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Polymer Characterization Using SEC-FTIR†

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Infrared spectroscopy combined with size exclusion chromatography has found wide acceptance in the study of deformation of samples of unknown origin, compositional distribution in copolymers, impurity profiling in polymers, and branching in polyolefins. Use of this technique is enhanced by the availability of new commercial instrumentation and by software that speeds data analysis. The new instruments are off-line solvent removal devices that provide samples in a simple, solvent free condition that are compatible with existing FTIR instrumentation. Two solvent removal approaches are described; a pneumatic nozzle and an ultrasonic/vacuum nebulizer. Both systems speed sample preparation and both work with the normal sampling methods and concentration levels expected in SEC. The utility of this technique is demonstrated using as an example a commercial adhesive sample.

Keywords: SEC, FTIR

INTRODUCTION

Combining infrared spectroscopy with HPLC and size exclusion chromatography is finding wide acceptance for the study of deformation of samples of unknown origin, compositional distribution in copolymers, impurity profiling in polymers, and branching in polyolefins. The utility of this technique has been enhanced by the availability of new commercial instrumentation and software that speeds data analysis. The new instruments are off-line solvent removal systems that collect the chromato-

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graphic eluents as solvent free solutes in a condition that is compatible with existing FTIR instrumentation. Normal HPLC/SEC sampling methods and concentration levels may be used. There are two solvent removal approaches currently available; the first uses a pneumatic nozzle with heated gas evaporation system, and the other that uses an ultrasonic/vacuum nebulizer.

In addition to enhanced hardware, software has been tailored for the analysis of time resolved spectra generated by the combination of HPLC/SEC and IR spectroscopy. The software, 3D/IR, may be used on any 486-based PC computer. 3D/IR consists of a series of program modules that allows for reduction of the large blocks of data into useful chemical and structural information about polymer samples. The process of reducing *data to information* then becomes a simpler and easier task.

SEC with online flow-through FTIR suffers severe limitations because the concentrations present in SEC are usually inadequate for IR analysis and mobile phases may blank out major regions of the useful IR spectrum. Furthermore, preparative SEC is labor intensive. Gagel and Biemann,^[1] Jinno, *et al.*,^[2] and others have described methods of removing the troublesome solvent in order to simplify IR analysis. The pneumatic heated nozzle system^[1] has been commercialized and solves both the solvent and the sample preparation problems. The details of this system, called the LC-Transform, have been described by Willis and Wheeler.^[3] (Figs. 1 and 2).

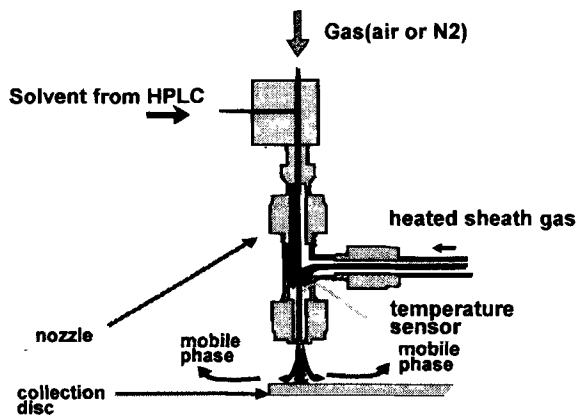


FIGURE 1 The pneumatic nozzle, Series 100.

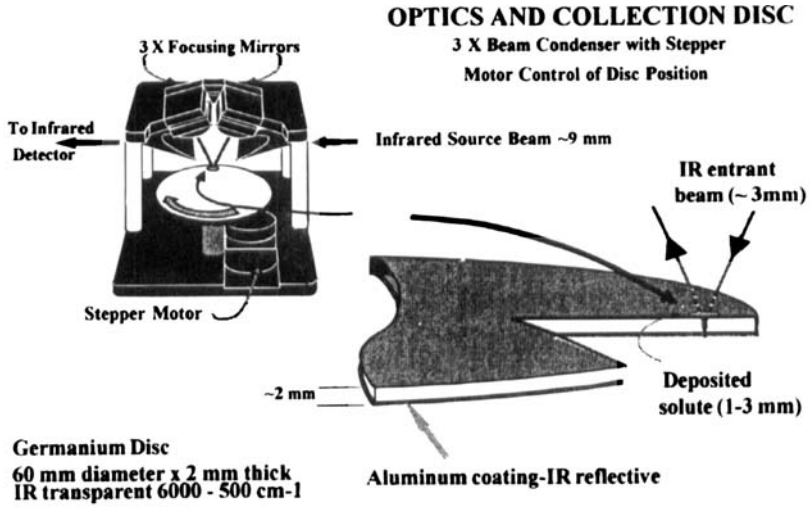


FIGURE 2 LC-Transform optics module.

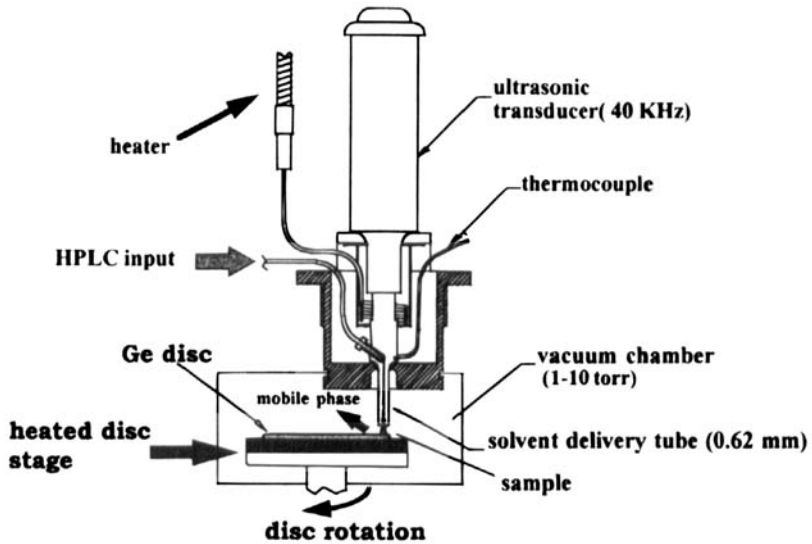


FIGURE 3 The ultrasonic nozzle/vacuum system, Series 300.

Dekmezian^[4] described an ultrasonic/vacuum method of solvent removal (Fig. 3). This system has the capability of removing a significantly higher flow of mobile phase than does the pneumatic system. The pneumatic system can evaporate up to 100 $\mu\text{L}/\text{min}$ of THF; whereas the ultrasonic/vacuum system can handle flow rates up to 1.0 mL/min of THF. For more difficult solvents, such as TCB or water, the rates of solvent removal are 50 $\mu\text{L}/\text{min}$ and 500 $\mu\text{L}/\text{min}$ for the pneumatic and ultrasonic/vacuum systems, respectfully. High-temperature solvents, such as TCB and DMSO, require a heated transfer line to transfer the SEC flow from the chromatography to a high-temperature cabinet of the collection module where the solvent is removed and the sample collected. Table I illustrates the sensitivity of each of the two systems using THF and water as examples of solvents with greatly differing properties.

All solvents including THF, toluene, water, and mixed mobile phases (*i.e.*, MeOH:H₂O, ACN:H₂O) effectively can be removed from a sample. The concentration required for satisfactory analysis is between 0.1 and 0.3 wt% assuming an injection volume of 400 to 100 μL , respectfully. Quantities down to 100 ng have been detected and identified although for routine analysis samples in the μg range are preferred. These conditions are consistent with normal methods used in HPLC/SEC analysis. With these concentrations and assuming a distribution of the sample over a 20 min time period, a signal level of between 0.1 and 1.0 AU will be observed in the FTIR spectrum. No special hardware or software is required for either the HPLC/SEC system or the FTIR.

In either the pneumatic or the ultrasonic/vacuum system, the sample must be nonvolatile, thermally stable below 100°C, and be a solid or a viscous liquid at room temperature. The mobile phase must not contain nonvolatile buffers. The solvent removal technique is most commonly used as a qualitative method, although by using calibrated standards it is possible to provide quantitative measurements for some samples.

TABLE I LC-Transform System Configuration

System	LC Mode	Nozzle Type	Nozzle Capacity
100	Reverse Phase (H ₂ O) GPC (THF)	Pneumatic	40 $\mu\text{L}/\text{min}$ 200 $\mu\text{L}/\text{min}$
300	Reverse Phase (H ₂ O) GPC (THF) GPC (TCB)	ultrasonic/vacuum	500 $\mu\text{L}/\text{min}$ 1 mL/min 500 $\mu\text{L}/\text{min}$

To demonstrate the utility of this instrument, a commercial adhesive was separated by SEC, collected with an LC-Transform, and analyzed by FTIR.

EXPERIMENTAL

Disc rotation in the LC-Transform was started immediately upon injection of the sample. The collection took approximately 25 min. Following collection of the sample, the sample collection disc was transferred to the FTIR spectrometer and the IR spectra collected. Data reduction was accomplished using Grams/386 (Galactic Industries, NH) and 3D/IR (Lab Connections, Inc., Marlborough, MA).

RESULTS

An examination of a 3D view of IR spectra, Figure 4, reveals the IR spectra of two main peaks and, in addition, another set of weak bands at approximately 22 min indicating the presence of a third material. The spectrum of the material eluted at 8.4 min, is very similar to that of the bulk material, which was identified as a styrene/isoprene block copolymer. The spectrum of the peak eluting at 17.9 min indicates that the material is an aliphatic ester which contains no styrene. A strong band at 2956 cm^{-1} indicates considerable branching. No other prominent features are found. The spectral features of the 22 min peak indicate that it is similar to the material found at 17.9 min but also exhibits strong bands at 3345 and 1025 cm^{-1} . This sample therefore contains the same backbone structure as found in the 17.9 min peak but with the ester groups being oxidized to acid functionality. Further improvements in the signal to noise could be obtained by acquiring additional IR spectra.

Further information is contained within the collected spectral data. For example, using a software routine (3D/IR), one can examine comonomer distribution and/or impurities. Because this sample is known to contain aromatic components, one can map the distribution of this species through all the deposits. To do this, first one determines an IR frequency that represents the molecular species of interest. Then the IR Chemogram of the band is calculated and extracted from all the IR spectra collected. The software then plots the distribution of the band of interest as a function of time.

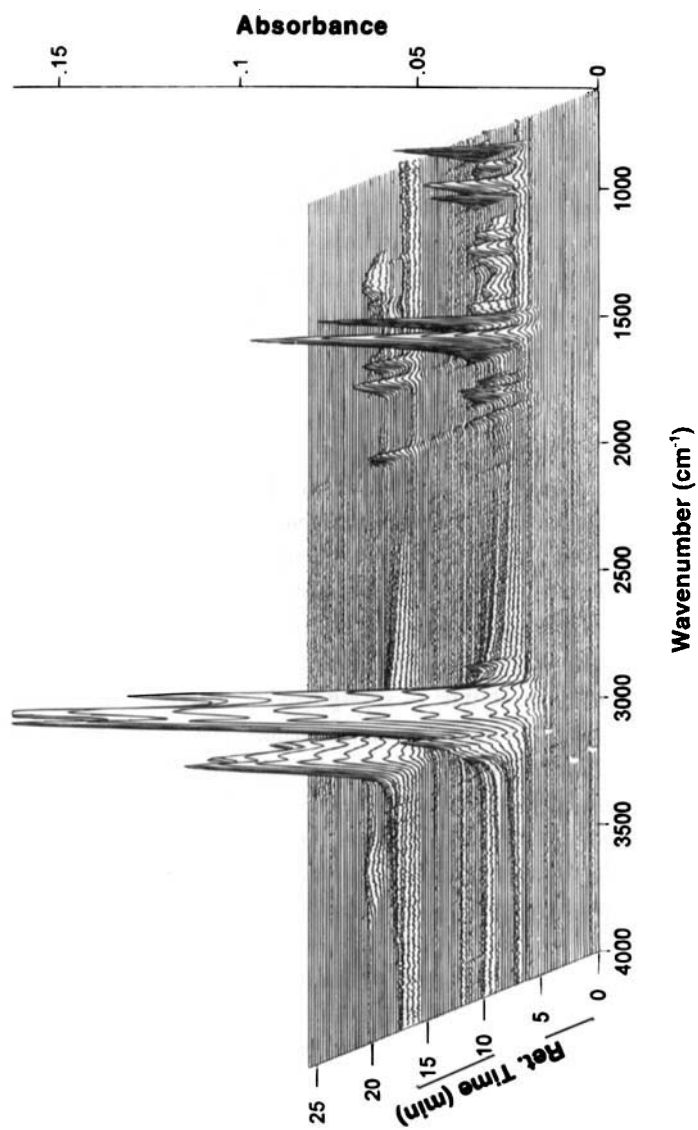
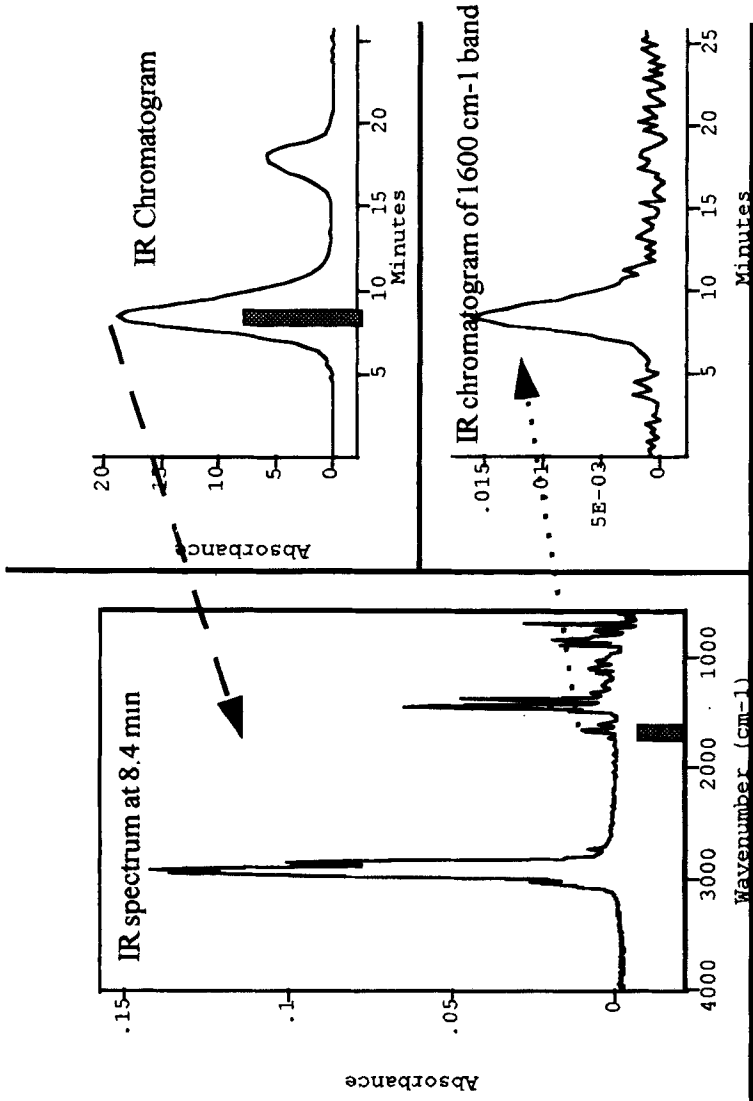
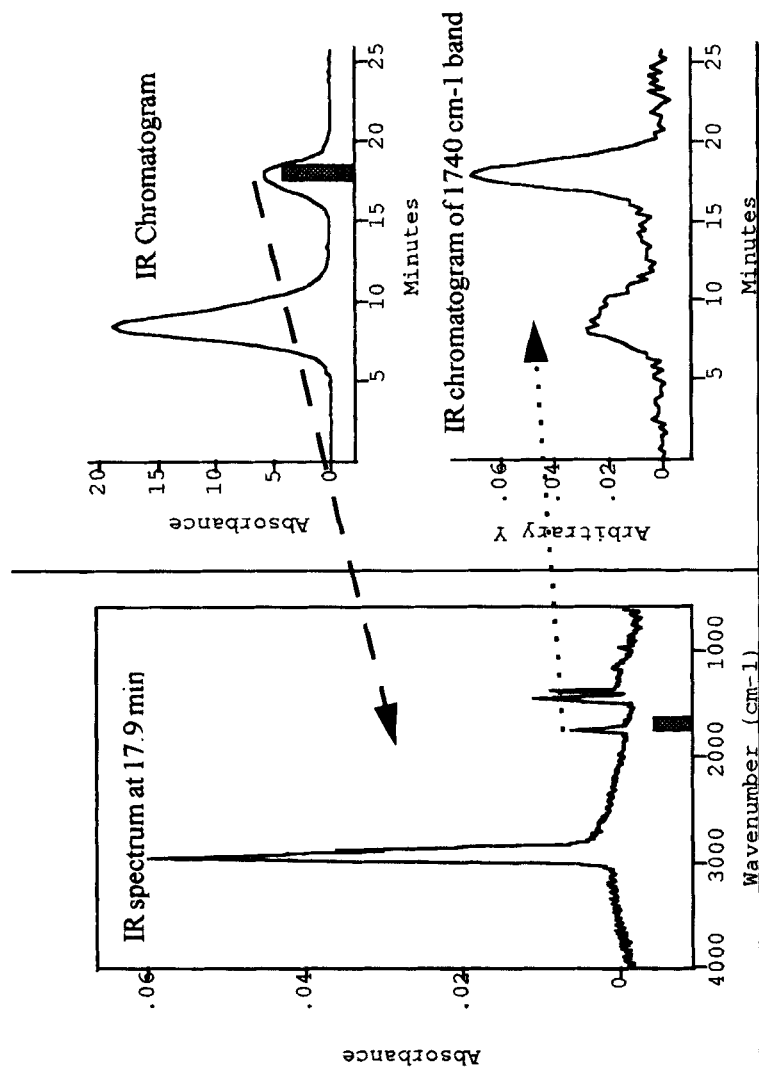


FIGURE 4 3D-IR spectra of adhesive.

FIGURE 5 3D/IR data extraction at 1600 cm⁻¹.

FIGURE 6 3D/IR data extraction at 1740 cm⁻¹.

In this case, the 1600 cm^{-1} band arising from the aromatic ring was selected. The distribution of that frequency then appears in bottom right box in Figure 5. This data confirms that only the sample deposit found at 8.4 min contains an aromatic containing species. Using a similar approach, one can determine the distribution of the aliphatic ester compound. Here the 1740 cm^{-1} band is selected as the representative band. The extraction and plotting of the distribution of this band is shown in Figure 6. This data clearly shows that there is little evidence of the ester compound in the main peak at 8.4 min but a significant amount in the second deposit. This method can be used to quickly map the distribution of any material collected from a chromatographic experiment. It should be noted that with this method is it not necessary to obtain complete separation via chromatography in order to map the distribution of a compound with a blend or a copolymer. Overlapping bands that contain differing materials can be deconvoluted with the available software.

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