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Article

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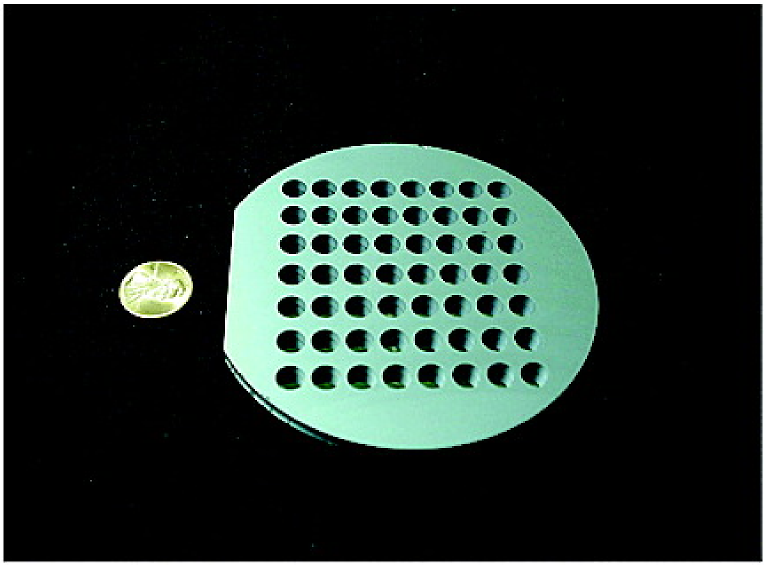

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High-Throughput Analysis in Catalysis Research Using Novel Approaches to Transmission Infrared Spectroscopy

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This study has demonstrated that high-throughput FTIR transmission measurements using a newly designed array-based support formed using silicon wells and a silicon wafer is a very useful and robust tool for the characterization of polymer composition for combinatorial materials research. The comonomer content in copolymers can be measured accurately with a fully automated throughput of >300 samples/day (8 h). The transmission measurement is more robust, reliable, and easier to automate than other spectroscopic methods. The support itself provides excellent resistance to aggressive organic solvents at elevated temperatures and allows the unattended deposition and preparation of polymer films for infrared analysis. Because of the excellent durability of the support with respect to the solvent, the support can be rinsed and reused many times. This high-throughput approach to infrared transmission spectroscopy can be used for measuring a wide array of polymer characteristics: vinyl content, geometrical isomers, crystallinity, and tacticity. As well, this IR approach can be used to predict the oxidative stability of the antioxidant packages. Because the support provides a means of containing hot polymer solutions while the solvent evaporates, the support is also suitable for high-throughput nanoindentation methods for the determination of modulus and other physical properties of the polymer.

Introduction

With the emergence of reaction tools for combinatorial chemistry, new characterization methods have been developed that hold considerable promise in speeding the process to identify attractive catalysts and reactions. This combination of synthesis tools and characterization tools allows the simultaneous generation and testing of a large number of compounds. One of the major difficulties lies in establishing general technologies for rapid and reliable screening of libraries to determine the catalytic activity. Infrared spectroscopy is a powerful, universal tool for the characterization of polymers, proteins, and many types of materials. A wide variety of infrared-based techniques have been investigated for interfacing the sample to the infrared beam of light used for high-throughput analyses. An excellent review of the technology highlights several recent publications addressing this need.[1] These techniques have been applied successfully not only to the high-throughput screening of parallel compound arrays but also to the screening of compound libraries developed from reactions and analysis of materials on microbeads. This review describes the methodologies used for the detection of catalytic events and places particular emphasis on the on-bead screening of one-bead-one-compound libraries.

Although IR microbead analysis has been used extensively as a characterization tool in the pharmaceutical industry, other approaches are more effective for the analysis of macrosized samples that are produced in materials and catalysis research. Fourier transform IR spectroscopy, using attenuated total reflection devices (ATR-FTIR spectroscopy) in conjunction with multivariate calibration, has been employed in order to determine the composition of olefin copolymers such as ethene/1-hexene and ethene/1-octene copolymers.[2] Snively and co-workers[3−5] demonstrated a major technology improvement in the characterization of catalytic activity using FTIR imaging approaches. This advancement dramatically decreases the time required for data collection without decreasing the data quality. With this new instrumental setup, an imaging data set consisting of 64 × 64 spectra with a 4-cm^{-1} spectral resolution over a 1360-cm^{-1} spectral range can be collected in 34 s. As a practical example, these authors demonstrated what they believed to be the first application of FTIR imaging to the screening of adsorbates on the elements of a combinatorial library containing different supported catalyst materials supplied with the same reactant feed. Photoacoustic FTIR (PA-FTIR) requires no sample preparation and can give high-quality spectra with minimal artifacts.[6] In PA-FTIR, a sensitive microphone measures an acoustic wave created by absorbed radiation diffusing as heat through the sample toward a boundary layer of gas. By

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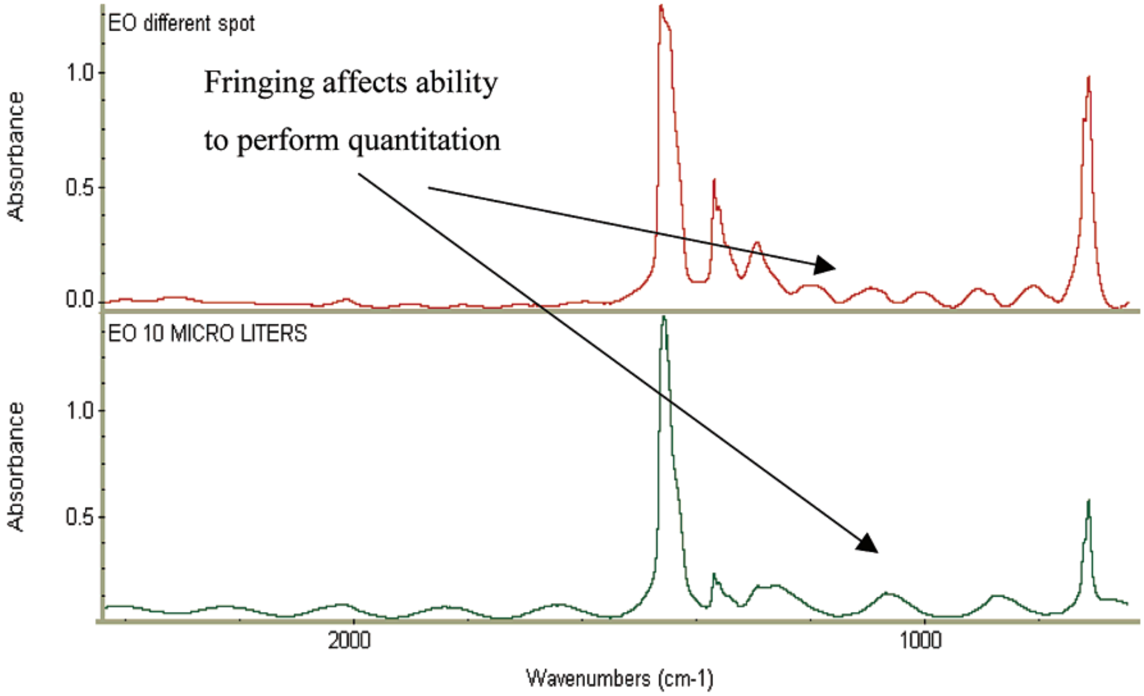

Figure 1. Sinusoidal baseline artifacts in micro-IR reflectance spectra of polyethylene films on gold substrate.

detecting only absorbed radiation via sound waves, PA-FTIR spectroscopy eliminates the spectral artifacts of light scattering and reflection. The authors demonstrated the use of PA-FTIR to effectively monitor the modification of solid supports as well as syntheses of polymer-bound organic compounds.

Feustel described the use of a Pike Technology XY autosampler for the direct IR spectroscopic analysis of liquids, powered solids, microbeads, and solid samples in microtiter wells in combinatorial chemistry.[7] It is based on the standardized 96-well architecture and is installed in the sample compartment of an FTIR spectrometer. The beam diameter at the focus was ∼2 mm, and measurements were performed in the transmission or in the diffuse reflection mode.

Researchers at Symyx Technologies (Santa Clara, CA) described the use of an arrayed wafer to determine the infrared spectra of an array of polymeric materials.[8] A polished silicon wafer containing an array of 3-mm gold dots is described. The silicon surface was treated with a silanizing reagent to increase the surface energy and render a nonwettable silicon surface. Polymer samples were deposited onto the gold dots of the wafer via evaporative deposition of heated polymer solutions. Reflectance FTIR spectroscopic methods were then used for analysis. This approach, however, presents potentially severe problems with regard to optical interference fringes produced in the spectra from thin, flat films on a reflective surface (Figure 1). While programmable mapping stages can be applied, it adds complexity and uncertainty to the method. Alternatively, this group proposed using a transmission substrate with transmission holes through the substrate into which the polymer “flows” or is transported. The problem with this approach is that the hole diameter would detrimentally constrain the beam geometry of the infrared instrument. In addition, the polymer viscosity would vary with molecular weight, and the transport of material into that capillary would be highly variable, leading to path length differences and concentration differences. These problems, which are inherent with the design of this instrument, would lead to highly inaccurate analytical results.

Although ATR spectroscopy has some advantages in terms of its flexibility with respect to sample geometry, the variation in the refractive index of the samples, pressure of the crystal against the samples, and long-term crystal abrasion can produce variables in the spectra that must be modeled in some way, usually using multivariate modeling approaches.

As with infrared spectroscopy, Raman spectroscopy provides information about the fundamental vibrational modes of the analytes and can be used for the quantitative measurements of composition. Hochloski and co-workers[10] describe the use of a polymer bead array holder device fabricated with a gold-plated silicon wafer. This approach is ideal for minute quantities of the analyte, since the focused laser beam is roughly 1−20 μm in effective size. Semicrystalline polymers frequently have spherulites that are tens of micrometers in diameter. To minimize the errors associated with probing these small regions of a heterogeneous material, the Raman instrument is generally programmed to acquire multiple spectra on each well in the array. This requires time, auto focusing, and averaging of spectra with lower than optimal S/N. Experiments in our laboratories have demonstrated that the size of the Raman probe beam is problematic for the fast, reliable quantitation of polymers and materials that are heterogeneous on this size scale. As such, every attempt was made to probe a large amount of material.

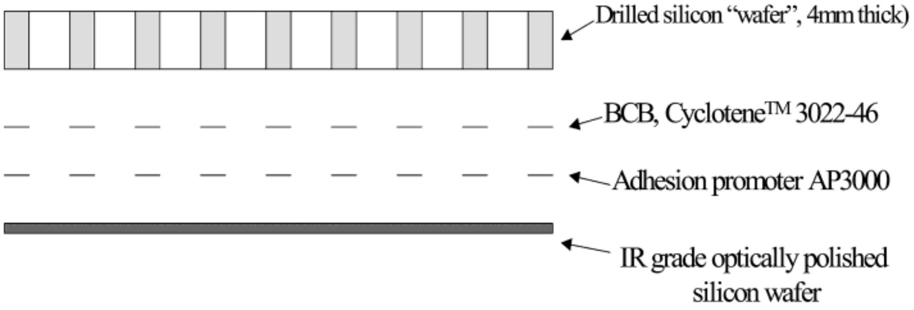

Figure 2. Exploded cross-sectional view of IR transmission substrate.

Infrared transmission spectroscopy typically probes a sample region up to 10 mm in diameter.

Current Approach. Given sufficient sample, IR transmission spectroscopy of macro-sized samples always yields the highest quality spectra with minimal artifacts if sample thickness is controlled.

Since the goal of this work was to develop a fully automated, robust measurement of comonomer content for newly synthesized polymers, well outside the universe of the calibration set in terms of molecular architecture, every effort was made to control the number of variables that needed to be modeled. Another essential feature of the analysis, from a practical standpoint, was the need for disposable, archivable, or simply reusable sample library holders.

Experimental Section

Sample Support Design. Common supports used for samples in IR transmission spectroscopy are typically salt plates, such as NaCl, KBr, CaF_2, AgCl, or ZnSe. While these materials have excellent transmission properties throughout the infrared range, they pose challenges with respect to constructing disposable or reusable supports for routine IR analysis of libraries of materials. One of the less commonly used materials for IR transmission spectroscopy is silicon. Although even high-purity silicon has measurable absorption bands in the mid-IR range, the uniformity of the material is so high that a reference spectrum in one region of the silicon support is highly reproducible with that in another region of the support. As such, this means that a reference spectrum obtained from a single spot on a wafer is representative of the entire wafer. This aspect of the support is important in that it is not necessary to obtain a complete library of reference spectra for each spot on the support before depositing the samples into the wells. IR grade silicon wafers can be made in a form that lend themselves to the fabrication of supports for liquids. The construction of such a support is shown in an exploded view in Figure 2 and a photo of the actual device in Figure 3.

Support Fabrication. A 3.937-in.-diameter × 0.020-in.-thick optical grade microcrystalline silicon wafer (purity >99.999%), which was polished on both sides to a scratch and dig specification of 80/50, was used as the first substrate (Lattice Materials Corp., Bozeman, Montana). The second substrate used was a 3.937-in.-diameter × 0.157-inch-thick silicon wafer with 56 holes or openings, mechanically drilled to a diameter 0.276 in., and arranged in a seven-column by eight-row array. Each wafer was machined with a flat edge 1.772 in. in length, which is used to align the substrates during preparation. Forty-eight of the openings are used for unknown samples, while the remaining eight openings are used for reference materials or background collection.

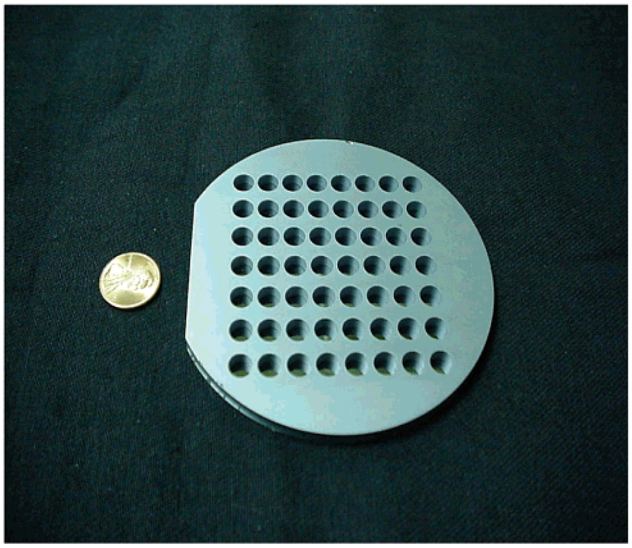

Figure 3. Photo of IR support for infrared transmission analysis.

To prepare the thin wafer for bonding, it was rotated to ~3000 rpm and a spin coat adhesion promoter, vinyltriacetoxysilane (AP3000, obtained from The Dow Chemical Company, Midland, MI), was manually added to the wafer. This produced an ~2−5-nm film of adhesion promoter onto the surface of the thin wafer. After drying, the wafer was rotated to ~500 rpm and benzocyclobutene (BCB, Cyclotene 3022-46, obtained from The Dow Chemical Company, Midland, MI) was manually poured onto the surface directly from the bottle to minimize contamination. Once the benzocyclobutene had been added, the rate of rotation was increased to 1000 rpm to yield a final film thickness of ~5 μm of Cyclotene. The thin wafer was then baked on a hot plate at 140 °C for 3 min to evaporate the solvent. The film produced in this manner was dry to the touch and storable for up to 1 month.

A programmable hot press was used to bond the two wafers together. The flat edges of the two wafers were aligned and placed in a machined holder to force the wafers to stay in alignment during the bonding process (Figure 4). The wafers were pressed together at 48.26 kPa (7 psi), and the platens were ramped to a temperature of 149 °C (300 °F) over 15 min to allow the BCB to soften. The pressure was increased to 3.447 MPa (500 psi), and the temperature

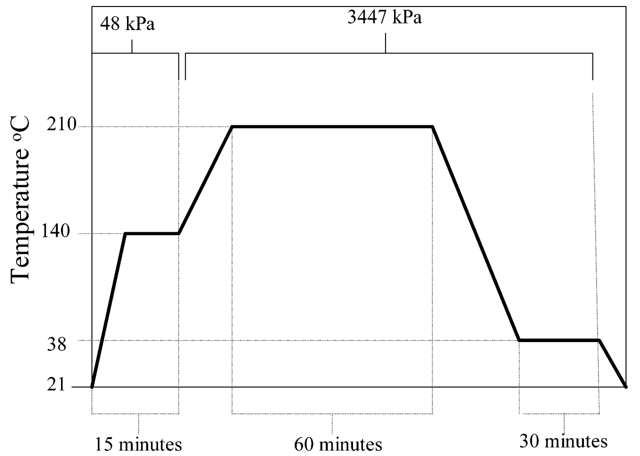

Figure 4. Temperature profile for high-pressure bonding of silicon wafers.

was ramped to 210 °C (410 °F) and maintained for 1 h to allow the BCB to cure. The temperature was then cooled to 38 °C (100 °F) and held for 30 min more. The pressure was then removed, and the arrayed wafer was allowed to cool to ambient conditions.

The cured Cyclotene was stripped out of the bottom of the cavities by soaking the arrayed wafer in benzenesulfonic acid for ~1 h at 80 °C. The arrayed wafer was rinsed with 2-propanol and then a distilled water rinse. A brass scribe was used to remove any minimal remaining bonding material.

The flat edges of the drilled silicon slab and the Cyclotene-coated polished silicon wafer were aligned and placed in a machined holder, which forced the two silicon flats to stay in alignment during the bonding process. The holder and silicon components were placed in a heatable press between two platens at room temperature. An automatic temperature program was started which ramped the platen temperature to 300 °F (140 °C). The operator then manually elevated the platen pressure to 4 psi (48 kPa). The assembly was held at this temperature for ~1 h in order to allow the Cyclotene resin to soften. After this period, the temperature was automatically elevated to 410 °F (210 °C), and the pressure was raised manually to 400 psi (3447 kPa). The assembly was held for 1 h under these conditions in order to allow the resin to undergo curing. After 1 h, the temperature program shut off the heat supply to the platens, and the press and assembly were allowed to cool to ambient lab conditions, with pressure maintained at 400 psi (3447 kPa).

The Cyclotene was stripped out of the bottom of the wells by soaking the assembly in Primary Stripper A, (benzenesulfonic acid) for 20 min at 80 °C. A rinse with 2-propanol and then a distilled water rinse followed this. The assembly was then heated on a hot plate at 160 °C for 1−2 h to drive off the residual cleaning solvents.

Calibration of the Method. A robust, high-throughput screening method that was amenable to a wide variety of catalyst systems was desired. The primary emphasis of this research was catalyst development for low-octene incorporation, so only polymers that had relatively low values of octene incorporation were included in the model. A total of 35 ethylene/1-octene copolymer samples were collected; 24 samples were from commercial sources, and 11 samples were from polymers prepared in a 2-liter batch reactor. One ethylene homopolymer sample was also used as a zero-octene data point. The commercial polymer samples were prepared via both homogeneous and heterogeneous catalyst systems in a continuous process mode. The batch reactor samples were made using a variety of homogeneous catalysts. All of the polymers were analyzed for 1-octene content using ^{13}C NMR spectroscopy. In the low octene-containing samples (<7 mol % 1-octene), all of the samples were well-represented by one curve. However, at octene incorporations above 7%, a disparity in the samples was observed for continuously produced, as compared to the batch-prepared, samples. The continuous samples showed consistently lower 1-octene incorporation values for the same absorbance measurement. Since the polymers prepared in 48-cell Symyx Technologies (Santa Clara, CA) Parallel Polymerization Reactors PPR-48 (PPR's) are prepared under batch conditions very similar to the 2-liter batch reactors, the 10 high ethylene/octene polymer samples prepared in a continuous reactor with mole percentages above 7 mole % were removed from the calibration line. As an initial check of the predictive power of the method, five additional polymer samples prepared in the 2-L batch reactor were then analyzed and found to fall on the calibration curve. These samples were then added the calibration curve to give a total of 31 samples.

Generation of the Polymer Samples in the Parallel Reactors. The IR wafer assembly and method was designed to analyze a library of polymer samples generated in the 48 PPRs.

These reactors are typically used for homogeneous and heterogeneous polymerization catalyst screening reactions. The PPR-48 is a collection of 48 Parr-like reactors, each having a 15-mL capacity, configured with six modules containing eight reactor cells per module.[9] The entire PPR-48 assembly is housed in an inert atmosphere triple glovebox. Custom control software allows for real-time in-situ monitoring of the catalyst activity by monitoring the consumption of monomer gas at typical polymerization conditions. Removable glass inserts are used in each cell during the reaction and are removed following the reaction. Postreaction samples containing solvent and polymer are then transferred to a rotary evaporator (Genevac Ltd., Suffolk, U.K.) to remove the solvent and any volatile materials. The library of polymer samples is weighed serially using a modified robot (Neptune, Mettler-Toledo Bohdan, Vernon Hills, IL), and the polymer weights are stored in a centralized database. Typically, 50−300 mg of polymer are produced in each cell.

Sample Preparation. Ethylene/1-octene samples were dissolved in 1,2,4-trichlorobenzene stabilized with butylated hydroxytoluene (BHT) (0.18 mg/mL) at 140 °C to a concentration of 30 mg/mL using a liquid handling robot (Cavro Scientific Instruments Inc, San Jose, CA) and shaken to completely dissolve the polymer. The polymer samples (50−100 μL each) were then deposited using heated robotic arms into the sample wells of the arrayed IR wafer. The samples were held at 150 °C for at least 30 min after the last deposition and the heating stage was turned off, allowing the large thermal mass to cool slowly to room temperature. The assembly was then mounted on the Pike Technology

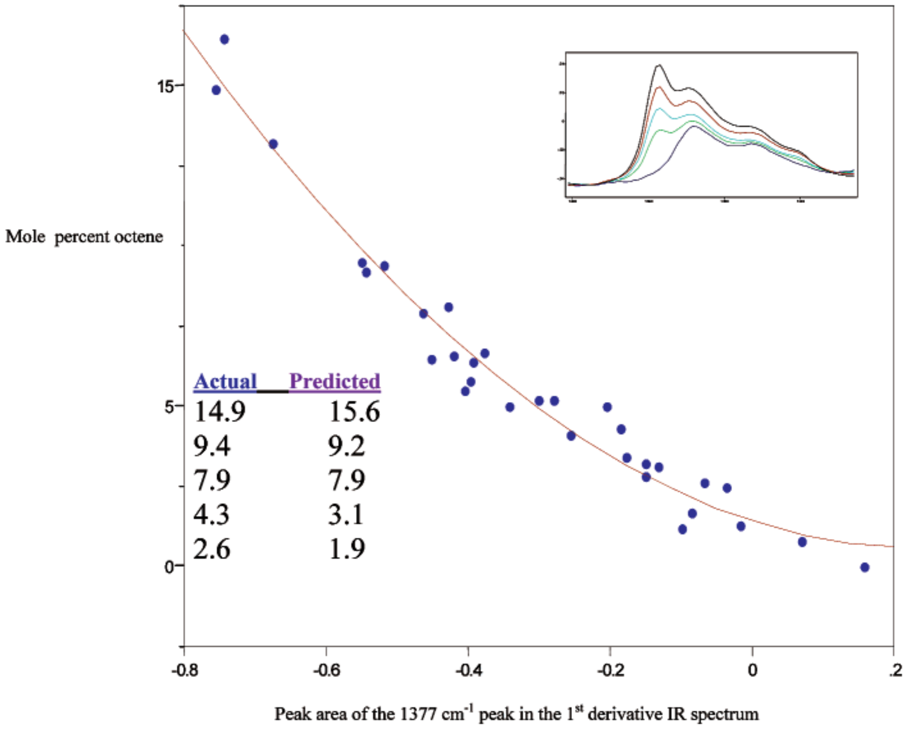

Figure 5. Calibration of mole percent of 1-octene ^{13}C NMR versus infrared measurements.

rotating wheel in the sample compartment of the Nicolet IR spectrometer.

Instrumentation. A nitrogen-purged FTIR spectrometer (Nexus model 870, Thermo Nicolet Corp., Madison, WI) was used for all infrared measurements. A 6-in. wafer holder accessory (Pike Technology, Madison, WI) was programmed with the position of all 56 spots on the assembly. The first position and the last position at the first column were left empty for background measurements and the average of these two spectra was used as background.. The background spectrum was remeasured after every 10 sample spectra were completed in order to ensure that long-term drift of the instrument did not cause quantitation problems. An OMNIC (trademark of the Thermo Nicolet Corporation) MACRO BASIC protocol was written which automatically sets the desired acquisition parameters and Excel file names for data export, purges the instrument with dry nitrogen for a fixed interval, collects average background spectra of different points on the wafer, and then collects spectra of individual samples in the wells. An additional aperture (4 mm in diameter) was positioned in front of the wafer to reduce the size of the incident IR beam. The distance between the aperture and the wafer is ~10 mm, which allows the wheel to rotate freely. The addition of the aperture is to ensure that 100% of the IR beam falls within the walls of each well. This also allows a wide tolerance of the well positions for the fabrication of wells.

During the initial installation of the rotating wheel and the AutoPRO software (Pike Technologies, Inc.), the coordination of the well positions needs to be defined. Once the four corner well positions are defined, all other well positions can be calculated. Each corner well position was defined by maximizing the intensities of interferograms in a series of positions (with ~1 mm interval) in *X* and *Y* directions. A polynomial curve fitting was used to find the maximum in the *X* or *Y* direction. The cross point of the *X* and *Y* maximums is the center position of the well. The *X*−*Y* coordination was then converted to $r-\theta$ coordinates.

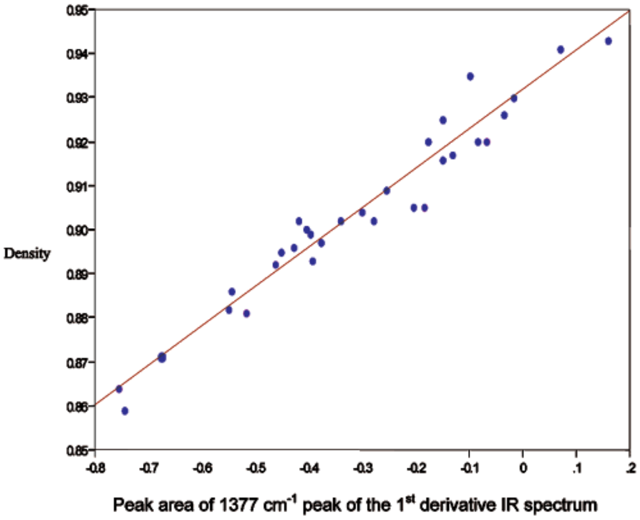

Figure 6. Calibration of density versus infrared measurements.

Results and Discussion

Calibration Results. The infrared spectral measurements of the set of 31 polyethylene standards were plotted versus the ethylene and octene incorporation values obtained from ^{13}C NMR spectroscopy, as shown in Figure 5. In this application, a direct least-squares curve fitting was used for the calibration. One of the inserts in Figure 5 shows the overlaid IR spectra in the 1377 cm^{-1} peak region. The octene contents (mole percent) of the samples in the insertion are 0, 5, 9.2, 13.6, and 16.5. Another insert in Figure 5 shows the results of the validation experiments, in which samples that were not included in the calibration were predicted with the model.

In this application, the CH_3 symmetric scissors band at 1377 cm^{-1} was used for the calibration and prediction of mole percent octene. Octene branches are the major structural characteristics of the octene/ethylene copolymer. Two functional groups in the polymer can be used to correlate the octene content, either the end group CH_3 or the tertiary carbon. While the spectral bands due to the tertiary carbon (either C−C or C−H) is very weak., the bands due to the CH_3 end group are significantly more intense. There are two relatively strong bands, which characterize CH_3 in this copolymer; the C−H asymmetric stretch at roughly 2956 cm^{-1}; and the C−H symmetric scissors deformation at 1377 cm^{-1}. The 2956 cm^{-1} peak is a broad shoulder on the side of a very strong CH_2 asymmetric stretch band at ∼2920 cm^{-1}. Because of this overlapping feature, directly measuring the 2956 cm^{-1} peak or derivative peak is very difficult. With a Fourier self-deconvolution, the 2956 cm^{-1} band shows a measurable peak. The peak heights and peak areas correlate to octene concentration. One problem associated with using the 2956 cm $^{-1}$ peak, however, is that this peak is very sensitive to the variations in film thickness. This problem is not completely resolved even after normalization of the spectra by either the 1464 cm^{-1} band or by the combination bands at around 2670 cm^{-1}. A calibration using the deconvoluted 2956 cm^{-1} peak shows a correlation coefficient of 0.976. Although this correlation is satisfactory, a better correlation is achieved using the peak area of the first derivative of the 1377 cm^{-1} peak, which shows a correlation coefficient of 0.998. A multivariate calibration using PLS/IQ from Galactic was tested to build a calibration and for prediction. Comparing the PLS calibration with curve fitting directly from peak area of the first derivative of the 1377 cm^{-1} band, the PLS calibration did not show an improvement of precision or accuracy. It is believed that the accuracy is mainly limited by the reference method, ^{13}C NMR.

Because of the high temperature of the solutions (160 °C) and high viscosity of the polymer solution in trichlorobenzene, the robot was not able to consistently deliver the desired amount of sample to each well. While the solvent evaporates from the well, the polymer tends to dry on the side wall of the well. For these reasons, the film thickness of the polymer at the bottom of the well varies over a relatively wide range. Under the experimental conditions used, the film thickness could vary more than 200%. To minimize the effect of film thickness variations, normalization of the spectra is necessary. Ideally, the normalization region should be independent of octene concentration. However, in the entire IR spectral region, there is no single peak or region that does not change as octene concentration changes. In this study, the 1464/1473 cm^{-1} region was used for the normalization. The reasons for choosing this region are (1) the absorbance is >0.1 absorbance unit, but <1 absorbance unit; (2) this region is very close to, but well separated from, the analysis region around 1377 cm^{-1}, and (3) this region is not affected seriously by crystallinity changes. A comparison of the peak area of the 1464/1473 cm^{-1} region was made before and after annealing. The total area change was found to be $<0.5\%$. In this study, the path length normalization is accomplished by dividing the whole spectrum by the net peak area between 1540 cm^{-1} and 1400 cm^{-1}.

Spectral resolution affects the speed of the analysis and the peak width. A spectrum acquired at higher resolution requires allowing the interferometer a longer time to scan but provides narrower bands and better peak separation. A high-resolution scan is especially important when derivative spectra are used, because narrower bands yield larger derivative peaks. In this study, the spectra recorded with 4 cm^{-1} spectral resolution were compared with 8 cm^{-1} resolution. Although the spectral acquisition time for spectra acquired at 4 cm^{-1} resolution is two times longer than that for spectra acquired at 8 cm^{-1}, the area of the first derivative of 1377 cm^{-1} peak is almost twice as large for the higher resolution than the peak recorded with 8 cm^{-1} resolution. On the basis of eight repeated measurements, the relative standard deviation of predicted mole percent octene is 2.6% for 4 cm^{-1} resolution and 3.7% for 8 cm^{-1} resolution, so the choice of spectral resolution is a balance between speed and analysis quality. In this application, the speed is not an issue, since the entire wafer assembly can be measured in 3 h. As a result, 4 cm^{-1} resolution was used for all analyses.

Polyethylene homopolymer and ethylene/octene copolymers are semicrystalline in morphology. The crystallinity of the solid polymer decreases as the octene content increases. This is because the increase in octene results in an increase in the number of branches, which hinder the formation of highly ordered chains that can fold into polymer crystallites. The crystallinity of the solid also depends on the heat history of the sample. Fast quenching of the molten polymer can freeze the chain into a wide array of nonequilibrium geometries, preventing the formation of fully formed crystallites. Annealing at proper temperature allows slow formation and growth of crystals, resulting in a higher volume fraction of crystallinity. The crystallinity change will be reflected in the vibrational bands across a wide spectral region in the mid-IR spectra, especially for the C−H rocking bands around 730 cm^{-1} region and the C−H scissors around 1473 cm^{-1} region. The effect of annealing was studied, in particular, with respect to the CH_3 symmetric scissors vibration at ∼1377 cm^{-1}. The samples were annealed by heating the samples at 120 °C for 2 h, then allowing the samples to slowly cool to room temperature. The peak areas at the 1377 cm^{-1} peak of 31 samples that contained 0−16.5% of octene were analyzed before and after annealing. It was found that all peaks were reduced; however, the changes were quite small. The predicted mole percent of octene after annealing reduces by 0.1% on average compared with that before annealing. This study indicates that the heat history does not seriously affect the octene measurement when the 1377 cm^{-1} spectral region is used for octene quantitation. This small difference is probably due to the fact that in the standard deposition method, the solvent is removed slowly from the sample, and the polymer film is cooled slowly to room temperature. As such, the polymer has undergone a reasonable degree of annealing during this procedure.

The effect of sample volume was also investigated. This effect was studied with two sample volumes, 50 and 100 μL. The 100 μL of sample fills almost 2/3 of the well. It was found that a large portion of the sample coated the walls of the well while it was drying, leaving only part of the sample on the bottom. It was also found that the film thickness from the deposition of 50 μL and from the deposition of 100 μL was not significantly different. Measurements based on the 1465 cm^{-1} band showed the averaged peak heights of 31 samples to be 0.43 absorbance units (AU) with 50-μL deposition, and 0.44 AU with 100-μL deposition. One potentially serious problem associated with the loss of the sample on the side wall is that the polymer material that solidified first may contain material of a higher molecular weight (higher melting point) than the material solidified later. As a result, the polymer at the bottom of the well may contain lower molecular weight material. This type of redistribution of the polymer during drying could cause the problem that the IR spectrum does not accurately represent the full original sample. Further research efforts are aimed at developing a coating to reduce the wetability of the side wall by trichlorobenzene/polymer solutions.

Conclusions

This study has demonstrated that high-throughput FTIR transmission measurements using an array-based support formed using silicon wells and a silicon wafer is a very useful and robust tool for the characterization of polymer composition for combinatorial chemistry. The octene content in octene/ethylene copolymer can be measured accurately with a high throughput of over 300 samples/day (8 h). The transmission measurement is more robust, reliable and easier to automate than other IR spectroscopic methods. The support itself provides excellent resistance to aggressive organic solvents at elevated temperatures and allows the unattended deposition and preparation of polymer films for infrared analysis. Because of the excellent durability of the support with respect to the solvent, the support can be rinsed and reused many times.

This high-throughput approach to infrared transmission spectroscopy can be used for predicting a wide array of polymer chemical and physical properties: vinyl content, cis and trans unsaturation, geometrical isomers, crystallinity, and tacticity. In addition, infrared bands appear in the carbonyl stretching region (1700−1600 cm^{-1}) when the polymer has undergone oxidative degradation after a significant time heating plate at 150 °C in air. As such, this method of carbonyl band quantitation could be used to predict the oxidative stability of the antioxidant packages.

Future Work. New high-throughput analysis tools continue to be developed in order to provide the maximum amount of information about the polymers being produced in the parallel reactors. Physical properties of the polymers produced, such as modulus, toughness, or impact strength, are highly desirable measurements because they reveal information about the morphology and the uses to which the material could be applied. High-throughput nanoindentation can be used for these types of measurements, but the method requires a stiff, highly polished surface for the probe tip to produce reliable results. Future research in the area of high-throughput analysis is now focusing on the use of the wafer assemblies described here for deposition and subsequent fully automated nanoindentation methodologies for the prediction of physical properties.

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