High-Resolution Electron Energy Loss Spectroscopy of Polystyrene Surfaces[†]

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The first detailed vibrational mode assignments for insulating polystyrene surfaces based on high-resolution electron energy loss spectroscopy (HREELS) are presented. Improvements in energy resolution based on low-energy secondary beam neutralization and spectral restoration algorithms allow an effective resolution of ∼6 meV (50 cm^{-1}) at relatively high loss intensities. This permits the assignment of eighteen vibrational modes for this material which are in good agreement with known IR and Raman bands.

I. Introduction

We recently reported the application of high-resolution electron energy loss spectroscopy (HREELS) to thick, insulating samples of polystyrene and poly(tetrafluoroethylene) (PTFE).[1] We presented a new, systematic method for the study of thick polymers by HREELS that combines modern instrumentation, low-energy secondary beam neutralization, and spectral restoration algorithms. This method for the first time allowed stable, reproducible spectra from these insulating materials at an effective resolution of ∼6 meV at relatively high loss intensities. The emphasis of the earlier work was a discussion of the methodology and salient results for polystyrene and PTFE. In the present paper we focus on two areas: (i) we show that the spectra obtained for polystyrene samples by this method in two different laboratories using different spectrometers and neutralization guns are in close agreement, and (ii) we present detailed mode assignments for insulating polystyrene based on comparison to infrared and Raman spectra. Using HREELS data we are now able to identify and assign eighteen modes for polystyrene whereas only seven modes were identified by HREELS in an earlier study of thin conducting films by Botelho do Rego et al.[2]

HREELS is a promising technique for the study of polymer surfaces due to its high surface sensitivity and wide spectral range, allowing a probe of both vibronic and electronic excitations. Nevertheless, until recently the method was severely limited in its application to thick, insulating polymers because of poor resolution and difficulty with charge neutralization.[1] The method of secondary electron beam neutralization at high (1 keV) beam energies and relatively high beam currents (μA), first discussed by Liehr et al.[3] and later by Cazaux et al.,[4] was extended by the present authors to a very low energy (130−170 eV), low-current (nA) regime. Furthermore, we applied commercially available spectral restoration techniques[5] to compensate for the broadening of the elastic beam attendant with rough, disordered surfaces and neutralization effects. This allowed for stable, reproducible spectra for both polystyrene and PTFE of previously unknown quality in terms of signal level and resolution.[1] The spectra were obtained with a

commercial LK2000 spectrometer,[6] which was modified for an input−output lens system of promising transmission characteristics and further enhanced by use of compression voltages on the cover plates of the cylindrical deflectors,[7] operating at an instrumental resolution of 5 meV. In the present paper we extended these results to a third generation commercial ELS3000 spectrometer,[8] capable of ∼1 meV resolution and very high signal intensity. We find that the neutralization method works equally well with this spectrometer and that, despite the broadening due to the rough, insulating surface, a definite improvement in spectral intensity and resolution in the loss region is achieved. This indicates that the method should be applicable to a variety of insulating polymer surfaces using second and third generation instrumentation at an effective resolution of ∼50 cm^{-1} and below.

II. Experimental Section

For these experiments, two different apparati were used. The first consisted of a standard ion-pumped stainless steel vacuum chamber (10^{-10} Torr) equipped with an LK2000 HREELS spectrometer with rotatable analyzer,[6] a normal incidence electron gun for sample neutralization, and a turbomolecular-pumped loading system for sample introduction. The second apparatus was similar to the first except the spectrometer was an ELS3000 HREELS spectrometer with rotatable analyzer.[8]

The samples studied were commercially available syndiotactic poly(styrene-co-paramethyl styrene). The copolymer contained between 4−7% paramethylstyrene. Samples were cut from sheets of 0.1 mm thick stock, cleaned in a series of ultrasonic baths of acetone, methanol, and ethanol, blown dry with nitrogen or air-dried, and loaded into the UHV system. The samples studied by both systems were sufficiently thick that the HREELS beam (4.5−6 eV) caused charge buildup. To compensate this effect, the low-energy flood-gun neutralization method, described earlier, was employed.[1] The secondary gun was operated at 170 eV beam energy and <5 nA beam current. The polystyrene was also examined with IR and Raman methods. Raman data were acquired for films using a Kaiser fiber optic process Raman system utilizing 785 nm excitation and a three inch focus probe. IR spectra were obtained using a Bio-Rad FTS-60A Fourier transform IR spectrometer with a DTGS

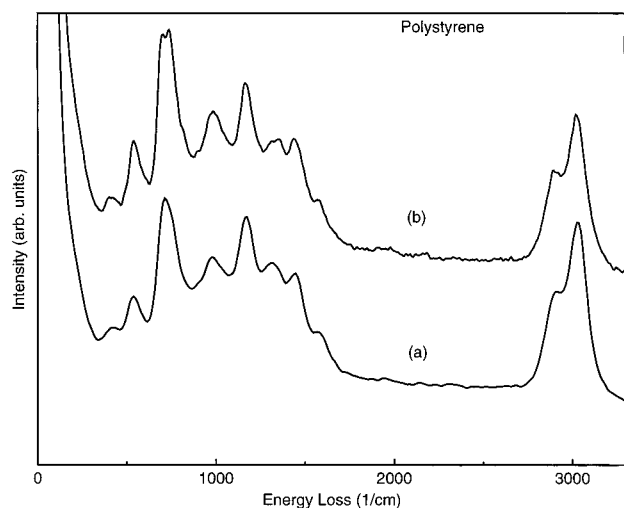† Part of the special issue "Gabor Somorjai Festschrift".

Figure 1. (a) High-resolution electron energy loss spectrum of a thick polystyrene sample at 6 eV impact energy under specular scattering conditions taken with the LK2000 spectrometer. (b) HREELS spectrum of thick polystyrene sample at 4.5 eV impact energy under specular conditions taken with the ELS3000.
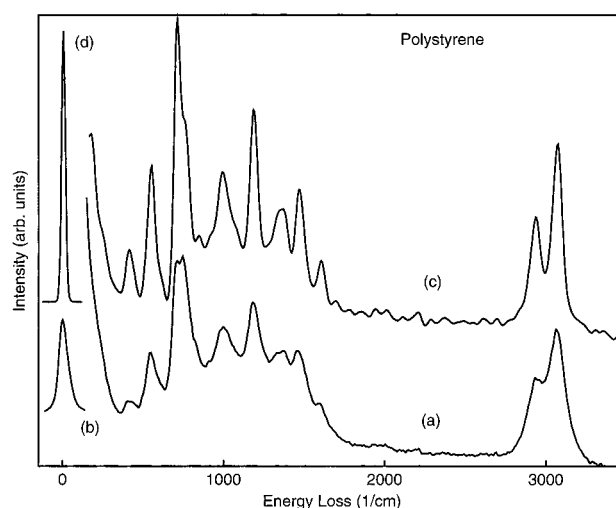

Figure 2. (a) Loss region of the raw data for polystyrene taken with an ELS3000 with (b) the elastic peak shown compared to the results of the (c) spectrally restored spectrum (50 iterations LUC) and (d) elastic peak. (a) and (c) have been enlarged by a factor of 90.

detector. Transmission spectra were obtained from film material dissolved in THF and coated onto Germanium windows. IR attenuated total reflections (ATR) spectra were obtained from films using a SPECAC Golden Gate diamond ATR accessory. The films did not exhibit orientational effects.

III. Results and Discussion

The main emphasis of this discussion will be on the mode assignments of thick polystyrene. Mode assignments for HREELS spectra of thin polystyrene films have already been presented by Botelho do Rego et al.[2] However, with the new low energy flood-gun technique[1] and spectral-restoration methods discussed elsewhere,[5,9] we have significantly improved the resolution thus enabling us to assign additional vibrational bands to the seven reported for the thin films.

Although two different spectrometers are used in the study, no appreciable difference is found between their data. Figure 1 shows a comparison of the raw data taken by the LK2000 and the ELS3000 instruments for the copolymer. Other than intensity and signal-to-noise, the spectra correlate very well. We cannot rule out that somewhat different operating and neutralization conditions in the two experiments led to slightly improved spectral resolution in the ELS3000 data. The quality of the data sets acquired with the LK2000 spectrometer was notable for thick polymer samples compared to previous studies. The fwhm ranged from 7.6−9.8 meV over the data sets and the elastic peak count rate varied from $1.2-4.0 \times 10^4$ cps with loss features between 200−1300 cps. Further improvement was made with the ELS3000 spectrometer. Although the fwhm of the elastic beam is 8−9 meV, there are several peaks resolved only by the ELS3000. The elastic peak count rate is 1.1×10^5 cps and the loss features have rates varying between 1900−3800 cps.

Even though the resolution of the data is noteworthy for thick polymers, further improvement can be made. The instrumental resolution on the LK2000 was set to 5 meV and the ELS3000 to 2 meV, but the resolution reported was between 7−9 meV. The peak width is increased due to the sample and the neutralization methods. The resolution improvement is accomplished by using spectral restoration methods that have been previously described.[5,9] The restoration method used is a commercially available deconvolution routine from the Razor
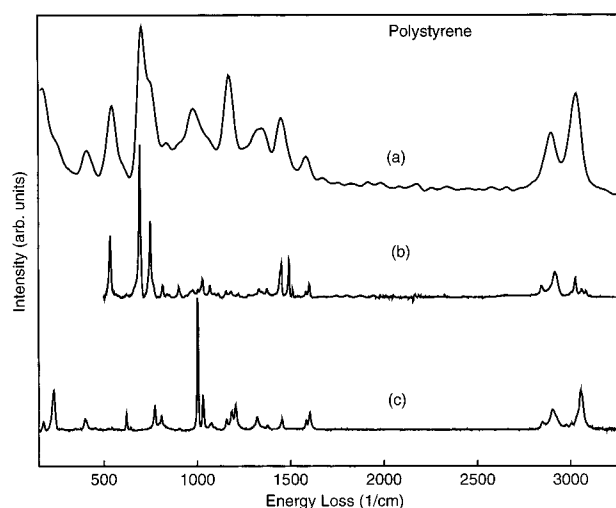
Figure 3. (a) 50 iterations of LUC applied to a ELS30000 spectrum compared to (b) diamond-ATR IR and (c) a Raman spectrum.

Library[10] called LUC, which employs iterative maximum likelihood methods. The routine uses the given peak-shape (a Gaussian, Lorentzian, or data shaped peak) and the data set to iteratively recreate the spectrum. The iterative procedure involves multiplication of a guessed object spectrum with the transfer function in the Fourier domain. The validity of the restoration methods for thick polystyrene were shown earlier by Kesmodel et al.[1] For the data presented, the peak shape used was the elastic peak from the data. This procedure does not involve any background subtraction methods. Figure 2 compares the raw data with 50 iterations of LUC applied to the ELS3000 data. The ELS3000 spectrum resolves several features that do not appear in the LK2000 spectrum. Only reproducible peaks are retained in the discussion of mode assignments below.

Figure 3 shows a comparison of the HREELS, IR, and Raman spectra for polystrene, and Table 1 shows the average of the HREELS data, IR, and Raman modes from the respective data, previous HREELS work on thin films,[2] and a list of the known frequencies and their assignments.[11] The standard deviation over the eight data sets varied between 5 and 20 cm^{-1}. The mode assignments have been separated into two major groups and their subgroups. The ring modes, the larger of the main groups, are divided into three subgroups: the ring skeleton in-plane bend

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TABLE 1: HREELS Data for PS in Comparison to IR, Raman, Thin PS HREELS, and Literature Values (all values in cm^{-1})

HREELS[a]	IR[a]	Raman[a]	thin PS[b]	$\bar{\nu}^{d}$	mode assignment[d]
218	c	230	c	216	ring out-of-plane deformation
410	c	401	c	410	ring out-of-plane deformation
543	536	c	c	540	ring out-of-plane deformation
623	c	622	c	621	ring skeleton in-plane stretch
708	694	c	700	700	ring out-of-plane deformation
764	751	772	760	760	ring out-of-plane deformation
854	840/852	c	c	842	ring out-of-plane deformation
916	901	905	c	906	ring out-of-plane deformation
983	964/977/1004	1003	999	999	ring out-of-plane deformation
1042	1029	1031	1027	1027	ring in-plane CCH bend
1083	1070	1075	c	1070	chain stretch
1172	1155/1182	1157/1184/1205	1157	1154	ring in-plane CCH bend
1336	1332/1348	1321	1333	1328	ring in-plane CCH bend
1375	1374	1378	c	c	not identified
1458	1445/1452	1454	1457	1450	CH$_2$ bending
1594	1583/1602	1585/1604	c	1585/1606	ring skeleton in- plane bend/ ring skeleton in- plane bend
2908	2916/2845	2904/2848	2900	2923	CH$_2$ stretching
3045	3027/3061/3084	3056	3062	3029	CH ring stretching

a This work. *b* HREELS on thin films.[2] *c* Not observed. *d* Bowers and Madams.[11]

or stretch, ring in-plane CCH bending, and ring out-of-plane deformation. The remaining modes are placed in the second major group. These include chain modes, CH$_2$ modes, and CH stretching modes.[11] One mode, however, does not fit into any of these categories. The 1375 cm^{-1} band had no listing in Bowers and Madams. This peak did have matches in the IR and Raman data at 1374 cm^{-1} and 1378 cm^{-1} respectively.

The largest number of ring modes belongs to the ring out-of-plane deformation group. Of the eight modes seen in this group, four are also known as R–C bending. The label R–C is used in polystyrene mode assignments by Bowers and Madams[11] where the authors approximated the modes of polystyrene by using monosubstituted benzene. The R can be several pieces of the backbone or just the first carbon. The four modes observed by HREELS include 218, 543, 916, and 983 cm^{-1}. The 543 cm^{-1} is listed as a strong IR peak and showed similar intensity in the HREELS spectra. The 983 cm^{-1} peak is visible only after the deconvolution; however, it appears normally in the IR as a medium-intensity peak and is the strongest Raman active mode. Both the 218 and 916 cm^{-1} peaks appear after deconvolution and are seen in the IR and Raman. The 218 cm^{-1} peak shows weak intensity in both the IR and Raman, while the 916 cm^{-1} mode displayed medium IR and a very weak Raman signal, and is only visible by the ELS3000. The 708 and 764 cm^{-1} peaks are both listed as very strong in IR intensity and the 764 cm^{-1} mode was also seen as being very weak in Raman intensity. The 708 cm^{-1} mode is the most intense peak in all the HREELS spectra. Although this peak is easily seen, the 764 cm^{-1} mode needed the higher resolution of the ELS3000. Even with the higher resolution, the peak is not completely resolved until the deconvolution is applied. The 854 cm^{-1} mode has medium–weak intensity in the IR and is accounted for in both LK2000 and ELS3000 HREELS spectra, while the 410 cm^{-1} peak is listed as having weak IR intensity and is a noted peak in the entire HREELS spectra prior to deconvolution. Although Bowers and Madams show no Raman activity for this mode, the present Raman data shows a mode at 401 cm^{-1}. This difference most likely arises from the different samples. Bowers and Madams report work done on atactic PS and our data is from a syndiotactic copolymer PS. The 1083 cm^{-1} and 1172 cm^{-1} bands also reflect this difference and will be mentioned with the respective bands.

The second set of bands belongs to the ring in-plane CCH bending group. The 1336 cm^{-1} peak is listed as a medium–strong IR and very, very weak Raman intensity. The 1172 cm^{-1}

is the second strongest mode in the HREELS spectra and has medium–weak intensity in the IR. Raman activity in this region was seen at 1157/1184/1205 cm^{-1}. However, Bowers and Madams reported this mode as being Raman inactive. Only visible after deconvolution in both LK2000 and ELS3000 spectra as a shoulder, the 1042 cm^{-1} mode has medium–strong IR intensity and medium Raman intensity.

The third group is the ring skeleton in-plane bend or stretch. The 1594 cm^{-1} peak is a ring skeleton in-plane bend and is visible in all HREELS spectra and well resolved after deconvolution. It is only medium in IR intensity and very weak in Raman intensity. The 623 cm^{-1} peak, an in-plane stretching mode, is seen only after deconvoluting the ELS3000 spectra. The 623 cm^{-1} peak displays medium Raman and very weak IR intensity. We should note here that the 1594 cm^{-1} peak may also be assigned to the 1606 cm^{-1} band associated with a ring skeleton in-plane bend.

The remaining modes include chain modes, CH$_2$ modes, and the CH stretch modes of the ring. The 1083 cm^{-1} peak labeled a chain stretch mode is a medium strength mode in the IR, and in HREELS spectra is visible only with the ELS3000. This mode, like the 410 cm^{-1} band, appeared in the Raman spectra at 1075 cm^{-1} but was not mentioned in Bowers and Madams as having a Raman mode. The 1458 cm^{-1} mode is very strong in IR intensity and has a very weak Raman intensity. This CH$_2$ bending mode is one of two CH$_2$ modes present in the spectra. The last modes pertain to CH stretching vibrations in the region 2900–3100 cm^{-1}. The two bands resolved are the 2908 cm^{-1} (aliphatic) and the 3045 cm^{-1} (aromatic). Both of these peaks are seen in all of the HREELS spectra and are also present in both IR and Raman spectra. The aromatic modes lie between 3029 and 3138 cm^{-1} and are labeled as the C–H ring stretching modes. The aliphatic modes lie between 2851 and 2923 cm^{-1} and are attributed to the backbone CH$_2$ stretching. This region therefore provides a convenient marker for documenting structural change in the polymer that separately affects the ring and backbone features.

IV. Conclusion

We have presented the first detailed vibrational assignments for insulating polystyrene surfaces by means of HREELS. Improved energy resolution has permitted the identification of eighteen vibrational modes whereas only seven modes were previously resolved in a thin film study.[2] These modes are in

good agreement with known IR and Raman bands. Although a detailed study of the electron excitation mechanism was not made it appears that both dipolar and impact interactions are present.

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