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Polycarbonates from Cyclohexene Oxide and Carbon Dioxide

$$\text{[cyclohexene oxide]} \xrightarrow[\text{catalyst}]{CO_2} \text{ALKYL POLYCARBONATE}$$
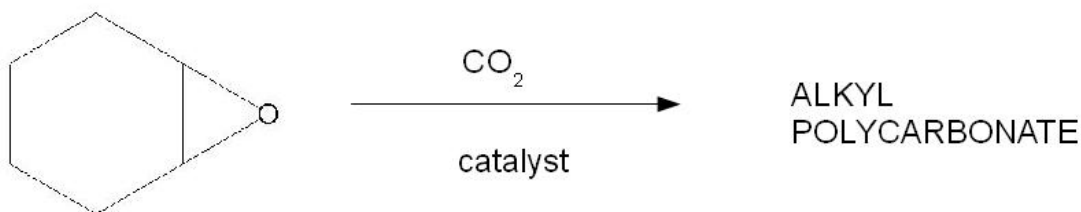
The manufacture of polycarbonates by polymerization of cyclohexene with carbon dioxide has been a topic of research for some time. The work described here uses a proprietary catalyst. CO_2 was bubbled through the heated cyclohexene for 16 hours, and the reaction was monitored using a ReactionView system with a ZnS ATR crystal.

Real-time data in the mid-IR spectrum allows us to follow the reaction as it unfolds, and can give immediate warning if something goes wrong. For example, during a preliminary run in our lab, the CO_2 supply was unexpectedly compromised. The problem was immediately apparent from the spectra, when the signal from dissolved CO_2 disappeared, and remedial action was taken.
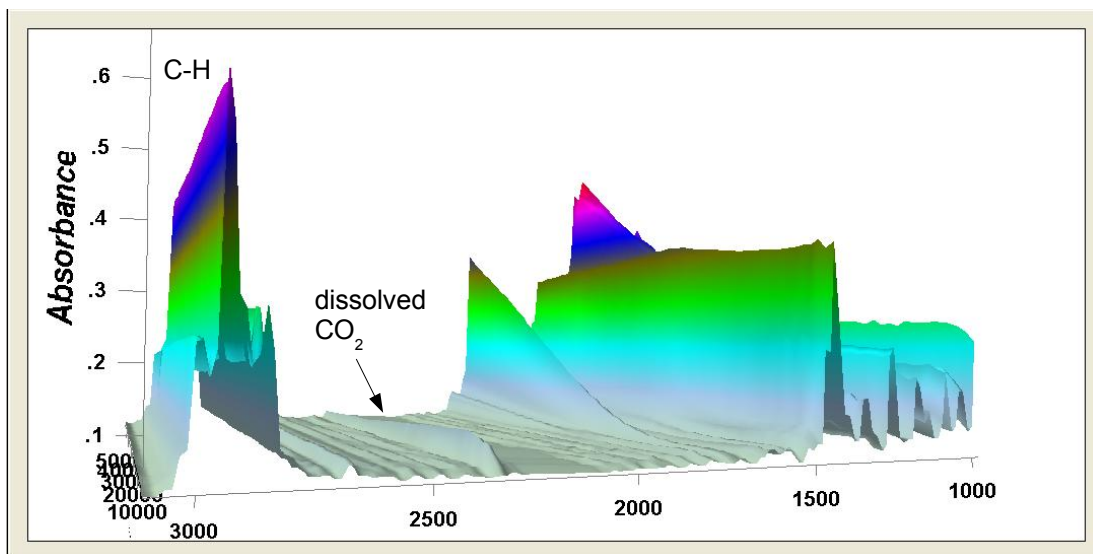
The 3D display of the ReactionView data from the completed reaction is shown here. There are three distinct regions:

- The C-H stretches between about 3000 and 2800 cm^{-1} are not usually very informative.

- The dissolved carbon dioxide appears at 2342 cm^{-1}. It is an isolated signal and provides a useful check on the reaction conditions. In this case, the CO2 concentration rises initially as the reactor is pressurized, then slowly drops as the reaction progresses. This may reflect a change in CO2 solubility as the cyclohexene oxide concentration drops.

- The region below 2000 cm^{-1} is information-rich, and provides detailed spectroscopic information about products and intermediates.
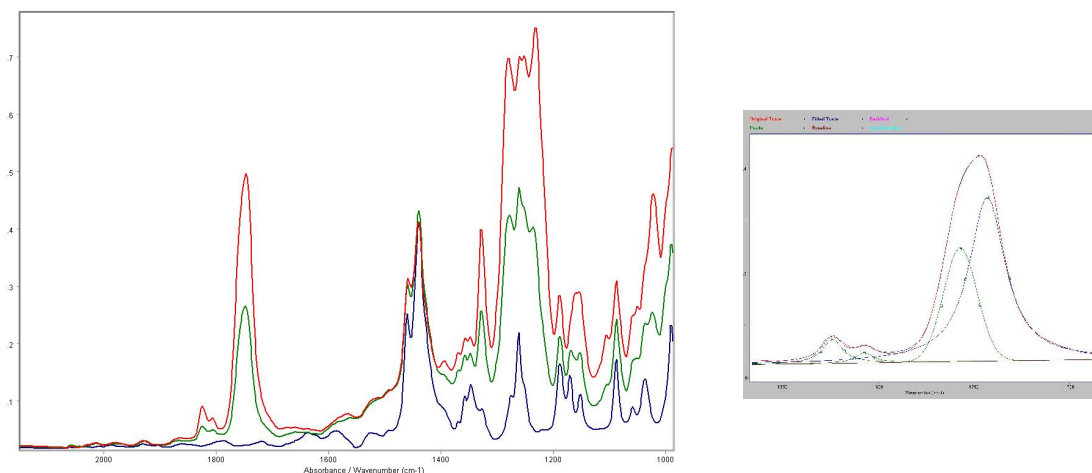
When the starting and ending spectra are overlayed with a spectrum from the middle of the reaction, it is clear that significant changes take place in the "fingerprint" region. In particular, an organic C=O feature near 1740 cm⁻¹ emerges as the reaction progresses. Close examination shows that this feature is not symmetrical. A peak-fit model can be built using two slightly displaced symmetrical peaks.

By fitting the model against each spectrum in turn—either in real time or in post-processing—it is possible to generate a trend line of peak height versus time for each peak in the model.
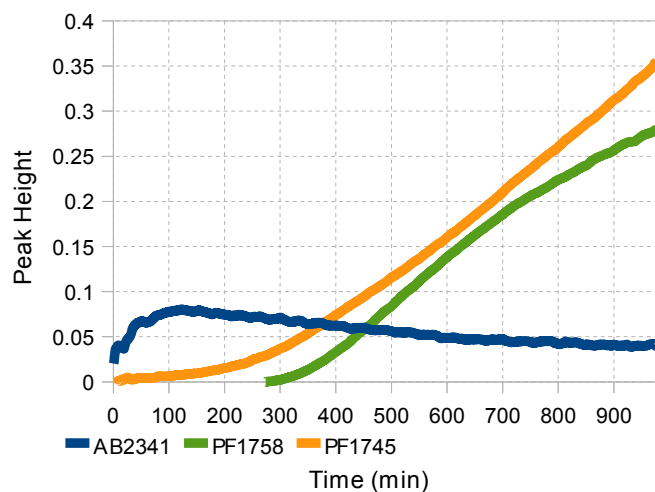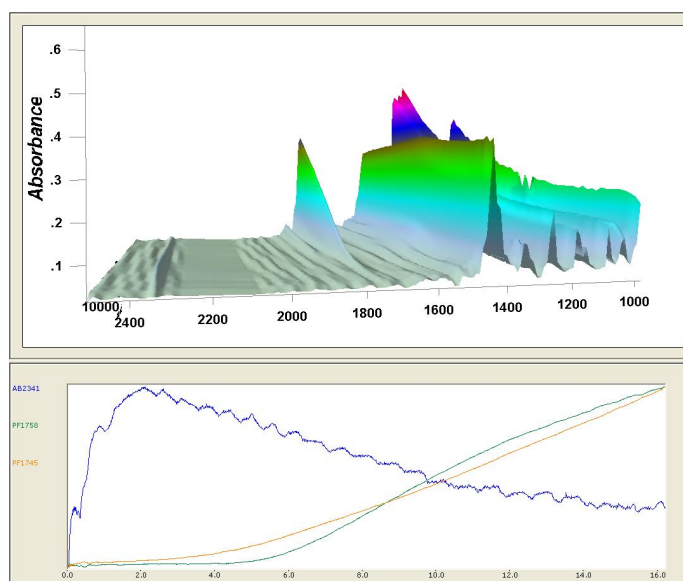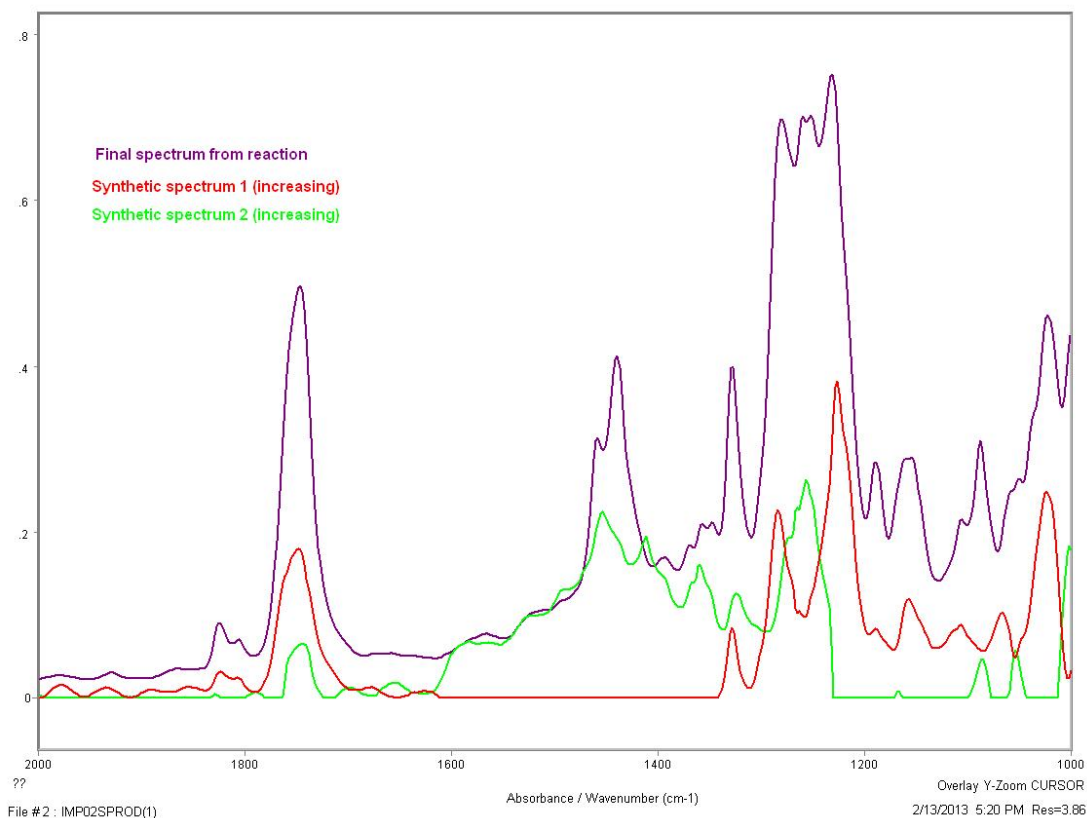
When the peak-fit model is graphed against time, it emerges that the two carbonyl peaks are associated with two slightly different reaction profiles. Here, they are displayed with a simple peak-height graph of the dissolved CO2 peak in an autoscaled display.

All of the calculated trend lines can be imported into a spreadsheet. They can be used to estimate relative reaction rates, even if fully quantitative calibrations are not available.

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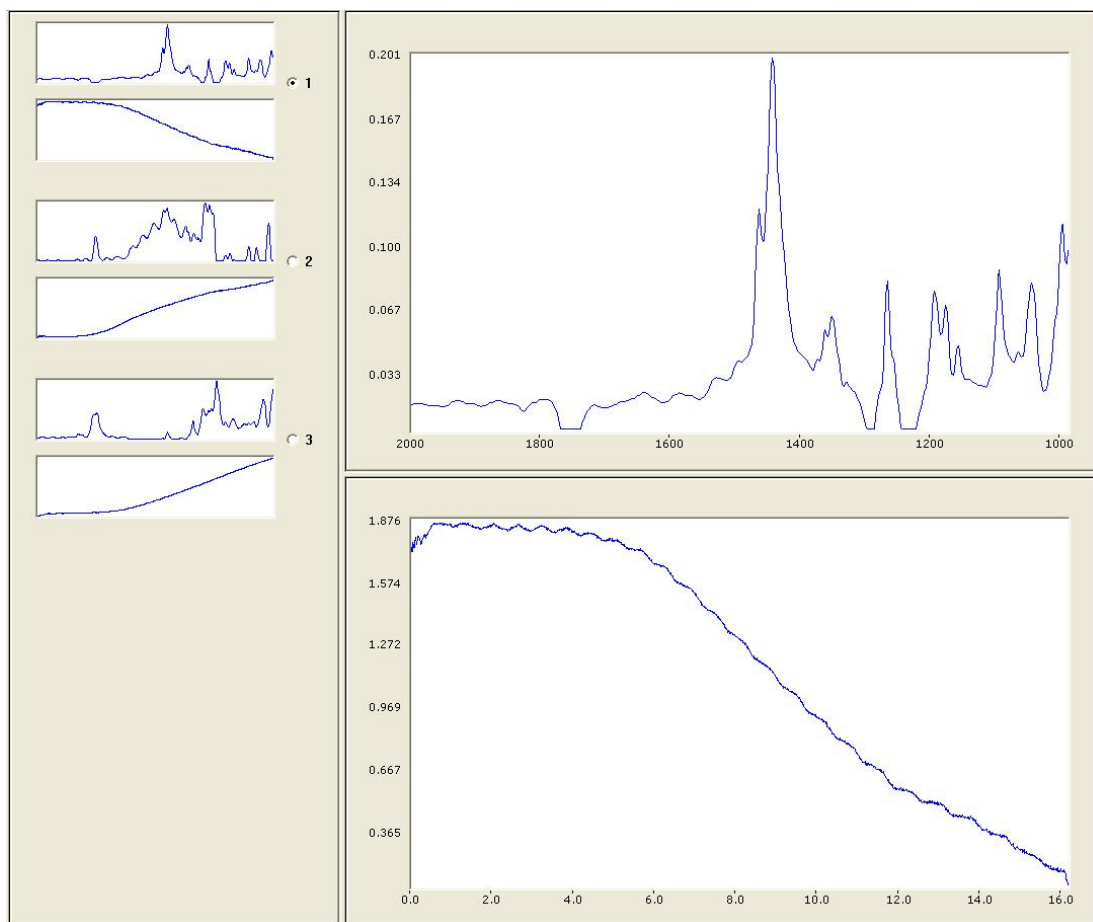
Remspec's ReactionSleuth™ software includes the ability to calculate "synthetic spectra" from complex data sets using a PCA/Target Transform method. The data from this reaction can be modeled successfully using three synthetic spectra, which are shown here with their calculated trend lines. The trace shown in the principal window matches the cyclohexene oxide starting material very well.

Final spectrum from reaction
Synthetic spectrum 1 (increasing)
Synthetic spectrum 2 (increasing)

File # 2 : IMP02SPROD(1)

Absorbance / Wavenumber (cm-1)

Overlay Y-Zoom CURSOR

2/13/2013 5:20 PM Res=3.86

When the two synthetic spectra that have product-like trend lines are overlayed with the the final spectrum from the reaction, it becomes clear that the the reaction product spectrum is a mixture of the two synthetic spectra.

Only a few minor features, like the small double peak near 1810 cm^{-1}, can be unambiguously identified with a single product. In cases like these, the ability to calculate spectra by the PCA/Target Transformation procedure can be very valuable.
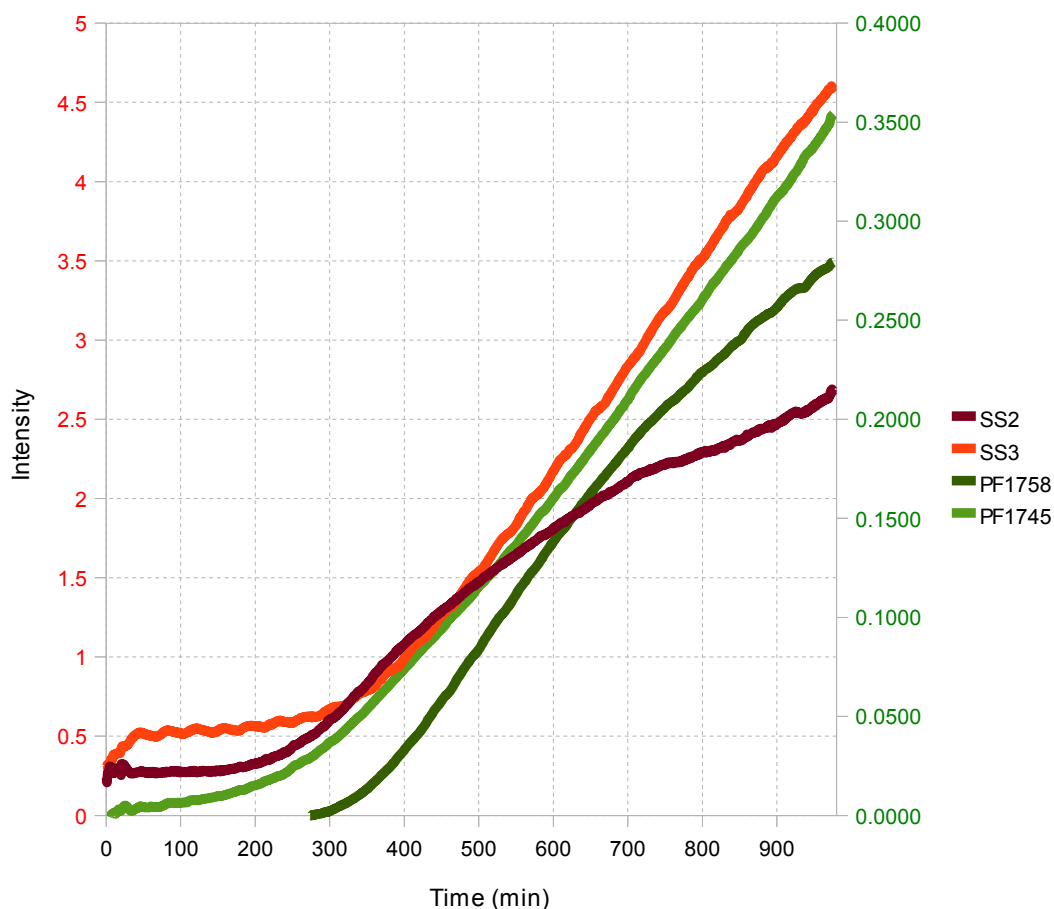
When we compare the "loadings", or trend lines, for the synthetic spectra (SS2 and SS3 above) with the trend lines for the two carbonyl peaks that were modeled, some similarities are obvious. SS3 and the peak at 1745 cm^{-1} both show essentially linear growth over time. SS2 and the peak at 1758 cm^{-1} exhibit more complex behavior.

Since the synthetic spectra loadings are mathematical constructs calculated in arbitrary units, there is no direct way to calibrate them quantitatively. The peak height from the peak model can be calibrated by measuring spectra from standard samples , if available.

The synthetic spectra are useful for characterization and identification of compounds (they are saved in spc format and can be run against spectral libraries), while the peak-fitting method is more suitable for quantitation.

Conclusions

- In-situ mid-IR spectroscopy with ReactionView® opens up a chemical "eye" inside a reactor to measure reactants like dissolved carbon dioxide, and products, directly and in real time.
- Problems with reactant feed can be picked up immediately.
- Real-time tools like peak fitting of emerging features allow for tracking of different products.
- Synthetic spectra of the products can be calculated in post-processing and correlated with the calibratable peak height measurements.

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