Monitoring Laboratory Scale Polymerisations

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Monitoring polymersiation reaction can be laborious, many of the analytical techniques used require sample preparation and long run times. Even using a spectroscopy technique with an immersion probe can have issues with probe fouling. Using a handheld Raman with Standoff capabilities can elevated the forementioned problems and give real time data though the reaction vessel walls, even when the reaction is at high temperature and under vacuum.

Objective

To track HMW polymer reactions in situ, through the walls of a double walled flask under vacuum and measure the decrease in free monomer throughout the reaction to a concentration of approximately 1%.

Equipment

The Metrohm Mira DS Raman spectrometer was coupled with the Standoff attachment, which is designed to allow the user to collect data from a substance 0.25 to 1.5 meters.

Mira DS 785	
Laser (excitation wavelength)	785 nm ± 0.5 nm
Laser Output Power	100 mW, 50 mW at sample, 5 adjustable laser powers down to 10 mW
Wavelength Range	400 to 2300 cm^{-1}
Spectral resolution	8 to 10 cm^{-1} (FWHM) across range
Collection Optics	5 mm working distance; 0.04 spot size, 2.5 mm raster size
Collection Techniques	Orbital Raster Scan (ORS™) to average over the sample
Exposure	Automatic modes (100 ms minimum)
Battery	2 AA Batteries, Lithium ion, >4+ hours operation
Weight	0.705 kg
Size	88.2 x 126.5 x 45.3 mm
Operating Temperature	-20 °C to +50 °C (continuous)
Ruggedization	MILSPEC 810G, IP67 Certified
Display	High visibility, glove compatible, color touch screen
Security Log in	PIN Code
Measurement Accessories	3 Position Point and Shoot, Right Angle Adapter, Cal Standard
Laser Class	Class 3B
Compliance	CE certification

Figure 1: The Metrohm Mira DS Raman spectrometer.

Experimental

The system was mounted on a tripod with the Standoff attachment positioned 0.25 metres from the interior of the reaction vessel focussed on the polymer.

Figure 2: The Standoff attachment.

Figure 3: The experiment set up.

Acquisition Parameters

Integration time	6 seconds
Laser Power	50 mW (full power)
No. averages	3
Working Distance	0.25m

The polymerisation reaction was carried out under vacuum for the purpose of monitoring the monomer conversion over time. Hot oil is circulated through an internal jacket sandwiched between the inner and outer walls of the vessel. Reaction temperature 160ºC.

Figure 4: The lab scale 4Kg reaction vessel.

The challenge for the instrument was to gather representative spectra through 2 glass walls and the circulating hot oil layer.

Standards

A series of standards were prepared in the HMW polymers and firstly scanned in glass cuvettes on the Mira DS. From this it was demonstrated that progress of the reaction could be followed by monitoring the reduction in the peak heights of the peaks at around 700-740cm^{-1} as shown in the adjacent plot.

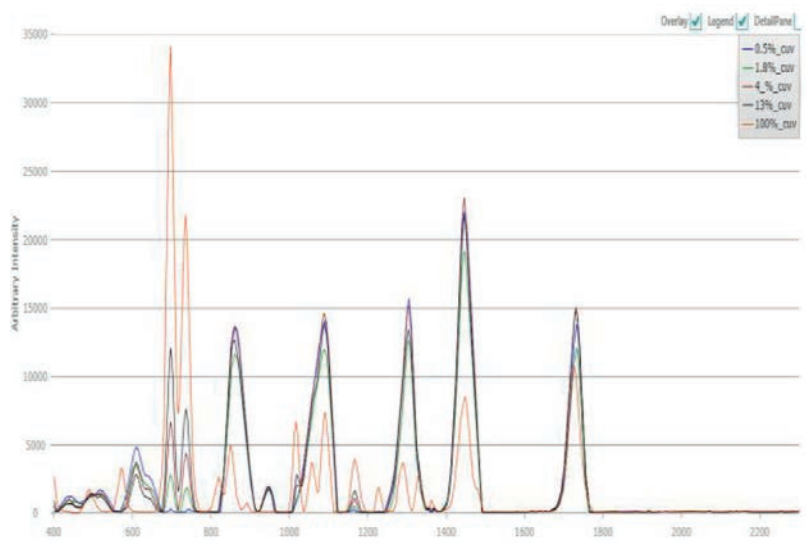

Figure 5: Monitoring the progress of the reaction.

Results

Reaction Progress – Flask

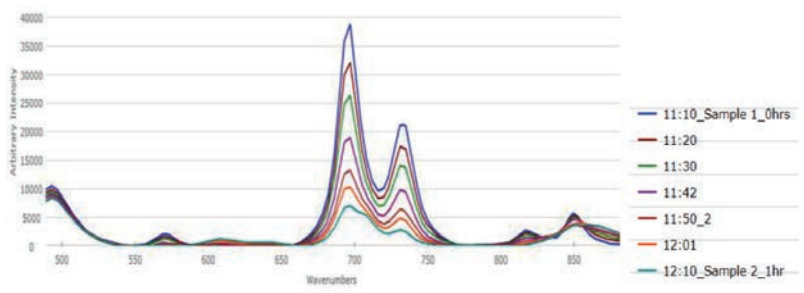

Figure 6: Spectra results in 1st hour.

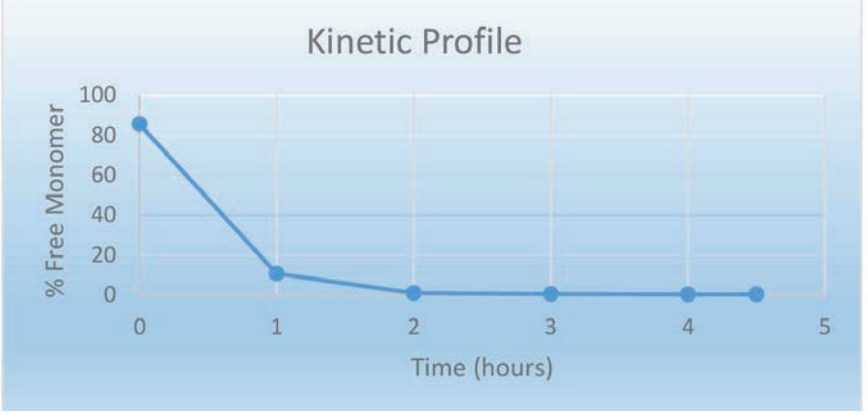

Figure 7: Reduction in monomer peak height at 700-740cm^{-1} v's time follows closely the kinetic profile of the reaction as shown above and in Table 1.

Table 1

Sample	Time (hr)	Visc @ 180°C & 10Hz	Monomer %	Peak Height
1	0	Liquid	85.6	38893
2	1	109.4	10.7	7088
3	2	412.5	0.92	4130
4	3	450.7	0.39	4007
5	4	481.4	0.28	4007
6	4.5	439.8	0.27	3995

The reaction proceeded quickly due in the main to good sparging, with the peak height being reduced significantly in the first hour of polymerisation. This was subsequently mapped using GC results from the grab samples taken over the 5 hour time period.

Conclusion

The Metrohm Mira DS hand-held RAMAN spectrophotomer successfully provided rapid, in-situ, real time analysis of the HMW polymer bench top reaction, through the wall of the flask, down to at least 1% monomer.

Using the RAMAN would eliminate the need to:

- release the vacuum and re-apply the vacuum in order to collect test samples (can be troublesome and take some time with HMW grades).
- dissolve a sample for testing (which can take around an hour),
- perform a GC analysis (which can potentially damage the syringe and contaminate the injector)

A massive time saving over the current methodology coupled with data in real-time.

Additionally, analysis of molten HMW in cuvettes using this method could also provide a faster result for free monomer in physical samples and could potentially eliminate the need to perform a GC until the reaction is complete.