Quantitative Analysis of Polymer Surfaces and Films Using Elastic Recoil Detection Analysis (ERDA), Fourier Transform Infrared Spectroscopy (FTIRS), and High-Resolution Electron Energy Loss Spectroscopy (HREELS)

Manuel Rei Vilar*

Laboratoire de Spectrochimie Infrarouge et Raman (CNRS), 2 rue Henri Dunant, F-94320 Thiais, France

Ana Maria Botelho do Rego and José Lopes da Silva

Centro de Química-Física Molecular da UTL, Instituto Superior Têcnico, Av. Rovisco, Pais, P-1096 Lisboa, Portugal

François Abel, Véronique Quillet, and Michel Schott

Groupe de Physique des Solides, Universitês de Paris 6 et 7, 2 Place Jussieu, Tour 23, F-75251 Paris Cedex 05, France

Serge Petitjean[†] and Robert Jérôme

Center for Education and Research on Macromolecules (CERM), University of Liêge, Sart-Tilman, B-4000, Liêge, Belgium

Received January 19, 1994; Revised Manuscript Received June 8, 1994[⊗]

ABSTRACT: A method of applying HREELS as a quantitative analysis technique to the study of polymer surfaces is presented. For this purpose, a series of random polystyrenes consisting of perdeuterated and hydrogenated monomers randomly distributed along the chains was synthesized and characterized by ERDA and FTIRS. Compositions determined from HREEL spectra of random polymers were then compared to those determined from ERDA and FTIRS. The agreement between HREELS results and the composition obtained by the other techniques is good: the isotropic composition of the polymer surface can be determined with an accuracy of the order of 5%.

Introduction

Films of polymer blends or of copolymers, their surfaces, and interfaces have been the subject of many recent studies. In these films, concentrations of the different molecular entities involved, their average values, their depth profile, or their surface values are quantities of interest in fundamental and applied fields (for a recent review see ref 1). For instance, among other properties, the nature and concentration of the functional groups present at the surfaces of the film govern the surface energy and the surface reactivity of the film.

Since the surface composition of polymer films differs in many instances from that of the bulk, there is a need for a specific method of analysis for this part of the film. The aim of this paper is to show that high-resolution electron energy loss spectroscopy (HREELS) can be calibrated and used for this purpose. To demonstrate this, we have chosen an example relying on the different properties of hydrogen and deuterium. Nevertheless, the potential generality of the method, i.e., the application to nondeuterated materials, is also discussed here.

Several techniques of analysis, such as nuclear magnetic resonance, vibrational spectroscopy, or thermal neutron scattering, make use of the different properties of hydrogen and deuterium. Selective deuteration of one type of chain in a blend or of a block in a copolymer can then be used to measure concentration profiles in films.

Although HREELS is largely used for phonon dispersion studies and for the characterization of molecules adsorbed on surfaces, we have shown that this technique can also be employed to characterize polymer film surfaces.[2,3] The depth of analysis of HREELS for organic films was found to be about 5 Å.[4,5] For instance, in a previous work[3] it was shown that the surface of a thin film of a mixture of hydrogenated and perdeuterated polystyrene is enriched in the deuterated component. More recently, using the results presented here, we were able to show that polymer chain ends segregate at the surface of a polymer film.[6] This research was motivated by the suggestions that chain end surface segregation can diminish polymer surface energy.[7,8]

The goal of the present work is to show that at the surface of a polymer film, of an average thickness of the order of 5 Å, the ratio between the hydrogen and deuterium atomic concentration (H/D) can be measured using HREELS. For this purpose HREELS results are compared with the bulk concentration measured using films whose bulk and surface concentrations are equal. It may safely be assumed that this is the case of films of random copolymers. Consequently, a series of random atactic copolymers of hydrogenated and deuterated styrene were synthesized.

To accurately determine the bulk H/D ratios of the copolymers, two different techniques were used: Fourier transform infrared spectroscopy (FTIRS) for random polymers in carbon tetrachloride solutions, and elastic scattering of swift ions, known as elastic recoil detection analysis (ERDA) or forward recoil elastic spectroscopy (FRES), for homogeneous films. The above results for bulk concentration were also used to calibrate SSIMS, another surface-sensitive technique.[9]

[†] Aspirant of the Belgian National Fund for Scientific Research (FNRS).

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1994.

0024-9297/94/2227-5900$04.50/0

Principles and Problems of HREELS

In a HREELS experiment a beam of monokinetic electrons of energy E_p impinges on a surface and the current intensity of the electrons backscattered by the sample in a given direction is measured as a function of their energy loss.[10]

The difficulty in determining cross sections in HREELS and in developing quantitative analysis stems from the very nature of the interaction of slow electrons with organic surfaces: elastic and inelastic channels, involving vibrational and electronic excitations (in a range of primary energies below 10 eV), operate in parallel.[11,12] Differential cross sections dependent on the energy of the primary electron and on the geometric parameters of the collision are associated with each type of excitation. Two basic processes are involved:[10] dipole and impact interaction.

Dipole interactions are essentially long range and characterized by high cross sections and low moment transfers and are produced by the action of the electromagnetic field associated with the incident electron on the molecular electrons present at the organic surface. Due to the nature of dipole interactions, electrons inducing vibrations of molecular dipoles adsorbed perpendicularly on metals or semiconductors are observed near the specular reflection.

Impact scattering involves short-range interactions characterized by high momentum transfers, lower cross sections, and isotropic scattering. During impact, the incident electron and the molecule form a new quantic system which relaxes in a vibrational or in an electronic excited state. One of the valence electrons of this excited system is then ejected carrying the characteristic energy loss. In this case, the spin state of the system may not be conserved. Since impact electron backscattering is fairly isotropic, the results are not strongly affected by slight variations of chemical bond orientations relative to the surface.

We shall analyze here only impact interactions, which are predominant in polystyrene HREEL spectra. In fact, the strong specularly reflected beam and the rapid variation of differential scattering cross section with scattering angle characteristic of dipole interaction are lacking in these spectra. The only known exception in the field of polymers where dipole scattering has been observed seems to be highly oriented PTFE.[13]

In the present work, use was made of well-isolated CD and CH bands corresponding in FTIRS and HREELS to stretching vibrations and in ERDA to well-characterized signals. This procedure can be adapted to other cases not involving deuterated materials if characteristic isolated bands appear in the spectra. For instance, C=O, C≡C, N—H, or O—H groups yield relatively isolated vibrational IR bands near 1700, 2200, 3400, and 3600 cm^{-1}. In the same way as ERDA was used to measure H and D concentrations here, characteristic nuclear reactions can be used for almost all light elements, notably carbon, nitrogen, oxygen, and fluorine, to determine accurately bulk concentrations.

Aliphatic and aromatic CH stretching vibrations are clearly separated bands in FTIRS but not in the present HREEL spectra. The instrumental resolution in recent HREEL spectrometers is better than 1 meV.[14] However, there are other possible causes of broadening in polymer HREEL vibrational spectra, which will not be discussed here.

Experimental Section

Random Copolymer Synthesis. A series of random copolymers of hydrogenated styrene and perdeuterated styrene of different isotopical compositions were prepared by living anionic polymerization (Figure 1). Molecular weights and polydispersities of the synthesized polymers are presented in Table 1.

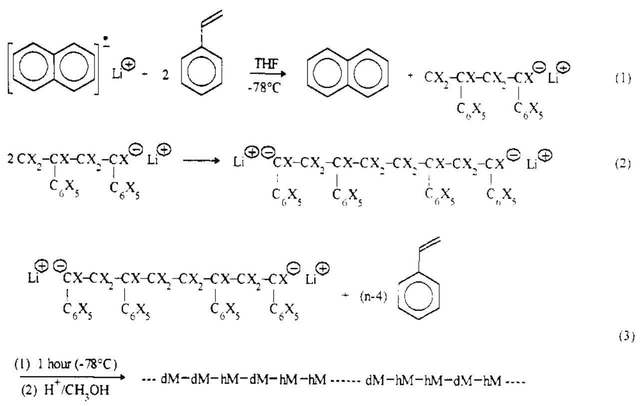

Figure 1. Polymerization scheme of random hydrogenated and perdeuterated polystyrenes. X stands for hydrogen in perhydrogenated monomers (hM) or deuterium atoms in perdeuterated monomers (dM).

Table 1. Molecular Weights and Polydispersities of the Synthesized Random Polystyrenes

polymer	M_n	M_n/M_w	polymer	M_n	M_n/M_w
1	35 000	3.05	5	29 000	1.83
2	26 000	2.69	6	27 000	1.89
3	53 000	1.66	7	50 000	1.55
4	39 000	1.72	8	54 000	1.46

Initiation was carried out by electron transfer rather than by the nucleophilic addition of an aliphatic alkyl metal to the monomer. The major drawback of the latter initiation technique is that it attaches an alkyl radical as an end group to each macromolecule, which might perturb the surface properties of the final copolymer. Freshly prepared naphthyllithium was used as an initiator. The copolymerization was carried out in THF at −78 °C for 1 h. The reaction medium was then deactivated by acidified methanol. Final polymer concentrations were 0.5 g/L. The ratio between the number of moles of hydrogenated monomers and the number of moles of deuterated monomers and the corresponding mole fractions of the deuterated component in the medium used in the reaction are presented in Table 2. The copolymer was then precipitated into methanol, filtered, and dried under vacuum. Polystyrene is known to be atactic when anionically prepared in THF.[15] Reactivities of hydrogenated and perdeuterated styrenes toward anionic polymerization were assumed to be identical.

As growing macroanions are very sensitive to protic impurities, such as water, both monomers and solvents had to be purified and dried before polymerization.[16]

Fourier Transform Infrared Spectroscopy (FTIRS). Polystyrene (M_n = 30000 and M_w/M_n = 1.05) and perdeuterated polystyrene (M_n = 27000 and M_w/M_n = 1.05) from Polymer Laboratories Ltd. (U.K.) were used to prepare calibrated solutions. Solutions of each polymer in carbon tetrachloride (spectroscopic grade) were prepared with concentrations of 2 g/L. Solvent purity was tested by infrared spectroscopy. From these mother solutions, a series of mixtures of variable isotopic composition (from ~75 to ~10% in weight of the deuterated polymer) were prepared.

Random copolymers having M_n and M_w/M_n comparable to those of the pure polymers were synthesized according to the procedure described above. Solutions containing 2 g/L of the different random copolymers were prepared in the same solvent.

At these concentrations all solutions are in the dilute regime where chains are independent of one another. The overlap threshold is $c^* \sim 270$ g/L.[17]

Infrared absorption spectra of the different solutions—pure polymers, their mixtures, and random copolymers—were then recorded with a 2 mm CaF$_2$ cell using a 1720 Perkin-Elmer Fourier transform infrared spectrometer. Polystyrene spectra were obtained by subtraction of the solvent spectrum.

Table 2. Comparison of the Compositions of Random Copolymers Expressed in Atomic Ratios *H/D* and Mole Fractions x_D Obtained via FTIRS, ERDA, and HREELS and the Values Expected from Synthesis

	synthesis		FTIRS		ERDA		HREELS		HREELS deviation[a]	
polymer	*H/D*	x_D	*H/D*	x_D	*H/D*	x_D	*H/D*	x_D	Δ*H/D*	Δx_D
1	21	0.05	18.6	0.051	21.8	0.044				
2	10	0.09	11.2	0.082	11.4	0.081				
3	6	0.14	8.0	0.11	7.9	0.11	8.1	0.11	2	<1
4	4	0.19	5.1	0.165	4.7	0.175	4.4	0.185	10	9
5	3	0.24	3.55	0.22	3.45	0.23	3.35	0.23	4	<1
6	1.1	0.48	1.15	0.47	1.1	0.48				
7	0.7	0.58	0.76	0.57	0.73	0.58	0.73	0.58	ref	ref
8	0.3	0.79	0.27	0.79	0.27	0.79	0.30	0.76	10	4

[a] Relative deviation between the HREELS values and the mean of those obtained via FTIRS and ERDA expressed in percent.

Elastic Recoil Detection Analysis (ERDA). Thin films of random polymers were spin-cast onto 2-in. silicon wafers from 30 g/L solutions in toluene. The solvent was removed by evaporation at room temperature. Resulting film thicknesses were about 1000 Å, as measured by ERDA and ellipsometry assuming the bulk concentration. This was also checked in a few cases by thickness determination using the interference fringes in neutron reflectometry.[18] To check the absence of solvent which would affect the *H/D* ratio, a similar nondeuterated polystyrene film from a perdeuterated toluene solution was prepared: no deuterium atoms were detected in the ERDA spectrum of that sample.

All measurements were performed using the 2.5 MeV van de Graaff accelerator at Groupe de Physique des Solides and the experimental setup described in ref 18. The incident ions were ^{4}He with an energy $E_1 = 1.8$ MeV.

High-Resolution Electron Energy Loss Spectroscopy (HREELS). After cleaning and removing the oxide film from silicon substrates, very thin films of polymers were cast by dipping these substrates in a 1 g/L solution of random polystyrene in carbon tetrachloride. The thickness of these films was determined by measuring the number density of H or D atoms by ERDA and of C atoms by nuclear reaction analysis, using the previously determined cross sections.[18] It was found to be around 100 Å. The samples must be thin enough to avoid electrical charging of the surface during the experiments. It was observed that for such thicknesses the incoming charge is easily transported to the substrate.

Each sample was introduced into an ultrahigh vacuum chamber ($\sim 10^{-7}$ Pa) through a fast insertion chamber.

HREEL spectra were recorded with two different spectrometers: a Kesmodel LK 2000R and a Leybold-Heraeus ELS-22. Incident energies were progressively varied from 2 to 10 eV. Steps of 1 meV were used in all spectra for the sweeping voltage. The geometry was chosen with incident and analysis angles of 30° with respect to the surface. The elastic peak fwhm was around 13 meV.

Data Analysis Method

In all three methods used here, the absorption (in FTIRS) or the scattering (in ERDA or HREELS) spectra contain well-defined bands corresponding to H and D, respectively. In each technique, the band area ratio A_H/A_D can always be related to a ratio between the number of hydrogen and deuterium atoms *H/D* through an appropriate factor σ_H/σ_D as follows:

$$\frac{A_H}{A_D} = \frac{\sigma_H}{\sigma_D}\frac{H}{D} \tag{1}$$

Quantitative analysis by means of infrared absorption spectroscopy is based on the Lambert–Beer law. The band intensity for a given wavelength is proportional to the number of oscillators through the absorptivity. The Lambert–Beer law can also be generalized to a spectral region by the sum of absorptivities corresponding to a certain domain of wavelengths. This corresponds to eq 1 (see for instance ref 19), where the σ_H and σ_D are associated with the weighted mean absorptivities of the spectral regions of CH and CD, respectively.

In ERDA, σ_H/σ_D is the ratio between the differential scattering cross section of hydrogen and deuterium, which depends on the mass and energy of the incident particle and on the scattering geometry.[18]

As in FTIRS, σ_H/σ_D for HREELS corresponds to the ratio between the mean differential cross sections of the different processes involved in the electron-induced excitations of CH and CD vibrations, respectively.[3]

H/D also has different meanings for each technique: in FTIRS and HREELS, it corresponds to the number of CH and CD bonds in the analyzed fraction of the solution or of the film, respectively, whereas for ERDA, it is the number of H and D atoms in the analyzed region of the film.

In the case of random copolymers composed of perdeuterated and perhydrogenated monomers, one can replace *H/D* in (1) by the molar fraction x_D *of* the deuterated component. Equation 1 can then be rewritten as

$$\frac{A_H}{A_D} = \frac{\sigma_H}{\sigma_D}\left[\frac{1}{x_D} - 1\right] \tag{2}$$

In each case, σ_H and σ_D or at least σ_H/σ_D must be known. For ERDA, σ_H, σ_D, and σ_H/σ_D were measured previously.[18] For FTIRS, σ_H/σ_D was measured using dilute solutions of mixtures of hydrogenated and perdeuterated polystyrenes with known mole fractions. However, for HREELS, mixtures of polymers cannot be used. In fact, films cast from polymer mixtures may exhibit segregation at the interfaces and, therefore, are not homogeneous in depth.[3] As HREELS is very sensitive to the surface, the measured composition depends on the amount of segregation. Hence, for this technique we took as reference a random copolymer whose composition was previously determined by ERDA. A film of this sample was used and a set of spectra were recorded. Values of σ_H/σ_D were then plotted as a function of the primary energy.

To take possible imperfect deuteration and/or hydrocarbon contaminants into account, eq 2 should be rewritten as

$$\frac{A_H}{A_D} = -\frac{\sigma_H}{\sigma_D} + \left(1 + \frac{n_D^{\,H}}{n_D^{\,D}} + \frac{n_c^{\,H}}{n_D^{\,D}}\right)\frac{\sigma_H}{\sigma_D}\frac{1}{x_D} \tag{3}$$

where $n_D^{\,H}$ is the CH molar concentration in the imperfectly deuterated chains, $n_c^{\,H}$ is the molar concentration of CH due to contaminants and $n_D^{\,D}$ is the CD molar concentration.[3]

In the absence of contaminants and for perfect deuteration, the ratio A_H/A_D is a linear function of $1/x_D$ where

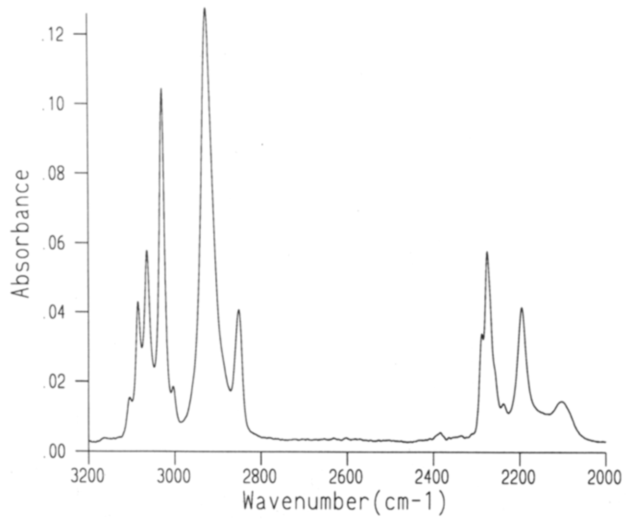

Figure 2. FTIR spectrum between 2000 and 3200 cm^{-1} of a mixture containing equal weights of hydrogenated and perdeuterated polystyrene.

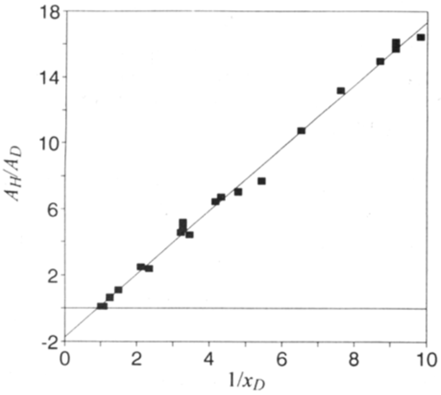

Figure 3. FTIRS calibration curve showing the linearity of the relation A_H/A_D versus $1/x_D$ for mixtures of hydrogenated and perdeuterated polystyrenes of different isotopic compositions.

the absolute value of the intercept and the value of the slope are equal to σ_H/σ_D.

Results and Discussion

FTIRS. Figure 2 shows the absorption spectrum recorded between 2000 and 3200 cm^{-1} of a mixture containing equal weights of hydrogenated and perdeuterated polystyrene. This region contains all the peaks corresponding to stretching modes of the carbon–deuterium (CD) and carbon–hydrogen (CH) bonds. Peaks corresponding to different stretching modes of aliphatic and aromatic CH are located between 2800 and 3000 cm^{-1} and between 3000 and 3100 cm^{-1}, respectively. On the other hand, peaks corresponding to the different stretching modes of CD can be observed between 2000 and 2300 cm^{-1}. The aliphatic CD peaks are located between 2000 and 2200 cm^{-1} at lower wavenumbers than the aromatic CD peaks, which are located between 2200 and 2300 cm^{-1}. CH and CD spectral bands are well separated from each other, and so they can be used for quantitative analysis taken as a whole. Moreover, comparison between the intensities of the aliphatic and the aromatic CH peaks enables us to conclude about the presence of possible contaminants, since most of these contaminants contain saturated CH bonds.

The calibration curve, presented in Figure 3, was established using standard solutions with known compositions in isotopic mixtures of hydrogenated and perdeuterated polystyrenes. The value of H/D for the perdeuterated polymer used here was measured by ERDA[18] and found to be 0.02. This value was used to correct x_D fractions in the mixtures. Values of A_H/A_D were then plotted versus $1/x_D$. A linear regression curve with a slope of 1.91 ± 0.03, an intercept of −1.8 [illegible] 0.4, and a square regression coefficient $R^2 = 0.995$ was obtained.

Compositions of random copolymers were then found by interpolating x_D values corresponding to the A_H/A_D ratios measured in the spectra (see Table 2).

Difficulties arising in quantitative vibrational spectroscopy are well known.[20] In the present work they are mainly due to compensation of CO_2 and CCl_4 absorptions in the spectra subtraction and to baseline definitions. Comparison of spectra of films deposited on CaF_2, where no subtraction of a reference is needed, and those of the respective solutions did not reveal additional uncertainties for the measurements. In any case, deficient compensations can always occur mainly in the CD region for polymers containing small amounts of deuterated monomers. In fact, relative deviations of FTIRS values from ERDA ones were always lower than 5% except for polymer 1 where they attained about 15%.

During spectra recording, special attention was also paid to the energy stability of the spectrometer. The solvent spectrum was recorded periodically to avoid imperfect compensations. Energy fluctuations were smaller than 0.1% during a period of 2.5 h.

The linearity of the setup response was tested using different polymer solution concentrations. No significant deviations from the proportionality between concentration and absorbance were observed in the concentration range used going from 2 to 15 g/L.

Other deviations from the Lambert–Beer law can be due, for instance, to stray radiation or insufficient resolution. Stray radiation is generally very low in most commercial FTIR spectrometers, and deviations due to a poor resolution (in the present case 4 cm^{-1}) are irrelevant in the analysis of broad bands.

The overall error on x_D values found by FTIRS has two main sources: errors in the parameters of the calibration curve and those in the evaluation of the spectral areas. The error in the preparation of the standard solutions is of the order of 5%. We have evaluated the errors resulting from the peak area determination to be less than 3%. The overall error is estimated to be less than 8%.

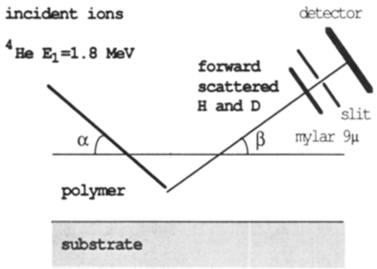

Figure 4. Schematic representation of the ERDA scattering geometry used. Incident ^{4}He particles of energy E_1 scatter H and D atoms at $\theta = \alpha + \beta$ (=30° in the present experiment) with energies E_2. Forward-scattered ^{4}He are absorbed by a 9 μm thick mylar film placed in front of the detector slit.

ERDA. In elastic recoil detection analysis light nuclei are scattered at forward angles by swift incident heavier ions (Figure 4). For a further discussion of the method, see ref 21.

The energy E_2 of a scattered particle of mass M_2 is a function of the energy E_1 and mass M_1 of the incident

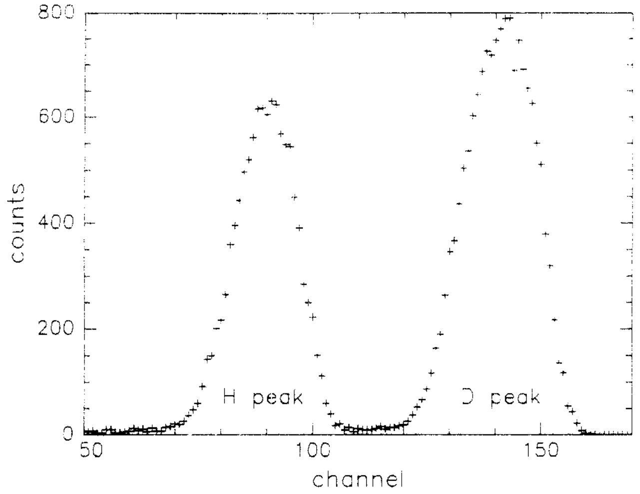

Figure 5. Typical ERDA spectrum showing well-separated H and D peaks. Channel numbers are a linear function of E_2.

particle and of the scattering angle θ:

$$E_2 = kE_1 = [4M_1M_2 \cos^2 \theta/(M_1 + M_2)^2]E_1 \qquad (4)$$

Forward-scattered particles are detected using a semiconductor surface barrier detector, sensitive to the particle energy, so that the number of scattered particles is measured as a function of their energy E_2. In the present experiments, ^{4}He ions were used as incident particles. The scattering angle θ was 30°, so that the ratio of the energies transferred to H and D respectively was $E_2(\mathrm{D})/E_2(\mathrm{H}) \sim 1.4$. Therefore, D and H nuclei can be easily discriminated in the detection. Ions are slowed down as they propagate into matter, so that the actual energy E_1 is a function of the depth z below the surface. But if the film is thin enough, the D and H peaks are still well separated, as shown in Figure 5.

The peak areas A_H and A_D can be accurately measured. In our experimental conditions, the energy loss of incident ^{4}He ions is small and constant throughout the film thickness and the scattering cross sections σ_H and σ_D vary slowly and linearly with energy,[18] so that eq 1 holds, σ's being taken at the mean energy of the ^{4}He ion at the mid-depth $z/2$ in the film. The value of $\sigma_\mathrm{H}/\sigma_\mathrm{D}$ in the experimental conditions used here was determined previously:[18] $\sigma_\mathrm{H}/\sigma_\mathrm{D} = 0.93$ (±2%).

This being known, the H/D ratio can be determined without comparison to a known standard. To obtain the true ratio for the polymer itself, the results should, however, be corrected for surface contamination and degradation during ion beam irradiation.

We shall briefly discuss the possible sources of error which essentially come from hydrogenous contamination, polymer degradation, and the uncertainties in data evaluation.

Since the present experiments are performed in a conventional vacuum (ca. 5×10^{-5} Pa), film surfaces are usually covered by a thin hydrogenous contamination layer. Study of perdeuterated polystyrene films showed that, under experimental conditions identical to those used in the present study, this contamination is always about 5×10^{15} H atoms/cm^2. This amount of H was therefore subtracted from the total measured H concentrations to compute the H content of the polymer. This was usually a 1–2% correction except for polymer 8, for which the correction was 4%.

All polymers degrade more or less rapidly under ion beam irradiation. In cross-linking polymers such as polystyrene, this degradation results in a change in atomic composition: whereas the C content remains constant under MeV ^{4}He irradiation to the accuracy of the measurements, H and D atoms are slowly released.[22] Moreover, we have found that polystyrene loses H and D atoms at different rates, so that the H/D ratio varies during measurement.[23] In our case, however, we were able to use experimental conditions in which <1% of H atoms and <0.5% of D atoms are lost at the end of the measurements and losses are linear functions of the dose, so that the effect can be accounted for by a small correction. However, this might be a more serious problem with materials such as PMMA which degrade more rapidly.

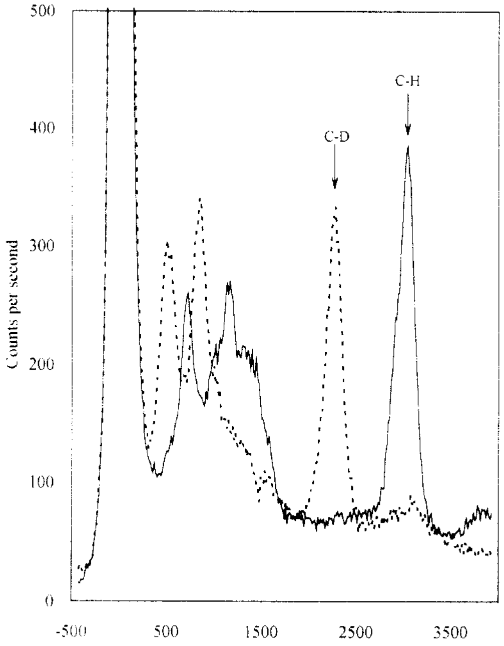

Figure 6. HREEL spectra of films of hydrogenated (—) and perdeuterated (- - -) polymers for a primary energy of 4.7 eV. Characteristic bands corresponding to stretching vibrations of CD and CH are indicated by arrows.

Other possible uncertainties in the determination of H/D are statistical counting uncertainties, which can be reduced below 1%, and the presence of a small amount of background counts under the ERDA peaks. This background was taken into account by assuming a linear slope under the peaks. This probably overestimates the background, so, as an upper limit of the corresponding error, the uncertainty was taken to be equal to the correction. In actual fact, it is certainly less.

The overall uncertainty resulting from all the causes mentioned above is then estimated to be ±4–5%, expect for H/D values which are much larger or much smaller than 1, for which the uncertainties reach 6%.

HREELS. For polystyrene samples the angular distributions of the elastic peak and the inelastic features are rather broad. This indicates that the interaction between the incident electrons and the surface is by impact rather than by a dipole mechanism; geometrical conditions are then not very critical to this work.

HREEL spectra of films of pure hydrogenated and deuterated polymers are presented in Figure 6 for a primary energy of 4.7 eV. Zero loss is centered at the maximum value of the elastic peak. The studied region of the spectra corresponds to the vibrational excitations induced by the incident electrons and can be easily compared with the FTIR spectra described above, although HREELS resolution is poorer.

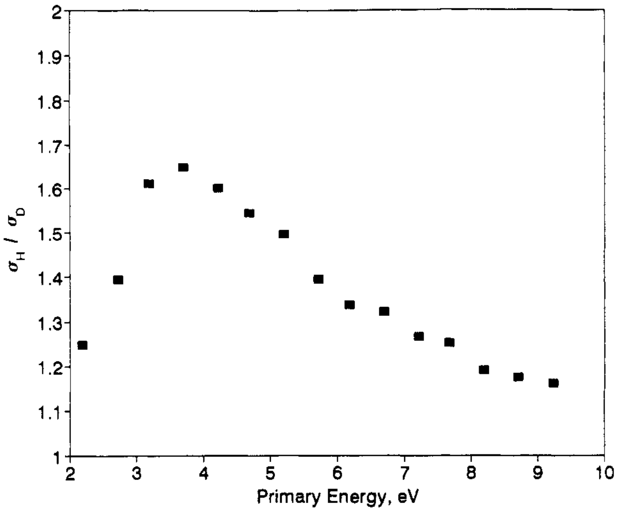

Figure 7. HREELS σ_H/σ_D as a function of the primary energy for polystyrene surfaces.

The identity of spectra obtained with two different spectrometers from samples independently prepared according to the above procedure and using the same polymer confirms the reproducibility of the experiment.

Between the elastic peak and the stretching vibrations, there are features containing the overlap of several vibration peaks including the out-of-plane modes of the benzene ring, bending modes of the aliphatic and aromatic bonds, and also those of the carbon skeleton.[2,12] This region is quite sensitive to variations of primary energy. A Gaussian decomposition of this part of the spectrum allows the separation of the different vibrational excitations. This will be the subject of a future publication.

Characteristic and well-separated peaks at 2200 and 3000 cm^{-1} corresponding to stretching vibrations of CD and CH, respectively, are indicated by arrows and will be used here, as in FTIRS, to quantify isotopic compositions of the surface of the films. The fluctuations of the positions of the fwhm of the characteristic peaks are lower than 20% of the fwhm of the elastic peak. Nevertheless these parameters can very more than 50% in the range of the primary energies used here, which is probably due to the cross section variations of the excited modes. The characteristic CD and CH peaks emerge from an exponential baseline due to multiple losses.[24] Each peak was therefore fitted with two Gaussian curves (aliphatic and aromatic) and an exponential function and the area was computed in an analytical way. A nonlinear least squares regression method was used for this purpose. Iteration was stopped when the least squares deviation variation obtained between two successive iterations was lower than 0.1%. The main error in the area so obtained was due to the baseline subtraction, which depends on the choice of the curve fitting limits. The uncertainty associated with this procedure is estimated to be <10%.

For a standard sample, polymer 7, A_H and A_D were measured for different values of E_p between 2 and 10 eV. Using the values of H/D determined by ERDA for this polymer (for which the uncertainty of the ERDA value is estimated to be <4%), the σ_H/σ_D values for HREELS were determined as a function of the primary energy (Figure 7). This calibration curve allows us to determine quantitatively via HREELS the mole fraction x_D at the surface of the polymer film using eq 2. Table 2 shows the results of the application of the method to the copolymers compared to the values determined via FTIRS and ERDA and to the values expected from the synthesis. The agreement between the mole fraction values obtained by FTIRS and ERDA is better than 6% except for polymer 1, where the difference reaches around 14%. The agreement between HREELS results and the compositions obtained by the other techniques is better than 10%.

σ_H/σ_D as a function of E_p was used elsewhere to show evidence for the segregation of chain ends at the surface of polystyrene films.[6] The same effect was also shown by SSIMS (static secondary ions mass spectroscopy).[25]

Conclusions

Comparison of FTIRS and ERDA results showed that both techniques have a high degree of accuracy in determining the bulk compositions of polymers, blends, copolymers, or block polymers. The high sensitivity and accuracy of ERDA and the possibility of performing measurements without a reference subtraction make this technique a very sure method for determining random polymer isotopic compositions. The remarkable performances of ERDA serve to guide further refinement of the FTIRS analysis of polymers. This can be very useful since FTIR spectrometers are more commonly used than ERDA, which requires particle accelerators.

ERDA and FTIRS results provided HREELS with a standard value, which could be used to infer the compositions of other random polymer surfaces.

To determine, using HREELS, the isotopic composition of polymer film surfaces containing hydrogenated and deuterated monomer sequences, a standard σ_H/σ_D vs E_p curve was established. From these same results, we also concluded that HREELS can be used to quantitatively analyze polymer surface. In fact, the values obtained for x_D by this technique are in good agreement with those measured with the other two techniques.

Methodologies used for ERDA and HREELS were different. In ERDA, knowledge of scattering cross sections enables the analysis of any sample irrespective of its chemical composition. This is not valid in HREELS, where σ_H/σ_D depends on the molecular nature of the polymers. So, standard samples for HREELS must always be of the same molecular nature as the sample to be analyzed. This can seem a handicap for HREELS studies but this difficulty is largely compensated by the HREELS possibilities of unraveling vibrational and electronic excitations in the extreme surface of the film and by its nondestructive character.

Acknowledgment. The authors thank the European Science Foundation (Additional Activity Program (Polymer Surfaces and Interfaces)), the Centre National de la Recherche Scientifique (France), and the Junta Nacional de Investigação Cientifica e Technológica (Portugal) for financial help. ERDA experiments were supported by GDR86 (CNRS). S.P. and R.J. are grateful to the "Services de la Programmation de la Politique Scientifique" (Belgium) for financial support. S.P. is also indebted to the FNRS for a fellowship.

References and Notes

(1) Sanchez, I. C. *Physics of Polymer Surfaces and Interfaces*; Butterworths: Boston, 1992.
(2) Rei Vilar, M.; Schott, M.; Pireaux, J. J.; Grégoire, C.; Thiry, P. A.; Caudano, R.; Lapp, A.; Botelho do Rego, A. M.; Lopes da Silva, J. *Surf. Sci.* **1987**, *189/190*, 927.
(3) Rei Vilar, M.; Schott, M.; Pireaux, J. J.; Grégoire, C.; Thiry, P. A.; Caudano, R.; Lapp, A.; Lopes da Silva, J.; Botelho do Rego, A. M. *Surf. Sci.* **1989**, *211/212*, 782.
(4) Sanche, L.; Michaud, M. *Chem. Phys. Lett.* **1981**, *80*, 184.
(5) Schreck, M.; Abraham, M.; Göpel, W.; Schier, H. *Surf. Sci. Lett.* **1990**, *237*, L405.

(6) Botelho do Rego, A. M.; Lopes da Silva, J. D.; Rei Vilar, M.; Schott, M.; Petitjean, S.; Jérôme, R. *Macromolecules* **1993**, *26*, 4986.

(7) Wu, S. *Polymer Interfaces and Adhesion*; Marcel Dekker: New York, 1982.

(8) De Gennes, P.-G. *C. R. Acad. Sci., Ser. B* **1988**, *B307*, 1841.

(9) Affrossman, S.; Hartshorne, M.; Jérôme, R.; Munro, H.; Pethrick, R. A.; Petitjean, S.; Rei Vilar, M. *Macromolecules* **1993**, *26*, 5400.

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

(11) Rei Vilar, M.; Heyman, M.; Schott, M. *Chem. Phys. Lett.* **1983**, *94*, 522.

(12) Botelho do Rego, A. M.; Rei Vilar, M.; Lopes da Silva, J.; Schott, M., to be published.

(13) Rei Vilar, M.; Bodõ, P.; Schott, M., to be published.

(14) Ibach, H. *Surf. Sci.* **1994**, *299/300*, 116.

(15) Kissin, Y. V. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989.

(16) Petitjean, S.; Ghitti, G.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Bull. Soc. Chim. Belg.* **1990**, *99*, 997.

(17) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(18) Quillet, V.; Abel, F.; Schott, M. *Nucl. Instrum. Method. Phys. Res.* **1993**, *B83*, 47.

(19) Griffiths, P. R.; de Haseth, J. A. *Fourier Transform Infrared Spectroscopy*; Wiley-Interscience: New York, 1986.

(20) Ferraro, J. R.; Basile, L. J. *Fourier Transform Infrared Spectroscopy*; Academic Press: New York, 1979; Vol. 2.

(21) Feldman, L. C.; Mayer, J. W. *Fundamentals of Surface and Thin Film Analysis*; North-Holland: New York, 1986. Agius, B.; Froment, M.; et al. *Surfaces, Interfaces et Films Minces: Observation et Analyse*; Dunod: Paris, 1990.

(22) Quillet, V. Thèse, Université de Paris VII, 1993. Dole, M. *The Radiation Chemistry of Macromolecules*; Academic Press: New York, 1973. Davenas, J. *Materials under Irradiation, Solid State Phenomena*; Transtech Publications: Aedermannsdorf, Switzerland, 1993; Vols. 30/31.

(23) Quillet, V.; Abel, F.; Schott, M., to be published.

(24) Botelho do Rego, A. M.; Rei Vilar, M.; Lopes da Silva, J.; Gonçalves da Silva, A. M. *Thin Solid Films* **1994**, *243*, 521.

(25) Affrossman, S.; Hartshorne, M.; Jérôme, R.; Munro, H.; Pethrick, R. A.; Petitjean, S.; Rei Vilar, M. *Macromolecules* **1993**, *26*, 6251.