

Improving slurry polymerization using in-line Raman Spectroscopy

Direct and fast visibility into reaction dynamics for earlier and more confident decisions

Agenda



The Technology - Raman Spectroscopy



The Application – Polymerization of Ethylene



Benefits using Raman for Polymer conversion

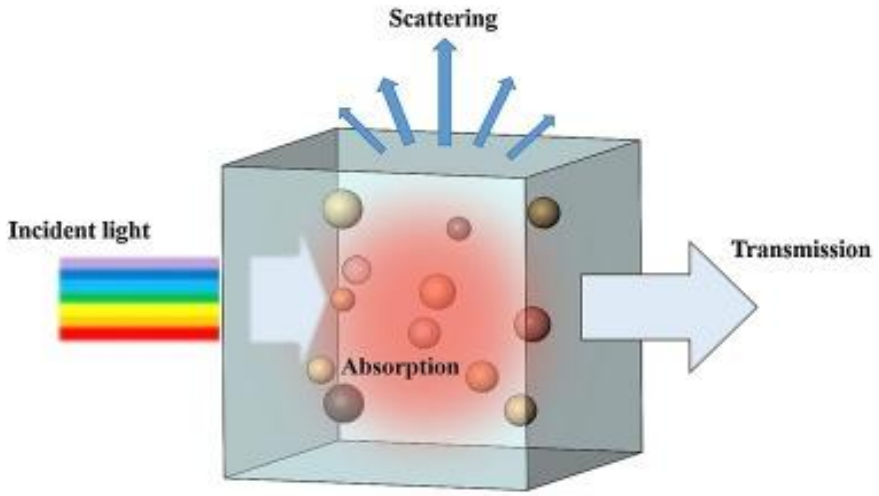


Q&A

Endress+Hauser

There are different interactions between light and matter

- Most of the light shines though (Transmission)
- Some light is absorbed (TDLAS)
- Some light is **scattered** (**Raman**)



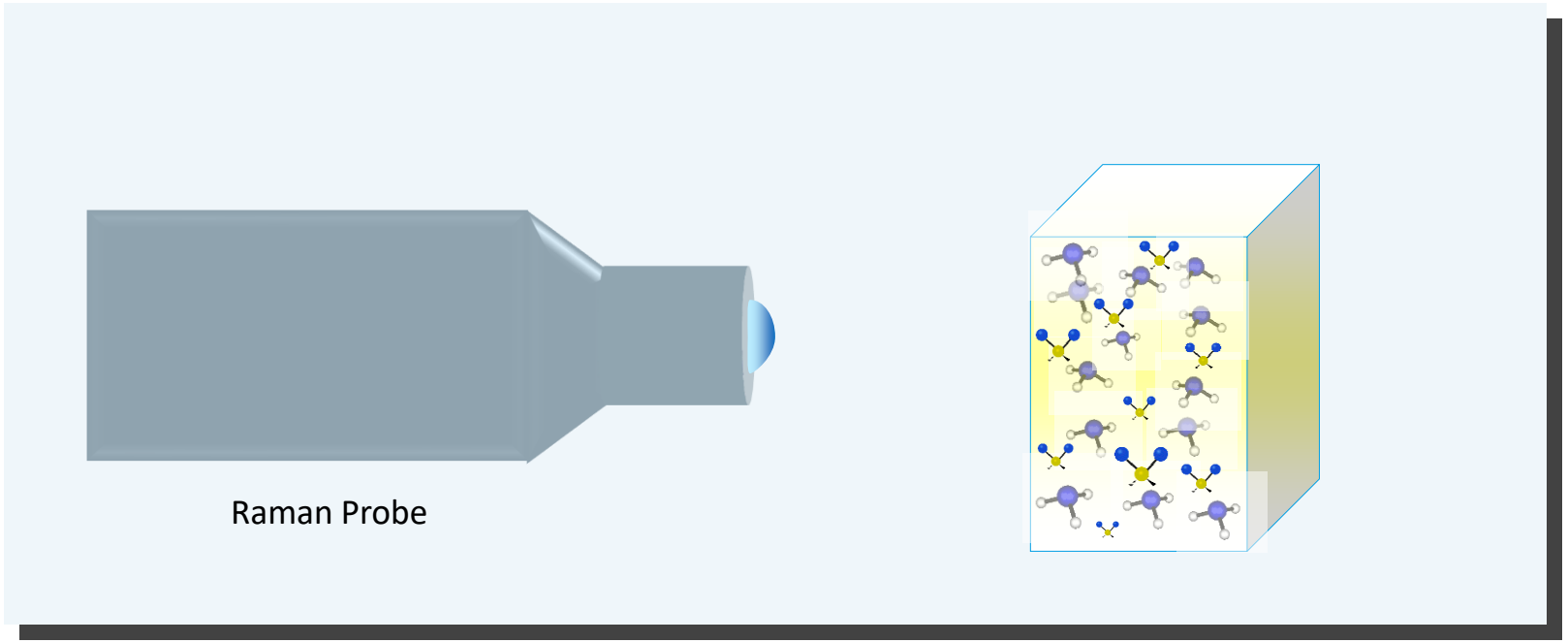
Raman's discovery:

- Light can transfer energy to molecules activating **molecular vibration.**



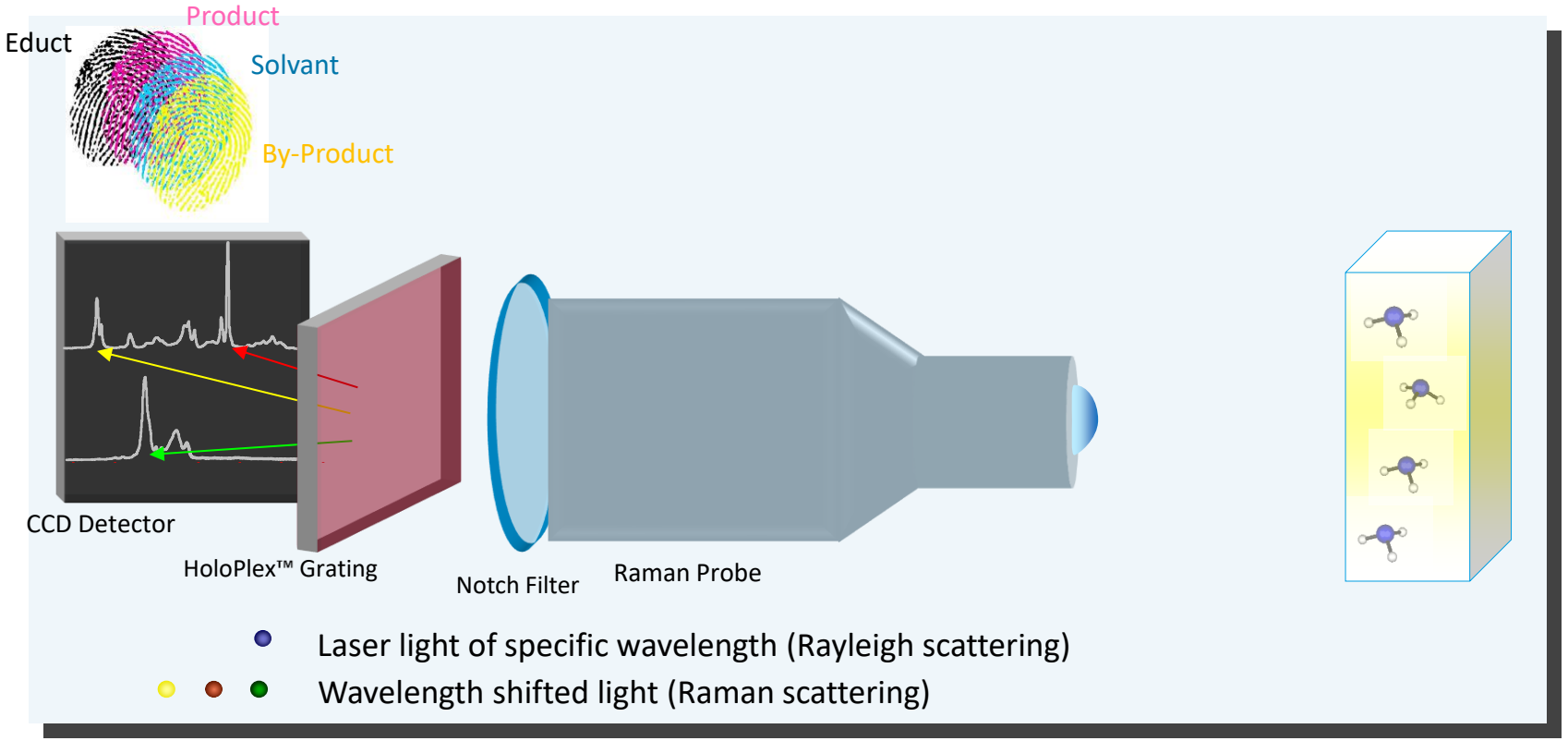
Raman : Laser Light is emitted - Excitation

- **Light** of specific wavelength (532, 785, 980…) interacts with molecules (**scattering**)
- A number of scattered photons are shifted in wavelength due to specific energy transfer (Raman shift)
- Result: Scattered Raman photons allow **identification & quantification**



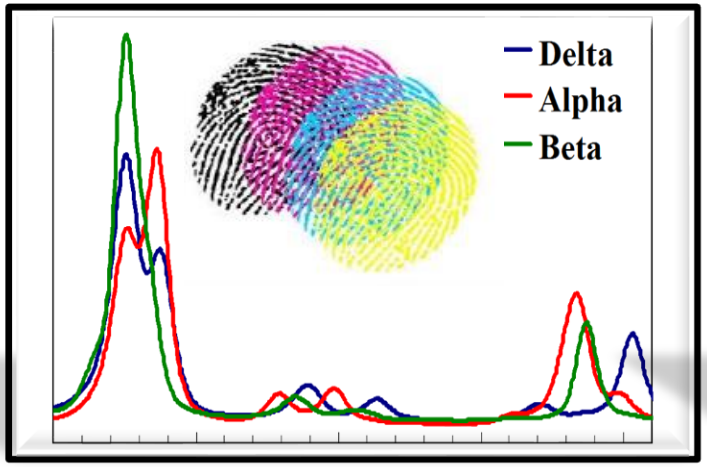
Raman Technology: Photon Collection

- Only back scattered photons are collected
- Notch® Filter filtering out original laser light
- Simultaneous diffraction through HoloPlex® Grating
- Raman photons are simultaneously detected on CCD detector

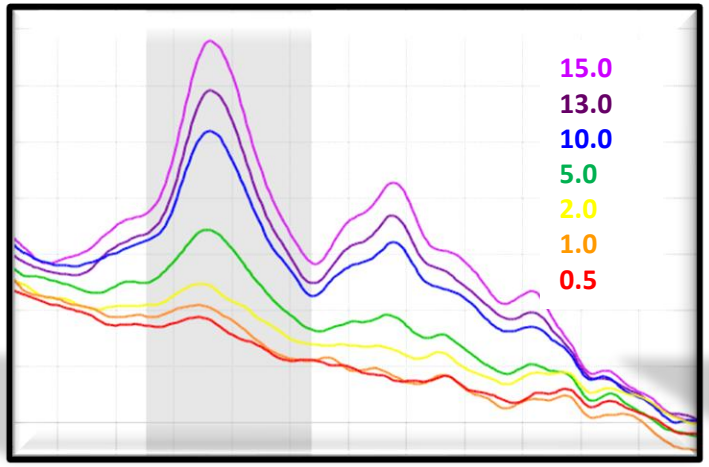


Raman spectra from a lab sample or process can tell us…

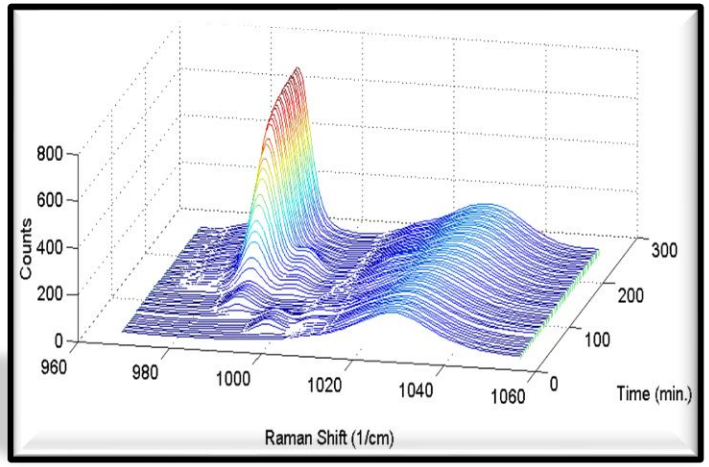
What is it?



How much?



Has it changed?



Endress+Hauser

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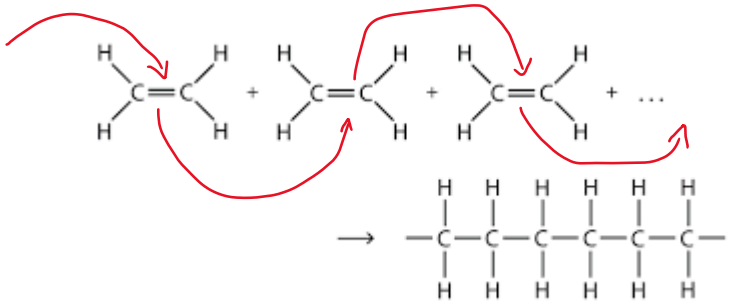


Q&A

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Polymerization of olefins

Monomers like **Ethylene** or **Propylene** are bonded together to form polymers – **Polyethylene** and **Polypropylene**



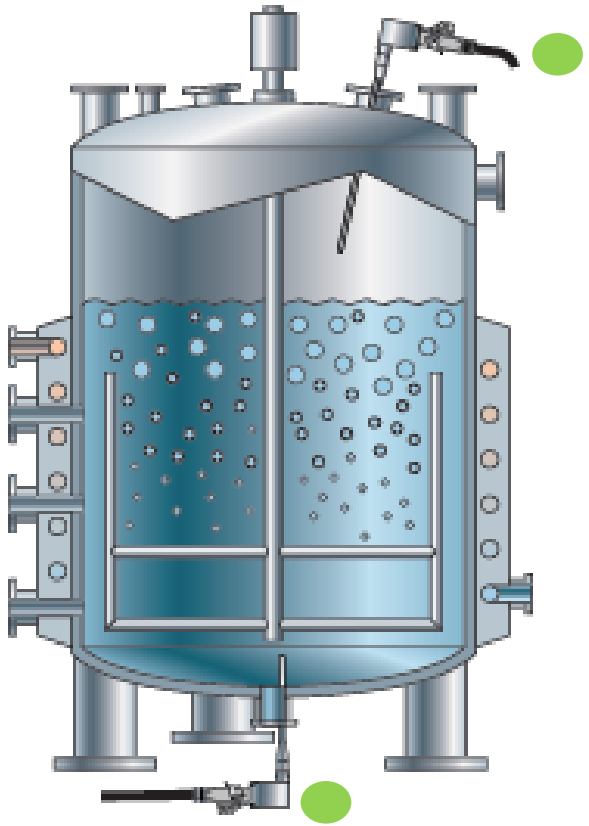
- **Addition polymerization**:
  - Monomers add to each other without the loss of any small molecules.
  - Catalysts, Temperature, Pressure and additives (like H_2) **control** the polymer structure, chainlength & properties

- Applications
  - **Plastics**: in packaging, containers, and various consumer goods.
  - **Fibers**: in textiles and industrial applications.
  - **Elastomers**: in rubber products and flexible materials



The process

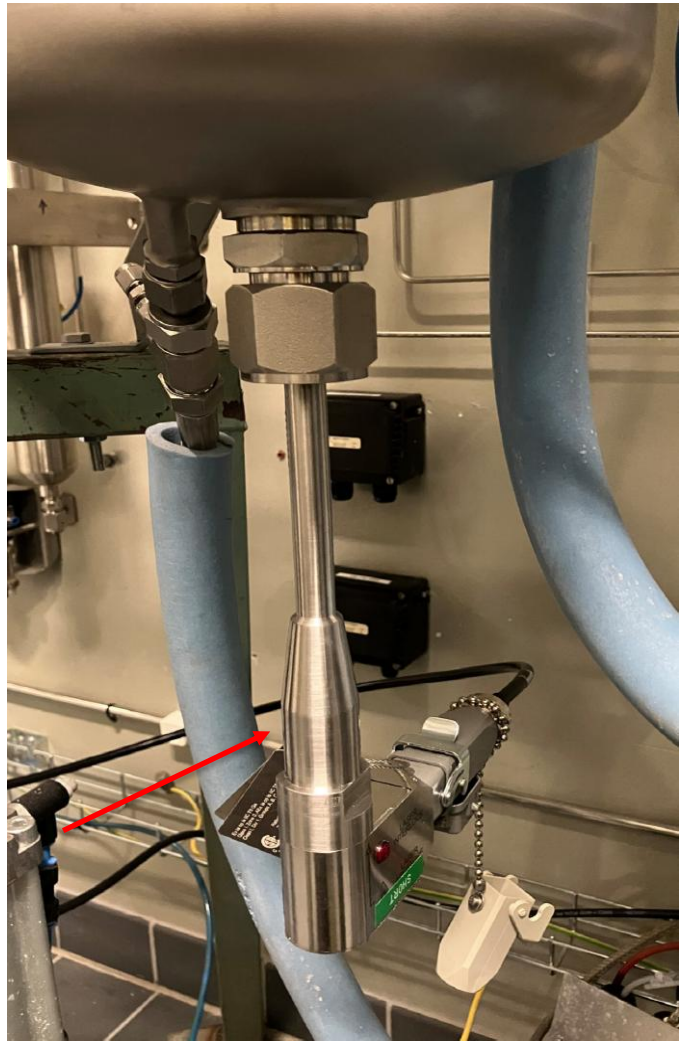
Raman Rxn-40: ***Gas Phase*** probe



Raman Rxn-40 probe: ***Liquid Phase***

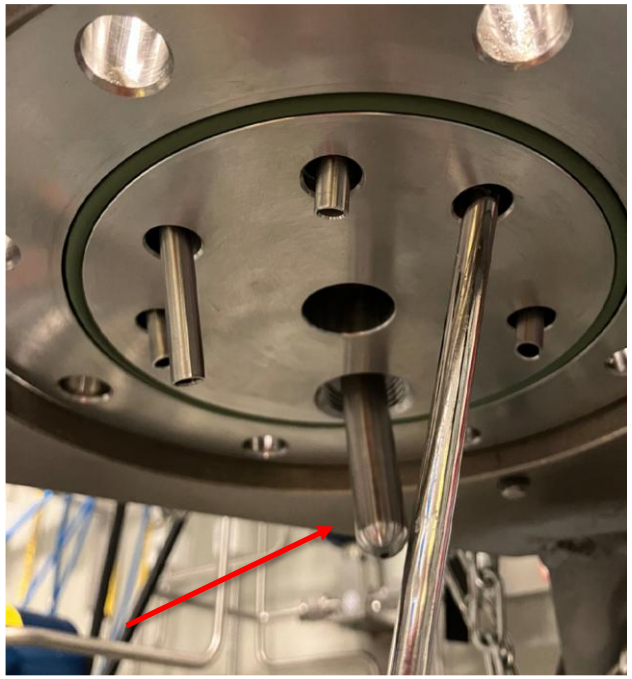
- The reactor is filled with liquid propane
- Dry Ethylene Gas is added to the reactor top
- Hydrogen is added for molecular weight control, together with diluent and catalyst.
- **Goal**: Monitoring the **H_2 consumption** and **formation of the polymers**
- Slurry polymerization conditions are evolving during the reaction
  - temperature gradients ~Δ 60° C
  - Increase of solid polymer content

The solution in real conditions



- ATEX Raman probes immersed in a lab-scale reactor
- 25m of fiber cable running from probe to analyser
- Raman analyser located in a control room connected to DCS by OPC





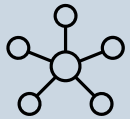
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Challenges: In slurry polymerization, critical variables are not visible in real time



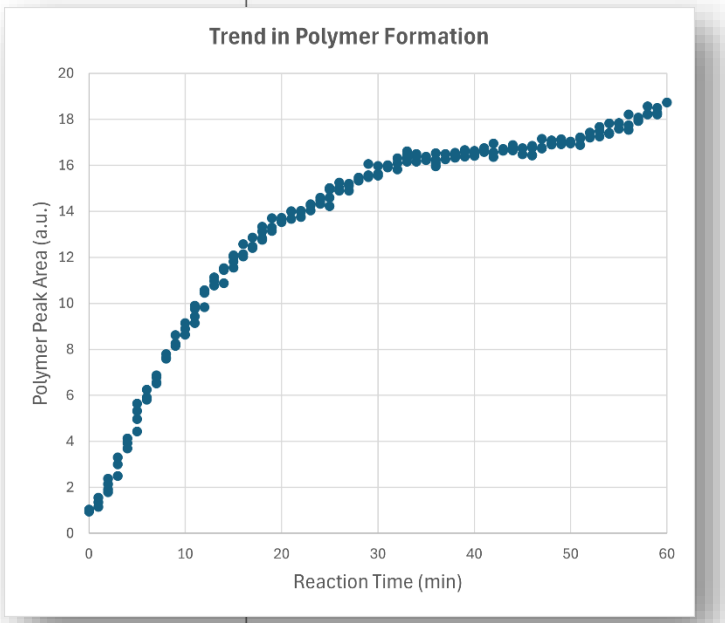
What do we need to see to make better decisions?

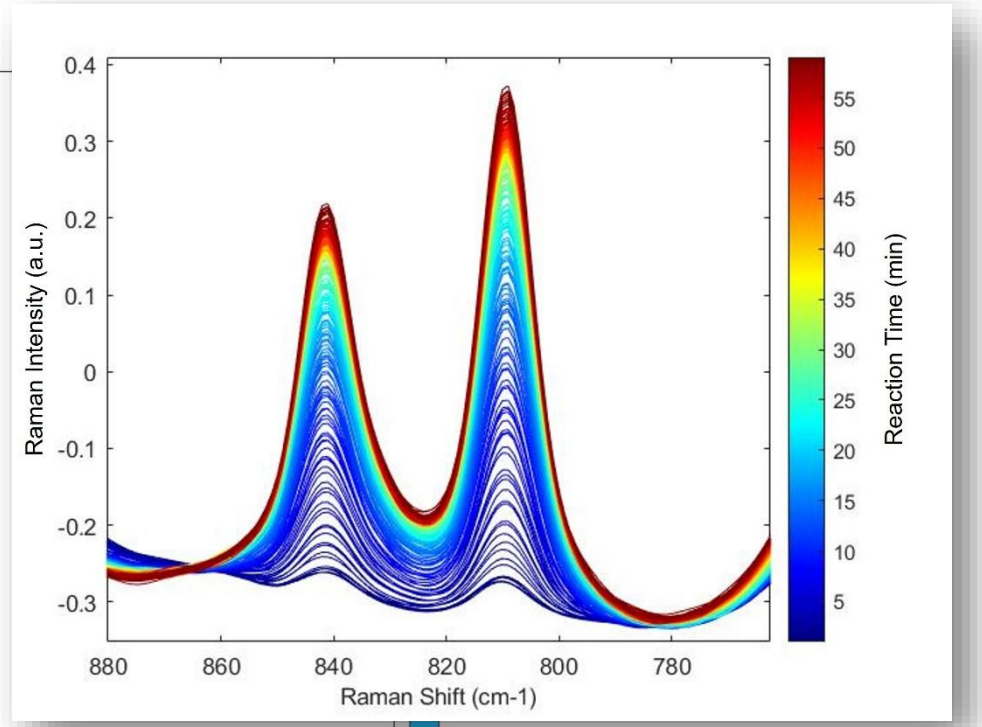
- **Monomer consumption rate**
- **Onset and speed of polymer formation**
- **Hydrogen effectiveness**
- **Deviation during transitions**
- **Distribution of reactants in the reactor**

If visible in real time, teams could:

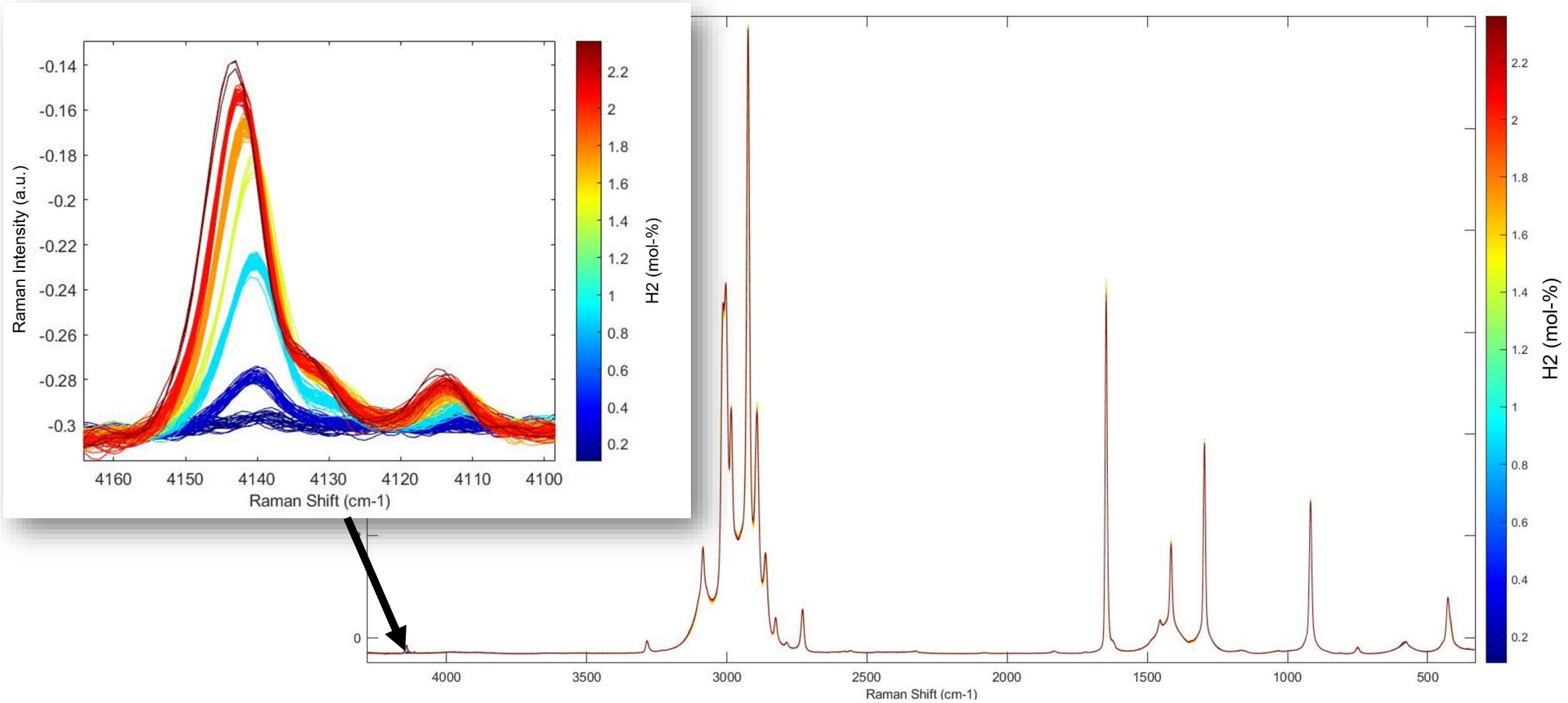
- Act earlier on reaction trajectory
- Control product properties before they drift
- Stabilize startups and transitions faster
- Correct while the product is still adjustable, rather than handling off-spec product after the fact

Raman spectra monitoring polymer formation within 60 minutes





Raman spectra with different H_2 concentrations during polymerization



Endress+Hauser

Raman spectroscopy reveals previously inaccessible information in slurry reactors



What do we see to make better decisions?

- Detect **early kinetic slowdowns**, accelerations and **when polymerization actually starts,** and how fast it evolves
- Distinguish normal degree of polymerization **from abnormal behavior** (e.g., fouling precursors or runaway paths)
- Correlate **hydrogen behavior** with **polymer growth dynamics**
- Identify small but **coherent deviations** that signal **upcoming quality issues**.



When would earlier insight change your decisions?

- *During startups*: acting on feeds, or catalyst **without confirmed reaction kinetics**
- *During transitions:* continuing a grade change **before trajectory drift becomes visible**
- *During early phases:* yield, molecular weight, or quality **locked in before confirmation**

The earlier you see, the earlier you decide, saving time, energy, and off-spec output



Customer benefits

Real-time, non-destructive measurements in a slurry for process characterization and feedback control

Slurry polymerization
a very fast (within an hour) multi-phase mixture reaction

monitored in real time with Raman spectroscopy in an ATEX environment → non-achievable with traditional techniques like GC	sensitive to monitoring inline monomer addition, polymer formation and H_2 addition – even low-level	estimating the melt flow rate (MFR) governing the physico-chemical properties such as viscosity

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