All data taken at the Pacific Northwest National Laboratory
FTS Operators: Tyler O. Danby and Paul L. Gassman
Data Analysis: Russell G. Tonkyn and Jerome C. Birnbaum

Composite spectrum for: Polystyrene

- First Column: Position in wavenumber (cm^{-1})
- Second column: Imaginary refractive index, $k(\tilde{\upsilon})$ (absorption index per unit length in centimeters)
- Third column: Real refractive index $n(\tilde{\upsilon})$ (dispersion index)

Where the complex refractive index $\hat{n} = n(\tilde{\upsilon}) + ik(\tilde{\upsilon})$

Following Bertie (in the references below) we define the absorbance as $A = -\log_{10}(I/I_0)$ and the linear absorption coefficient K = A/d, where d is the path length. The connection between the imaginary refractive index and the absorbance coefficient arises from the following: $2.303K = 4\pi\tilde{\upsilon}k$

See the following references for a detailed description of terms and units:

1) Bertie, J. E., Zhang, S. L., Eysel, H. H., Baluja, S., & Ahmed, M. K. (1993). Infrared Intensities of Liquids XI: Infrared Refractive Indices from 8000 to 2 cm^{-1}, Absolute Integrated Intensities, and Dipole Moment Derivatives of Methanol at 25°C. *Applied Spectroscopy, 47*(8), 1100-1114. doi:10.1366/0003702934067973
2) Bertie, J. E., Zhang, S. L., & Keefe, C. D. (1995). Measurement and use of absolute infrared absorption intensities of neat liquids. *Vibrational Spectroscopy, 8*(2), 215-229. doi:10.1016/0924-2031(94)00038-i

Sample:

- Chemical name, formula and CAS number: Polystyrene, $[CH_2CH(C_6H_5)]_n$, [9003-53-6]
- IUPAC name: Polystyrene
- Synonyms: PS
- Physical properties: FW = Avg. 800 g/mole; mp = n/a; bp = n/a; ρ = n/a
- Supplier and stated purity: Sigma-Aldrich, analytical standard (Lot # MKBW0708V)
- Temperature of sample: 26 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: 10.3, 12.2, 27.9, 51, 52, 192, 213 and 1004 micrometers (μm). Final data are a composite of these spectra.
- Sample cell window material is potassium bromide (KBr).
- Preparation: Sample was viscous so the sample, syringes, and cells were heated above 100 °C in order to fill the cells. The cells were then allowed to cool to room temperature.

Instrument Parameters:

- Bruker Tensor 27 FTIR, purged with UHP nitrogen
- Spectral range: 7800 to 400 cm^{-1} (1.282 to 25 microns)
- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10 kHz
- Folding limits: 15802 to 0 cm^{-1}
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4823 cm^{-1}
- IR source: Silicon carbide glow bar
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm

Measured Refractive Index:
The refractive index for Polystyrene was measured at 27 °C using an Atago model DR-M2/1550 Abbe refractometer. Notch filters were employed in front of a white light source to make measurements at multiple wavelengths. An InGaAs camera was used to detect signal at 1550 nm. The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm: $n = 1.5921$	486 nm: $n = 1.5912$	546 nm: $n = 1.5821$
589 nm: $n = 1.5778$	644 nm: $n = 1.5737$	656 nm: $n = 1.5727$
1550 nm: $n = 1.5520$		

The refractive index, *n*, vs. wavelength in microns, λ, was fit to an equation similar to that of Sellmeier:

$$n(\lambda) = \{a + b/(\lambda^2 - c)\}^{1/2}$$

The resulting best-fit equation was used to find the refractive index at the highest energy data point in our experimental spectra. For Polystyrene, the result was

$$n(7800\ \text{cm}^{-1}) = 1.5542 \text{ at } 27\ °\text{C}.$$

a) b)

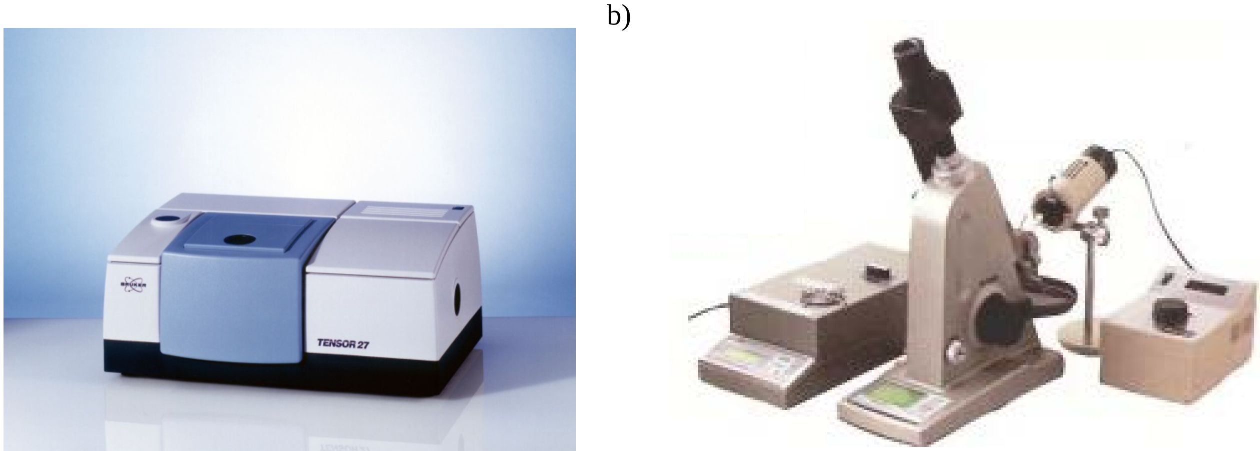

Figure 1: The Bruker Tensor 27 FTIR (a) and Abbe refractometer (b).

Post Processing and Related Parameters:
A composite spectrum was created from 8 absorbance spectra (base-10) taken at 8 path lengths: 10.3, 12.2, 27.9, 51, 52, 192, 213 and 1004 micrometers (μm). At each path length several spectra were measured and the results averaged for better signal to noise. The measured cell lengths were adjusted using Beer's law plots.

1) The imaginary part of the refractive index, or *k* vector, was determined for each absorbance file as per Bertie's program "RNJ46A" (see reference above). This takes into account the reflective losses due to the KBr windows.
2) A composite *k* vector is created via a classical, weighted, linear, least squares fit using the output files of program "RNJ46A": Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values ≥ 2.5 are given zero weight. Three composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 192, 213 and 1004 μm cells. This *k* vector determined the final values for the range from 7800 to 3200 cm^{-1}.
   b) The second *k* vector used the results from the 10 through 52 μm cells. This *k* vector determined the final values for the range from 3200 to 2800 and 1640 to 400 cm^{-1}.
   c) The third *k* vector used the results from the 51 through 1004 μm cells. This *k* vector determined the final values for the range from 2800 to 1640 cm^{-1}.

3) The resulting composite *k* vector and the refractive index at 7800 cm^{-1} were used to create the real or *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
   a) Calculated and estimated errors: Type A = 0.7%.
   b) Frequency correction (already applied): $\tilde{\nu}$(corrected) = [$\tilde{\nu}$(instrument) * 0.99975+.00389] as determined by comparing measured spectral lines of vapor phase water to values from the Northwest Infrared Spectral Library Database.
   c) Axis units: X = Wavenumbers (cm^{-1}); Y = Absorbance (base 10).

Photograph of Sample Polystyrene:

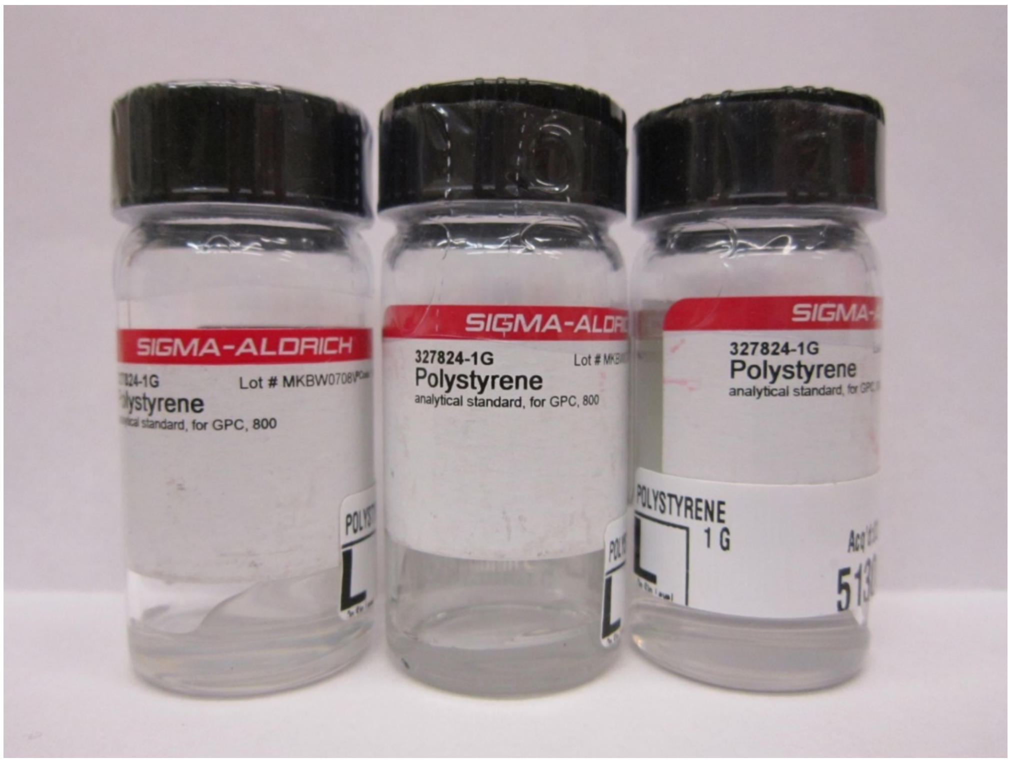

Figure 2: Polystyrene in Sigma-Aldrich containers with PNNL CMS #s 513042-513044.