Application Note

Novel Silicone Synthesis

Via Precisely Controlled Polymerization

Based on work presented by **Dow Toray Co., LTD**

In-situ Raman reaction monitoring affirms targeted chain length is achieved

For a wide range of industries, silicone's diverse properties enable companies to design products with specific, fit-for-purpose characteristics. These products exploit the varied properties of silicone rubbers such as strength, thermal resistivity and stability. Typically, silicone is produced via hydrolysis of a chlorosilane followed with a terminal functional group addition (figure 1a), or through polycondensation of a cyclic siloxane (figure 1b). Each of these methods are equilibrium reactions that produce low-molecular-weight products with a wide range molecular weight distribution.

Dow researchers have developed an alternate means of producing silicone, based on a precisely controlled polymerization, to yield product with targeted, uniform chain lengths (figure 2). In this synthesis, a lithium-based reactant serves to open a cyclic tri-siloxane ring, followed by addition of another cyclic siloxane reagent, to yield a monodispersed silicone polymer.

Gas Chromatography is the traditional means of tracking silicone polymerizations, but due to the kinetics of this Dow Toray silicone synthesis, a new analysis method was required. Time delays associated with the offline G.C. method resulted in polymer chain length information only becoming available after the synthesis was complete. Therefore, the researchers wished to determine if in-situ Raman analysis of this fast reaction would provide actionable feedback on the polymerization and affirm that the targeted silicone chain length is achieved. Other benefits of in-situ Raman analysis include the elimination of potential errors associated with offline analysis such as irreproducible sampling of an increasingly viscous polymer reaction, and the need for sample pretreatment before injection into a GC.

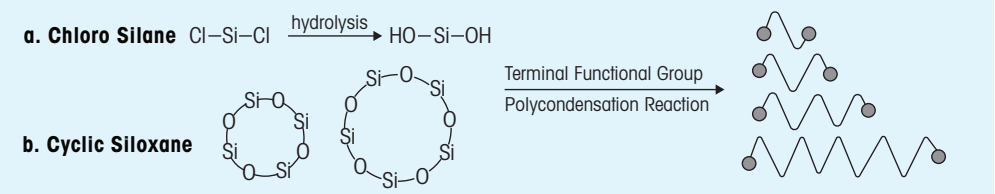

Figure 1. Conventional method to produce silicone

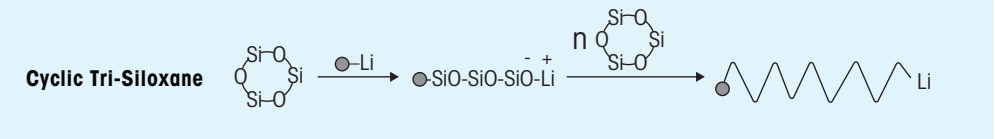

Figure 2. Silicone production based on precise polymerization

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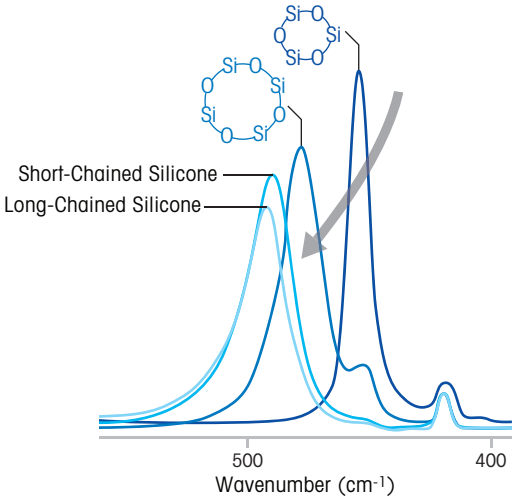

Figure 3. Raman spectra overlaid at increasing points in time of the reaction. Arrow indicates the peak shift of Si-O-Si as a function of increasing polymer length and time.

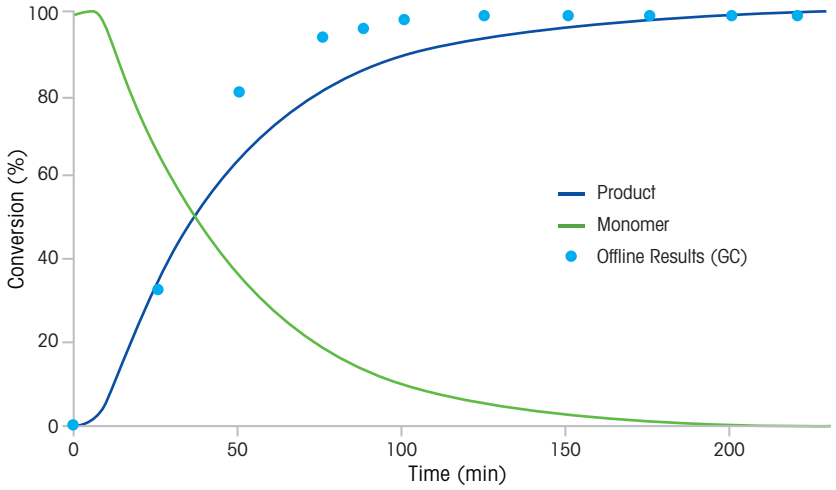

Figure 4. Raman trend profiles for Product and Monomer. Offline GC samples to validate the Raman measured results.

Results

A ReactRaman, in-situ Raman spectrometer, equipped with an optical fiber probe was used for investigating this new silicone synthesis. The ability of ReactRaman to distinguish the key molecular species in this polymerization reaction is evidenced by the shift of low frequency peaks in the spectra of cyclic siloxanes and polymeric silicone (figure 3). Notably, as the chain length increases, the Si-O-Si peak shifts to higher frequency, and thus can be used as an immediate indicator for reaction initiation. By in-situ Raman tracking of the Si-O-Si band in the silicone product (figure 4), reaction progress and reaction completion are readily determined. This provides real-time feedback to prove that the targeted silicone chain length is achieved, eliminating the need to use offline analysis.

Conclusions

This novel silicone polymerization, which results in monodispersed product with precisely controlled chain lengths, is readily tracked by ReactRaman, eliminating the delays and reaction uncertainties associated with off-line GC analysis. Reaction initiation, progress and kinetics are all readily measured by the Raman method, providing continuous, real-time verification that the reaction is proceeding as expected.

ReactRaman™

Application of ReactRaman include:

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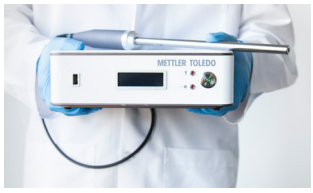
- Polymorphism
- Polymer Synthesis
- Hydrogenation
- Bioprocess Monitoring
- Biocatalysis



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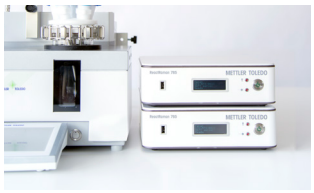

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