On-line coupled SEC - Pyrolysis-GC-MS for copolymer characterization and additive analysis

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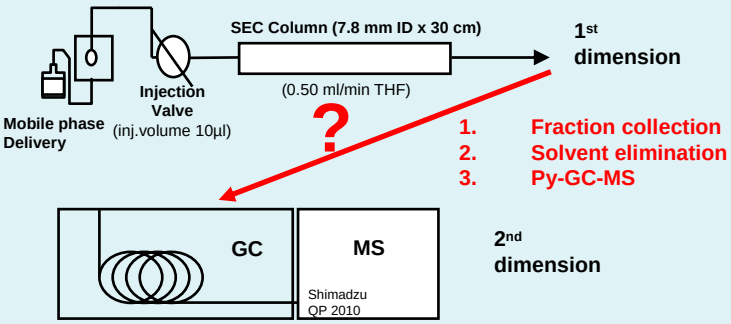
Introduction

Knowledge of the physical and chemical properties of polymers as well as the molecular weight distribution is very important for product development and the later production of polymeric materials. In this study SEC and (pyrolysis-)GC-MS are coupled on-line and fully automated to allow the determination of the molecular weight distribution, the average chemical composition, and the identification and quantification of additives in one a single run.



Experimental

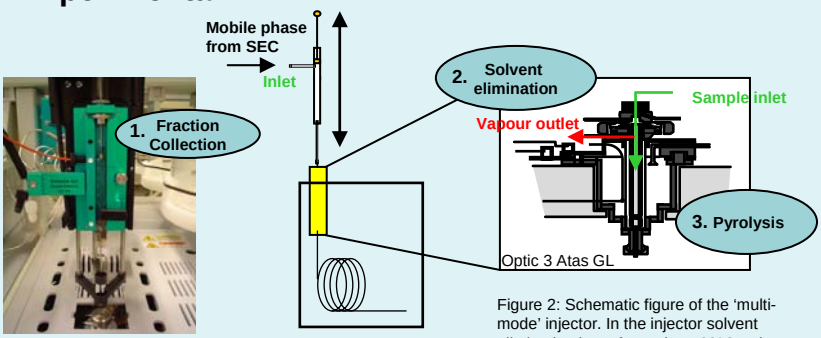


Figure 1: Example of a "side port" syringe used for collection of the SEC fractions. Fractions of the SEC effluent are collected in the syringe. After 15 seconds the flow is stopped and the collected fraction is transferred into the injector for solvent elimination and pyrolysis.

Figure 2: Schematic figure of the 'multi-mode' injector. In the injector solvent elimination is performed at 100°C. When all the solvent is evaporated, the split-exit is closed and pyrolysis is performed by ramping the injector to 600 °C at 30 °C/min.

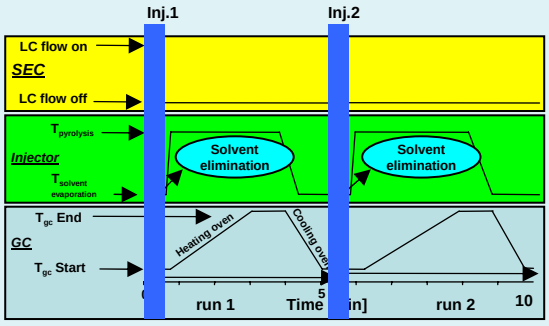


Figure 3: Injection diagram of the SEC – Py-GC-MS experiments. First the SEC flow is started and stopped for collection of a fraction. Then the fraction is injected into the injector. Now the solvent is evaporated. When all the solvent is eliminated pyrolysis is started. The fragments of the pyrolysis are refocused in the cold analytical column. When the pyrolysis is finished the GC-program is started. After completion of the GC-run, the GC-oven and the injector are cooled to T_{start} and the next fraction is transferred.

Results

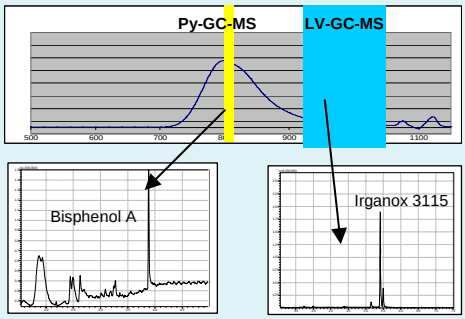
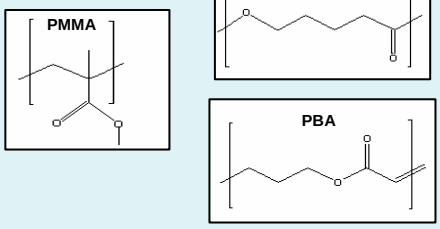


Figure 4: Analysis of Polycarbonate (PC) and Irganox 3115 in a single SEC - Py-GC-MS run. One fraction of PC is taken and analyzed by Py-GC-MS. The second fraction is analyzed without pyrolysis for identification and quantification of smaller molecules like additives.



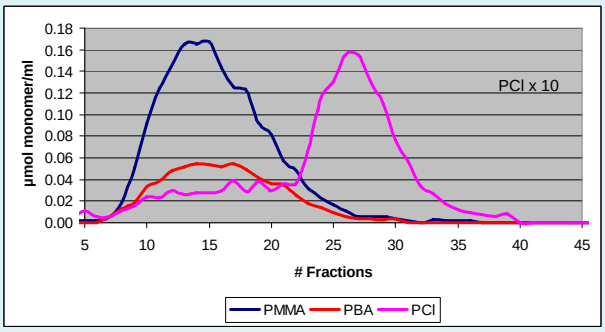


Figure 5: Characterization of a complex *ter*-polymer, PCl, PMMA and PBA. System conditions:
SEC column, 2 PL mixed C (7.8mm x 30 cm); Mobile Phase, THF; fractions, flow 0.50 ml/min for 15 seconds (split 1:5); $T_{Injector}$ solvent elimination, 100°C; $T_{injector}$ pyrolysis, 600°C; GC-column, GL Sciences TC-5 (30m x 0.25 mm ID, film thickness 0.25 µm); GC-program, T_{start} 70°C (2 min), 100°C/min to 150°C for 2 min; He flow 30 kPA (constant pressure).

Conclusions

- Automation of SEC - Py-GC-MS is possible using a "multi mode" injector with ramp rate of 30°C/sec.
- Py-GC-MS can be used as a polymer-selective detector.
- With SEC - Py-GC-MS it is possible to obtain compositions of complex copolymers as function of the Mw.
- Copolymer characterization and quantification of additives can be done in one single SEC - Py-GC-MS run.

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