Direct Gas-Phase Derivatization by Employing Tandem μ-Reactor-Gas Chromatography/Mass Spectrometry: Case Study of Trifluoroacetylation of 4,4′-Methylenedianiline

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Abstract:

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is a promising technique allowing the rapid characterization of the polymer structure and additives of microgram-scale plastics. However, the Py-GC/MS analysis of polymers with urethane bonds is challenging because they produce highly reactive pyrolyzates such as amines and isocyanates polymerizing in the GC column, which limits the efforts to elucidate the pyrolysis mechanism and plastic characterization by online GC analysis. Herein, a novel pyrolysis-gas-phase derivatization-GC/MS (Py-GPD-GC/MS) technique was developed, allowing the pyrolysis of polymers and the subsequent direct gasphase derivatization of pyrolyzates, employing a modified tandem μ-reactor-GC/MS system. This work conducted the gas-phase trifluoroacetylation of 4,4′-methylenedianiline (MDA), which is one of the major polyurethane (PU) pyrolyzates, using N-methylbis-trifluoroacetamide (MBTFA) as a derivatization agent. The trifluoroacetylation gas-phase reaction was monitored by *in situ* GC/MS analysis and the effects of derivatization conditions were investigated. The highest MDA conversion observed was 65.6 area %. Furthermore, the sequential PU pyrolysis and direct trifluoroacetylation of PU pyrolyzates in the first μ-reactor and second μ-reactor, respectively, were successfully operated, achieving the inhibited polymerization and detection of trifluoroacetylated derivatives. Thus, the Py-GPD-GC/MS method has a significant potential to be applied for other combinations of pyrolyzates and derivatization reactions, enabling deeper characterization of plastics producing highly reactive pyrolyzates that cannot be accurately analyzed by conventional Py-GC/MS analysis.

* Excerpted from online journal website (Click the title)

Frontier Labs Products used:

Multi-Shot Pyrolyzer (EGA/PY-3030D, UA$^+$-5, Tandem micro-Reactor (Rx-3050TR), UADTM