical groups at the interface with the outside world. However, some attention will be given to preliminary results assessing the very high surface sensitivity—to the first 25 Å below the surface—of electron-induced vibrational spectroscopy.

(2) Pireaux, J. J.; Grégoire, Ch.; Vermeersch, M.; Thiry, P. A.; Caudano, R. *Surf. Sci.* 1987, 189/190, 903.

(3) Pireaux, J. J.; Thiry, P. A.; Sporken, R.; Caudano, R. *Surf. Interface Anal.* 1990, 15, 189.

(4) Pireaux, J. J.; Grégoire, Ch.; Vermeersch, M.; Thiry, P. A.; Rei Vilar, M.; Caudano, R. ACS Symposium Series 440; Sacher, E., Pireaux, J. J., Kowalczyk, Eds.; American Chemical Society: Washington, DC, 1990; p 47.

(5) Gardella, J. A., Jr.; Pireaux, J. J. *Anal. Chem.* 1990, 62, 645A.

(1) Ibach, H.; Mills, D. L. *Electron Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, 1982.

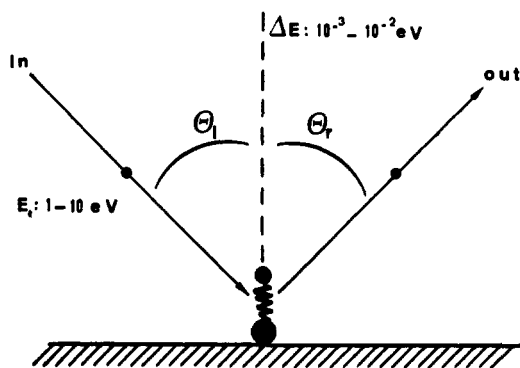


Figure 1. Schematic of the HREELS experiment. In ultrahigh vacuum, the backscattered part of a well-monochromatized low-energy electron beam is used to probe vibrational excitations from a polymer surface.

Table I. Principal Characteristics of Surface Analytical Techniques

properties	XPS (ESCA)	HREELS	sSIMS
element detection	for $Z > 2$	no	all
chemical information	no hydrogen by chemical shift	especially good for H, C, N, O, containing bonds	molecular ions and fragments
structural information	no	yes	? yes (molecular ions)
depth sensitivity	$\approx 50 \text{ \AA}^a$	$\approx 25 \text{ \AA}$? 10 \AA
quantification	accurate	qualitative	very difficult
sample damage	small with monochromatized X-rays	no	low (static SIMS)

^a Less at grazing exit angles ($< 20^\circ$).

Instrumentation

Basically an ultrahigh vacuum external reflection spectroscopy (Figure 1), HREELS studies the backscattered part of a well-monochromatized low-energy electron beam that is used to probe the vibrational excitations from a material surface; it does not require any peculiar tool except very high performance electron energy analyzers. Indeed, a very low energy electron beam (between 1 and 10 eV), must be monochromatized and analyzed to achieve an intrinsic energy resolution that ranges—today—from 2 to 10 meV (10^{-3} eV); as a comparison with optical spectroscopies, this corresponds to 16–80 cm^{-1} ($1 \text{ meV} = 8.066 \text{ cm}^{-1}$), what might be sufficient, as infrared or Raman spectra of polymers usually consist of peaks which vary in width from about 5 to 30 cm^{-1} . However, a resolution below 10 meV is seldom achieved on polymer surfaces, because of roughness and poor reflectance from the samples and because of charging effects. It has been shown that polymers prepared as thin films on conducting substrates are workable samples, but there might remain transient and very local charges to perturb the electron probe beam.

HREELS vs XPS and SIMS

Table I summarizes most of the practical attributes of X-ray photoelectron spectroscopy (XPS or ESCA), secondary ion mass Spectrometry (SIMS), and HREELS: these advantages are pertinent for the study of polymer surfaces. Electron-induced vibrational spectroscopy appears particularly suited for polymer research, because it is especially sensitive to the light elements (H, C, N, O, ...) involved in chemical bonds. HREELS can easily detect hydrogen (as C–H, N–H or O–H bonds) and distinguish between single, double, and triple bonds; heavier elements

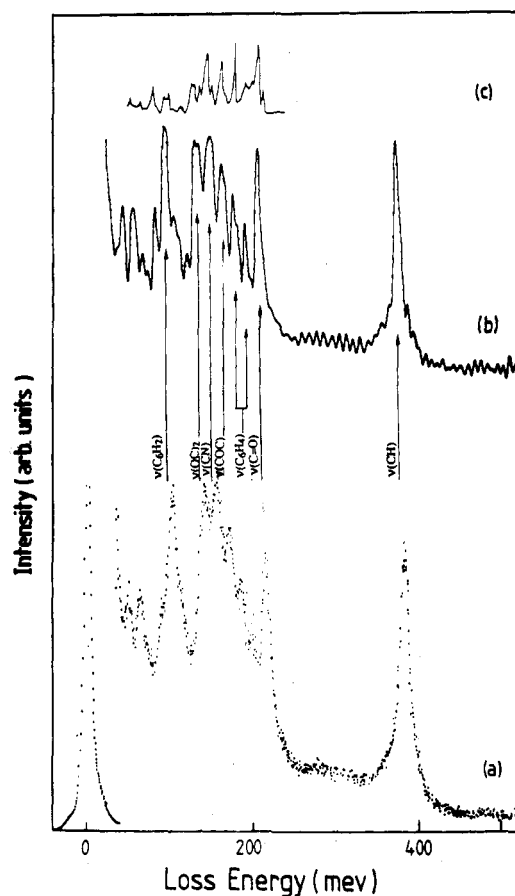


Figure 2. Electron-induced vibrational analysis of a clean, cured polyimide film: spectrum a is the original raw data, curve b is a FT-resolution enhanced curve, to be compared with spectrum c, the infrared absorption spectrum of the same polymer.

are difficult to detect, because the associated vibrations are at low loss energy in a narrow energy range, very close to the elastic peak. As will be shown here, HREELS is still more surface sensitive than XPS (at normal exit angle); it is in fact quite common that a sample labeled “clean” for this spectroscopy presents a very significant carbon and/or oxygen contamination in HREELS. As for the structural information to be gained on the extreme polymer surface (see the examples given in this paper) they are presently at the qualitative level; indeed, the excitation mechanisms of the molecular vibrations have not yet been exactly identified: without selection rules, intensity analysis of vibrational bands rests on the use of spectra collected from reference materials.³

The potentialities of infrared and Raman analyses are well-known from the spectroscopists. Vibrational spectra excited by an electron beam should be as informative, either as soon as the experimental resolution is mastered and improved or as soon as sensitive enough computer codes will allow a meaningful resolution-enhanced analysis. Progress in this direction is currently being made,⁶ and Figure 2 compares the HREELS spectrum of a clean, cured polyimide surface, together with one computer analyzed spectrum, and an (absorption) infrared fingerprint of the same material. Clearly, the majority of the IR bands of interest are accessible to the electron-induced vibrational spectrum; noteworthy however is the fact that the relative band intensities cannot be transferred from the optical to the electronic spectra. This confirms that both spectroscopies do not obey the same selection rules.

(6) Pireaux, J. J.; Ghijsen, J.; Sporken, R.; Grégoire, Ch.; Gardella, J. A., Jr. In preparation.

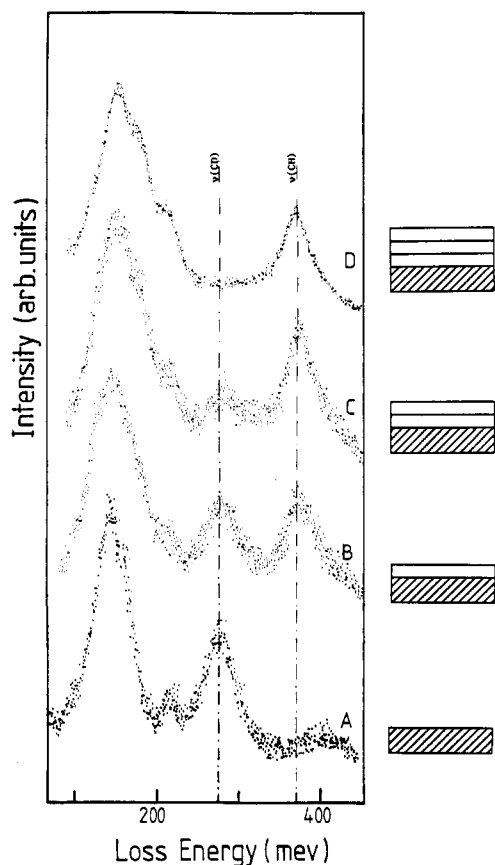


Figure 3. HREELS spectra of LB-PMMA sandwich structures: (A) pure d_3 deuterated polymer; (B \rightarrow D) sample A covered with one, two, and three normal PMMA layers (12 Å thick), respectively.

HREELS Surface Sensitivity

The probed depth in organic materials by very low energy electrons is still an open question.^{2,5} A sensitive way to solve the problem appears to study very thin organic layers, with a marker at a given controllable depth; the extinction of a signal versus depth should measure the surface sensitivity of the spectroscopy.

It has already been shown a few years ago that fatty acid layers (Langmuir-Blodgett (LB) films) presented no carboxyl stretch band around 1650 cm^{-1} , when these (usually very IR intense) dipoles are located some 25 Å below the extreme surface.⁷

In order to precisely define this figure, a program has been launched on the study of alternating normal and perdeuterated layers (sandwich structures) of poly(methyl methacrylate).⁸ These films can be prepared by the LB technique, with individual thickness of about 12 Å. As an example—to be further analyzed⁸—Figure 3 compares four spectra collected respectively from a thick layer of pure deuterated PMMA (please note the absence of $\nu(\text{C-H})$ signal just below 370 meV; the broad peak at 410 meV is a combination band from the 140-meV peak and of the 270-meV C-D stretch) and then for a fully deuterated layer covered with one, two, and three normal LB-PMMA films. The attenuation of the $\nu(\text{C-D})$ stretch signal at 270 meV is very clear; without waiting for a detailed analysis of the results,⁸ where electron impact energy and scattering geometry will have to be taken into account, it is already possible to safely bracket the total

(7) Wandass, J. H.; III; Gardella, J. A., Jr. *Langmuir* 1986, 2, 543; *Langmuir* 1987, 3, 183.

(8) Brinkhuis, R.; Schouten, A. J.; Grégoire, Ch.; Pireaux, J. J.; Caudano, R. In preparation.

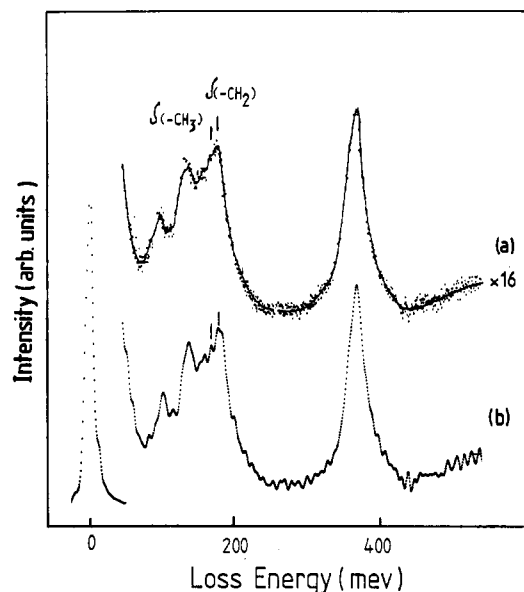


Figure 4. Electron-induced vibrational spectrum (a) and its computer resolution enhancement analysis (b) of high-density polyethylene. The intense 1370- cm^{-1} band is attributed to the methyl bending band of the chain-ends.

effective electron probed depth between 24 and 36 Å, for the $\nu(\text{C=O})$ vibrational stretch band at an electron impact energy of 6.0 eV. A similar experiment with normal PMMA covered with multiple deuterated PMMA LB layers gave the same result.

Molecular Structure of Polymer Surfaces

The four sets of data presented here have already been published separately in some similar format (full references will be cited in due time). The purpose of this presentation is to juxtapose individual cases and let them converge to a unique conclusion. HREELS is capable of retrieving some useful information on the molecular structure at the extreme surface of polymers.

(1) **Chain Ends Segregation at Surfaces.** One of the first HREELS spectra recorded from the "simplest" polymer, polyethylene, was very surprising.⁹ Besides the relatively large number of bands (or shoulders, due to the poor energy resolution of the electron spectrum), their intensities were striking (Figure 4). Focusing particularly on the deformation bands between 1300 and 1500 cm^{-1} , it is known that polyethylene is optically fingerprinted by an intense $\delta(\text{CH}_2)$ bending mode at 1440 cm^{-1} and a very weak $\gamma(\text{CH}_2)$ wagging band at 1370 cm^{-1} .¹⁰ The electron-induced vibrational spectrum of polyethylene on the contrary presents an intense band at 1370 cm^{-1} (Figure 4). The literature shows the infrared spectrum of polypropylene also has a strong peak at 1378 cm^{-1} —in fact, as strong as the $\delta(\text{CH}_2)$ at 1440 cm^{-1} —which is assigned to the $\delta(\text{CH}_3)$ bending vibration. Without knowing any mechanism that could enhance a $\gamma_w(\text{CH}_2)$ mode in the electron spectrum of polyethylene and supposing that a $\delta(\text{CH}_2)$ or $\delta(\text{CH}_3)$ band would have about the same excitation probability, it is therefore tempting to attribute this band to the methyl groups of polyethylene. As the studied material is a high molecular weight, high density, crystalline polyethylene where branching should be very low, the relative number of $-\text{CH}_3$ end groups are largely

(9) Pireaux, J. J.; Thiry, P. A.; Caudano, R.; Pfluger, P. *J. Chem. Phys.* 1986, 84, 6462.

(10) Bower, D. I.; Maddams, W. F. *The Vibrational Spectroscopy of Polymers*; Cambridge University Press: Cambridge, 1989.

outnumbered by the $-\text{CH}_2-$ skeleton units. Knowing the extreme surface sensitivity of HREELS, one could suggest that the intense $\delta(\text{CH}_3)$ band at 1370 cm^{-1} on the electron spectrum corresponds to chain ends of polyethylene, terminating preferentially on the surface. The driving force to push the chain ends to segregate at room temperature preferentially at the surface might be their lower surface energy. To be convinced of the effect, in Figure 6 (to be discussed later on), one can compare the relative intensities of the $\delta(\text{CH}_2)$ and $\delta(\text{CH}_3)$ bands recorded from PMMA surfaces.

(2) Chain Segregation at Surfaces. There are now numerous examples of surface segregation in blends of miscible polymers. Electron-induced vibrational spectroscopy has also contributed into this very exciting field of research.¹¹ Indeed, physical mixtures of normal and perdeuterated polystyrene solutions of the same average molecular weight (MW $\approx 40\,000$), mixed with different molar ratios were used to cast thin films to be studied by HREELS. The electron spectra produced intensity ratios of the $\nu(\text{C-H})$ and $\nu(\text{C-D})$ stretch bands, proving a net surface enrichment in deuterium (Figure 5), for low deuterated species concentrations; Fourier transform infrared (FT-IR) spectra attested to the correct composition of the solutions, showing a linear relationship between the band intensities and the inverse of deuterium molar fraction.

The origin, the driving force (probably related to a difference in surface energy), and the dynamics of this selective diffusion are worthwhile to study. Similar experiments using polymers with higher molecular weights, and with mixtures of polymers with different molecular weights, are underway. Is this effect genuine? Is it caused by the film casting, by the air-drying, or by the ultrahigh vacuum (UHV) environment? Surprising results were recorded with the same polystyrene films (inset of Figure 5): the $\nu(\text{C-H})$ and $\nu(\text{C-D})$ intensity ratios were seen to evolve with time; this was in UHV, under the low-energy electron beam (intensity $\approx 10^{-11}\text{ A}$), for a sample temperature probably around 30°C . Samples containing more deuterium were much less affected than the sample ($1/X_D = 8$) shown on the inset; the continuous monitoring of its A_H/A_D ratio showed it evolving from 4.0 to 6.0 in less than 2 h—this last number is still significantly less than the nominal bulk concentration of the solution. The quite rapid variation of the hydrogen/deuterium ratio might perhaps be used to learn about the dynamics of the selective diffusion of deuterated material to (back from) the surface, unless we are just monitoring a progressive hydrocarbon contamination on the surface of the polymer film. A rapid evaluation, neglecting probed depth effect, of this extra hydrocarbon content would suggest that the surface is contaminated at 30%, after 2 h, in UHV (ion pumps, operating pressure around $2 \times 10^{-10}\text{ Torr}$); this supposes a contamination sticking coefficient on the polymer surface close to one, suggesting that this polymer surface would be as reactive as a clean single-crystal metal surface. Such an effect cannot be completely ruled out for the moment, except that Figure 3 (bottom) presents a counterexample of such a possible contamination; a perdeuterated PMMA LB-layer showed no hydrogen contamination after a similar analysis time.

Further studies are therefore mandatory to clarify this issue. But all the data discussed above are undoubtedly arguing in favor of the extreme surface sensitivity of the electron-induced vibrational spectroscopy.

(11) Rei Vilar, M.; Schott, M.; Pireaux, J. J.; Grégoire, Ch.; Caudano, R.; Lapp, A.; Lopes Da Silva, J.; Botelho do Rego, A. M. *Surf. Sci.* 1989, 211–212, 782.

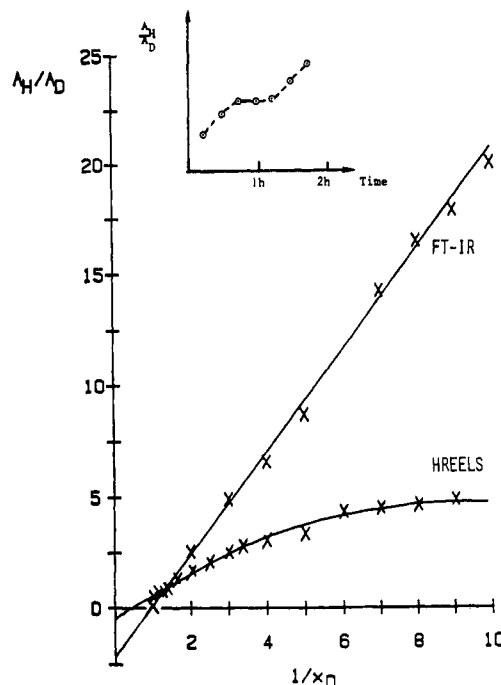


Figure 5. FT-IR and HREELS analysis of the composition of mixtures of normal and deuterated polystyrenes with different molar ratios (X_D): the intensity ratios of the (C-H) and (C-D) stretch bands show a deuterium enrichment on the surface. The inset shows for sample ($1/X_D = 8$) a time dependence; see the text.

(3) Polymer Surface Tacticity. Tacticity—the orderly placement of side groups on the polymer skeleton—can physically distinguish chemically identical polymers. The predictable relative orientation of chemical groups for tacticity-different polymers has already been shown to extend up to the extreme surface of the materials. XPS valence band studies,¹² more recently low-energy ion scattering spectroscopy (ISS),¹³ and a combination of XPS and static SIMS results¹⁴ have evidenced such effects.

Staying at the fingerprinting level, as it is presently premature to try to quantify the observations, HREELS spectra have undoubtedly shown that atactic and isotactic polystyrene films were presenting on their surface, i.e. within the depth probed by the technique, a different amount of $\nu(\text{C-H})$ aromatic signal; this suggests a relative enrichment of phenyl groups on the surface of the isotactic material.¹⁵

In the same type of analysis, Figure 6 compares the electron-induced vibrational spectra of two PMMA layers, an isotactic (bottom) and a syndiotactic one (top); without going into the detail of a complete interpretation of all the recorded vibrational bands, it is clear that, at the fingerprinting level, the two polymer surfaces are easily distinguished. For a similarly intense carboxyl stretch band (around 1700 cm^{-1}), the $\nu(\text{C-H})$ stretch is significantly reduced for the syndiotactic PMMA, with a concomitant

(12) Pireaux, J. J.; Riga, J.; Caudano, R.; Verbist, J. *Photon, Electron and Ion Probes of Polymer Structure and Properties*; ACS Symposium Series 162; Dwight, D. W., Fabish, T. J., Thomas, H. R., Eds.; American Chemical Society: Washington, DC, 1981; 169. Pireaux, J. J.; Riga, J.; Boulanger, P.; Snauwaert, P.; Novis, Y.; Chtaib, M.; Grégoire, Ch.; Fally, F.; Beelen, E.; Caudano, R.; Verbist, J. *J. Electron Spectrosc. Relat. Phenom.* 1990, 52, 423.

(13) Hook, T. J.; Schmitt, R. L.; Gardella, J. A., Jr.; Chin, R. L. *Anal. Chem.* 1986, 58, 1285. Hook, T. J.; Gardella, J. A., Jr.; Salvati, L., Jr. *Macromolecules* 1987, 20, 2112.

(14) Caster, D. G.; Ratner, B. D. *Surf. Interface Anal.* 1990, 15, 479.

(15) Rei Vilar, M.; Schott, M.; Pireaux, J. J.; Grégoire, Ch.; Thiry, P. A.; Caudano, R.; Lapp, A.; Botelho do Rego, A. M.; Lopes da Silva, J. *Surf. Sci.* 1987, 189/190, 927.

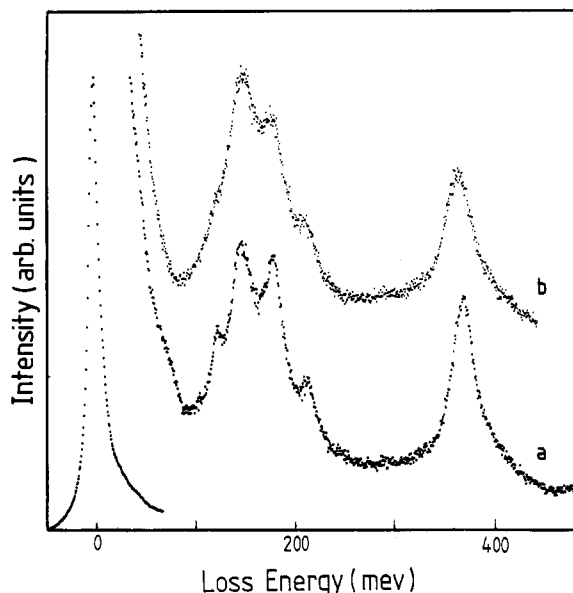


Figure 6. Electron-induced vibrational spectra of tacticity controlled poly(methyl methacrylates): (a) isotactic polymer; (b) syndiotactic polymer.

reduction of the vibrational intensity at about 1400 cm^{-1} ; we know that this spectral region is a combination of $\delta(\text{CH}_3)$ and $\delta(\text{CH}_2)$ deformation bands. We have therefore a consistent scheme suggesting a larger $\text{C}=\text{O}/\text{CH}_n$ ratio on the syndiotactic polymer surface.

Again, it is not possible at the moment to go to the quantitative level. Even so, a qualitative picture should be considered with great care, because other effects might have to be taken into account. Indeed—this is just an example to be discussed further in another paper—we have experimental evidence that the crystalline or amorphous state of the surface is reflected in the electron-induced vibrational spectra; e.g. the same crystalline isotactic PMMA layer is presenting a very different $\nu(\text{C}-\text{H})$ band intensity, depending on the orientation of the polymer chain versus the electron scattering plane.

(4) Molecular Reorientation during Polymer Metalization. For the study of the adsorption of small molecules on well-ordered and clean single crystalline metal surfaces, HREELS is known to be capable of disclosing adsorption site plus symmetry, and molecule orientation, through the collection of angular resolved loss spectra. A similar data analysis procedure has been attempted for a clean film of cured, crystalline polyimide (PMDA-ODA type). Surprisingly, for such a complicated macromolecule, an average statistical order was disclosed (Figure 7a): when collecting the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{H})$ stretch band intensities at different angles measured from the normal to the sample surface, a preferential relative orientation of those groups is deduced, differentiating the ODA and PMDA planes of the monomeric unit. (It is presently very difficult to quantify precisely this observation, as the excitation mechanisms of the two $\nu(\text{C}=\text{O})$

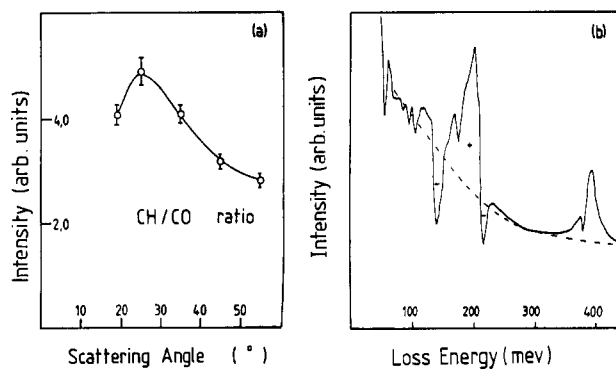


Figure 7. (a) $\nu(\text{CH})$ and $\nu(\text{CO})$ stretch ratio obtained from an angular analysis of a clean polyimide film. This anisotropy vanishes when covering the polymer surface with a thin (0.5 monolayer) aluminum layer. (b) Difference HREELS spectrum (covered-clean) obtained during the incipient metalization of polyimide: all the (C-H) bands are increased in intensity.

and $\nu(\text{C}-\text{H})$ modes may be—and probably are—different. However, if the C-H mode has a high impact scattering cross section, its angular distribution cannot be anything else than isotropic, with a possible intensity increase in the direction of the scattered beam; the $\text{C}=\text{O}$ mode would preferentially be dipole-excited, with high intensity in the specular direction.¹⁶ However, when a small amount (the equivalent of about half a layer) of aluminum is deposited onto the polymer, this anisotropy completely disappears, suggesting a now whole planar monomeric unit; in addition, the global intensity increase of the C-H vibrational bands after partial aluminum coverage (Figure 7b) is corroborating a major conformation change. Intensities of bands corresponding to C_6H_4 units are enhanced, whereas a typical $\nu(\text{C}_6\text{H}_2)$ vibration at 800 cm^{-1} is stationary; the intensity decrease of the $\text{C}=\text{O}$ associated vibrations is related to the bonding of aluminum atoms.

Conclusions

At this stage, the fundamental research program on the study of the potential of electron-induced vibrational spectroscopy, to be applied into the analysis of the extreme surface layer of polymers, looks extremely promising. As a complement to ESCA (XPS) and ion spectroscopies (SIMS/ISS), the technique will most probably add some unique capabilities characteristic of infrared or Raman spectroscopy.

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(16) Pireaux, J. J.; Vermeersch, M.; Grégoire, Ch.; Thyry, P. A.; Caudano, R.; Clarke, T. C. *J. Chem. Phys.* 1988, 88, 3353.