PYROLYSIS-GC-MS FOR STUDYING POLYMER SOLUBILITY

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Introduction

Pyrolysis gas chromatography – mass spectrometry (Py-GC-MS) can be used to study synthetic polymers. In recent years it has been demonstrated that a programmed-temperature-vaporization (PTV) injector can be used to quantitatively determine the amounts of monomeric units present[1]. This makes it possible to use Py-GC-MS for determining the composition of copolymers and for determining the concentrations of polymers in solution. The PTV injector allows samples to be injected as liquids (solutions) and its coupling with a state-of-the-art GC-MS system allows the analysis of very small amounts of polymers. Thus, Py-GC-MS with a PTV injector is a promising new tool for quantitative solubility studies of (co-) polymers. Py-GC-MS can be used to study polymer solubility as a function of solvent composition, temperature, *etc*.

Experimental

GC-MS: QP 2010 Plus, Shimadzu, Duisburg, Germany
PTV-injector: OPTIC 3, ATAS GL, Veldhoven, The Netherlands
Auto sampler/interface: FOCUS (combi-pal), ATAS GL

Py-GC conditions:
T injection 40°C; T solvent elimination 150°C;
T pyrolysis 550°C; GC-column, GL Sciences TC-5 (30 m x 0.25 mm ID, film thickness 0.25 µm);
GC-program, T_{init} 35°C (3.5 min hold), T_{final} 200°C (rate 10°C/min) and hold for 2 min ; He pressure 30 kPA.

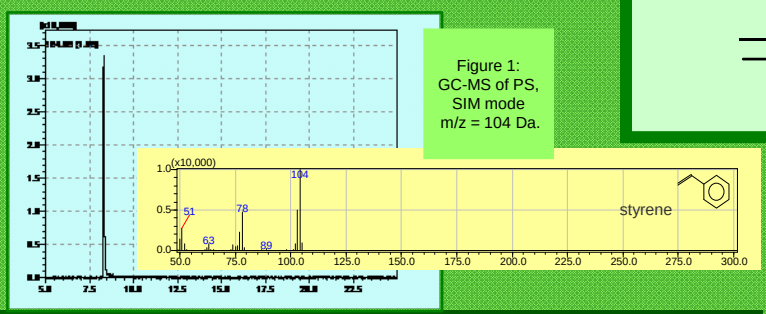

Figure 1: GC-MS of PS, SIM mode m/z = 104 Da.

Instrumentation

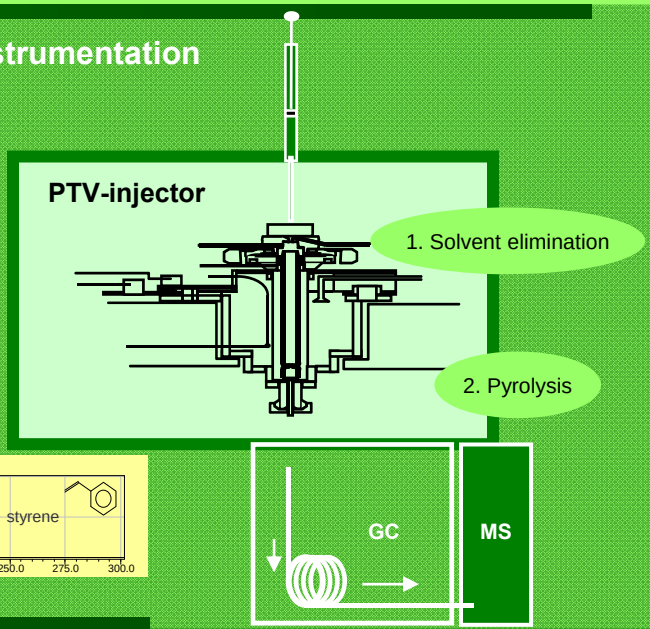

Figure 1: Schematic diagram of the automated Py-GC-MS. Programmable – temperature-vaporization (PTV) injector controls the programmed Py-GC-MS.

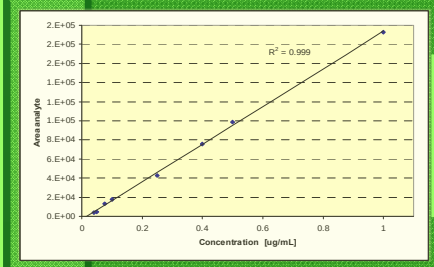

Figure 2: Calibration curve of PS M_r = 300,000 1 µL injection.

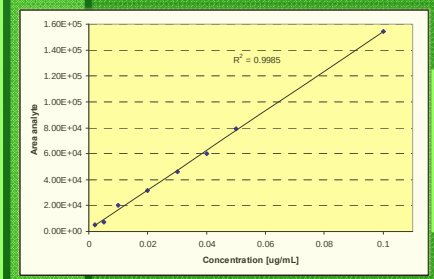

Figure 3: Calibration curve of PS M_r = 300,000 50 µL injection.

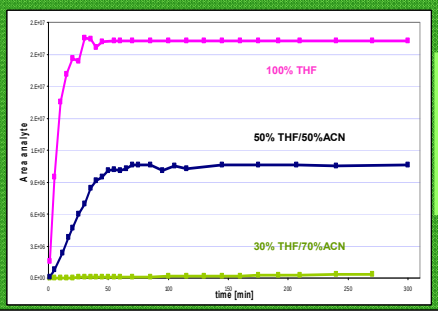

Figure 5: Dissolution curve of PS in THF/ACN M_r = 300,000

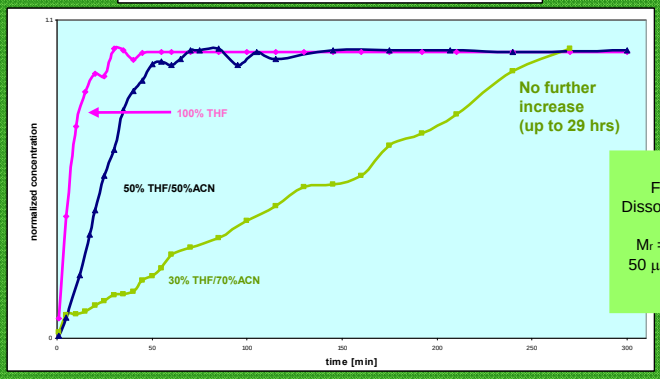

Figure 6: Dissolution curve of PS M_r = 300,000 50 µL injection.

Conclusions

- **With Py-GC-MS we can measure dissolution curves and solubilities.**
- **Lower solubility corresponds to slower dissolution.**
- **Using large volume injections (50 µL) we can measure concentrations below 10 pg/mL for PS.**
- **The Py-GC-MS method is especially useful when the solubility of polymers is low (poor solvents) and it can be used to measure very slow dissolution processes.**
- **Precision is acceptable (and will probably be improved in the future).**

Reference

[1] Erwin R. Kaal, Geert Alkema, Mitsuhiro Kurano, Margit Geissler and Hans-Gerd Janssen *On-line size exclusion chromatography–pyrolysis-gas chromatography–mass spectrometry for copolymer characterization and additive analysis* Journal of Chromatography A, Volume 1143, Issues 1-2, 2 March 2007, Pages 182-189.

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