INTEGRITY Application note: A02-004A

The Online Monitoring of a Gas/Liquid Reaction.

Introduction

For more than 70 years the condensation reaction products of melamine and formaldehyde have been used in technical applications. In 2004 formaldehyde was declared a carcinogen and therefore it was necessary to find alternative ways to produce melamine based macromolecules. A very interesting approach is the radical polymerization of melamine monomers containing a double bond. Vinylation with acetylene at atmospheric pressure is a very simple way to get these monomers in high yield. The reaction works at temperatures from 80°C up to boiling temperature in a superbasic system containing dimethyl sulfoxide or *N*-methyl pyrrolidone as the reaction solvent and potassium-*tert*.-butoxide as the catalyst. Figure 1 shows the reaction scheme of the vinylation of pentamethyl melamine where one vinyl group can be added.

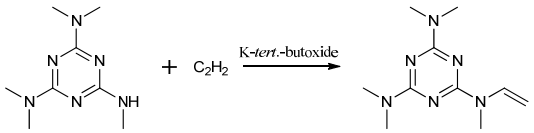

Figure 1: Vinylation reaction scheme

Working with a highly reactive gaseous reagent in the laboratory leads to several problems. In the experiments two specific instrumental problems with heating and stirring were observed. Due to the injection of the gas it was difficult to get accurately defined reaction temperatures, both in the constant and gradient temperature experiments. Furthermore, stirring is known to have a big influence on the dispersion of gas in the solution and therefore this variable needs to be accurately controlled. Additionally, there are analytical problems during the reaction. Generally identification and quantification of the educts and products with gas chromatography and mass spectrometry works very well but as first indications showed that the reaction starts very fast, on-line monitoring of the reaction would allow a lot of additional information about the conversion and reaction kinetics to be determined. Therefore it was necessary to find additional analytical techniques and equipment. It was decided to perform the experiments using an Integrity 10 STEM Reaction Block from Electrothermal as this instrument allows the user to accurately define the experimental reaction conditions. A Thermo Scientific Antaris FT-NIR instrument was used to collect on-line NIR spectra.

Experimental Methods

An Integrity 10 STEM Reaction Block from Electrothermal was programmed with reaction conditions between 50 and 130°C and stirring speeds between 500 and 1000rpm. The reaction temperature was monitored and controlled using the optional in-situ temperature probes to ensure that inaccurate temperatures, caused by the cooling effects of the added gas, were avoided. During all reactions NIR spectra were collected with a Thermo Scientific Antaris FT-NIR instrument. The analysis conditions used were: scan range 4000-10000cm^{-1} using 8cm^{-1} resolution with 15 scans averaged giving an analysis time of approximately 10 seconds. Each spectrum was automatically integrated using characteristic peaks.

Several temperature screening experiments were performed at temperatures between 70 – 130°C, with catalyst concentrations between 10 – 30 %(w/w), in order to get information about the ideal starting temperature and optimum catalyst concentration of the reaction. Further experiments were performed to show the conversion of the reaction at constant temperatures as a function of time. Additional experiments were performed where different concentrations of the starting material (pentamethyl melamine) were used. The following examples describe two experiments in detail. The rest of the experiments were done in a similar way with varied reaction parameters.

Example 1:
2g Pentamethylmelamine and 0.2g potassium-*tert.*-butoxide 10%(w/w) as catalyst were dissolved in 10ml dimethyl sulfoxide. Acetylene gas was bubbled through the solution, stirring

speed set to 500rpm and the temperature increased from 70 to 130°C at 1.5°C min^{-1}.

Example 2:
1g Pentamethylmelamine and 0.33g potassium-*tert.*-butoxide 30% (w/w) as catalyst were dissolved in 10ml *N*-methyl pyrrolidone. Acetylene gas was bubbled through the solution, using a stirring speed of 1000rpm. The temperature was held at 100°C for 83 minutes.

Results

Figure 2 shows the typical NIR spectra recorded at the beginning and end of the reaction. By integrating the peaks of the methylamino (6800cm^{-1}) and the vinyl group (6200cm^{-1}), the conversion of the reaction could be determined at any time.

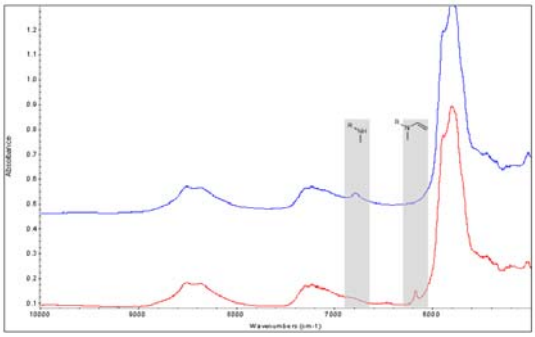

Figure 2. NIR spectra at the start (blue) and the end (red) of the reaction.

Using both pieces of equipment, the Integrity 10 STEM Reaction Block and the Antaris FT-NIR, it was possible to determine the best reaction parameters and the dependency of the conversion on the reaction parameters. The minimal starting temperature of the reaction was found with the temperature screening experiments and was determined to be at about 85-90°C. The impact of a change in catalyst concentration, as well a change in the temperature of the reaction was very significant. Figure 3 shows the result of an experiment at 100°C. The reaction starts very fast and it takes about 1hr to get more than 90 percent conversion. Raising the catalyst concentration causes the reaction speed to rise rapidly. Furthermore it seems as if the final conversion degree is dependent upon the catalyst concentration as the reaction slows down gradually. The maximum concentrations in these experiments were limited by the solution's viscosity as higher concentrations gave solutions with higher viscosities and it became increasing difficult to stir and collect NIR spectra in these samples.

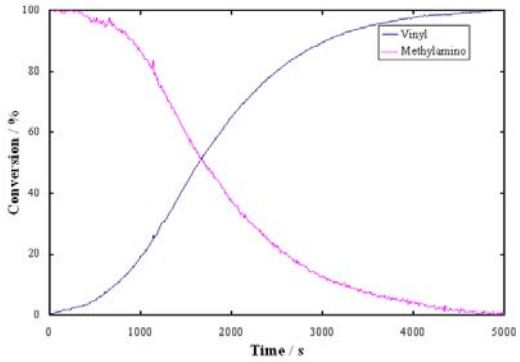

Figure 3. Progress of the conversion.

Conclusion

Both instruments were successfully used for on-line monitoring of the conversion of a gas/liquid reaction. The Integrity 10 STEM Reaction Station from Electrothermal is an excellent way to create reproducible reaction conditions, especially in temperature screening experiments. In combination with the Antaris FT-NIR instrument it is possible to get information about the progress of the reaction in real time as long as there are characteristic peaks in the NIR spectra.

Acknowledgements

The contents of this application note are adapted from a report of the same name written by Dr. M. Irrgeher[1].

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