

Analysis of nylon-6,6 by reactive pyrolysis at high temperatures and high pressures using Online micro Reaction Sampler

[Background] Nylon is one of the general purpose plastics. Therefore, the characterization of unknown nylon samples is very important in forensic chemistry. The differentiation is generally made through a variety of thermal analysis techniques and/or pyrolysis (Py)-GC/MS. In Py-GC/MS, the reactive pyrolysis GC/MS in the presence of organic alkali such as tetramethylammonium hydroxide (TMAH) is useful to characterize condensation polymers. However, in the analysis of polyamides such as nylons, there is a problem in which reactive pyrolysis – derivatization reactions are inherently inefficient. On the other hand, chemolysis in a sealed vessel at high temperatures and high pressures is expected to solve this issue, but the reaction mixture is generally worked up offline. Described in this note is online analysis of nylons by chemolysis at high temperatures and high pressures using Online micro Reaction Sampler^{1,2)} that is fitted to Multi-Shot Pyrolyzer.

[Experimental] 50 µg of a nylon sample and 10 µL of 25 wt% methanol solution of TMAH were placed in a glass tube (id.=1.9 mm, od.=2.4 mm, L=40 mm), and the tube was sealed with a torch flame. The tube was then heated in a muffle furnace at 300°C for one hour. The glass tube was fitted to Online micro Reaction Sampler (PY1-1050, Frontier Labs), followed by attaching the sampler to Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Labs) which was directly interfaced to the injector of GC/MS. The glass tube was then physically crushed under He atmosphere and the reaction products were fed to the GC separation column.

[Results] Products formed by chemolysis of 9 nylon samples were analyzed, and methyl derivatives of the monomers were observed in all of the samples. An example of the pyrogram of nylon-6,6 obtained by Py-GC/MS is shown in Fig. 1. Also, the chromatogram of chemolysis products obtained using the Online micro Reaction Sampler is shown in Fig. 2. In the chemolysis at high temperatures and high pressures, the tetramethyl derivative (M1) of hexamethylenediamine, a comonomer of nylon-6.6 and dimethyl derivative (M2) of adipic acid, another copolymer, were clearly observed along with the methyl derivative (D1) of mixed dimer. Also the reproducibility of the peak areas of M1 and M2 was found to be about 2% (n=3) in relative standard deviation (RSD), which should be more than sufficient for quantitative analysis of monomer. As described above, the chemolysis in a sealed vessel using the Online micro Reaction Sampler was demonstrated to be useful for characterization of nylons.

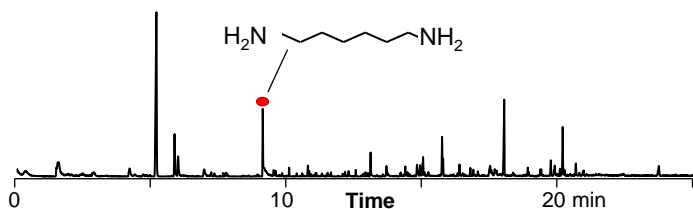


Fig. 1 Pyrogram of nylon-6,6 obtained by pyrolysis GC/MS

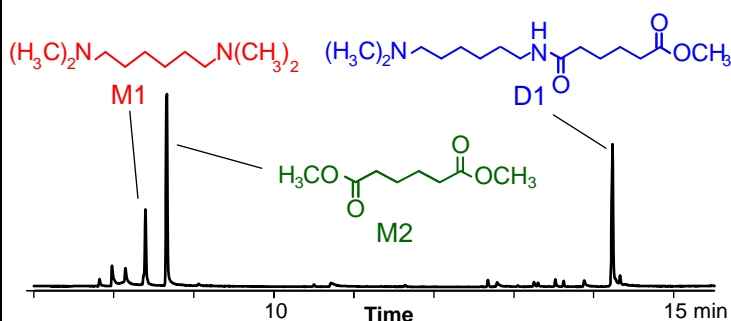


Fig. 2 Chromatogram of chemolysis products of nylon-6,6 obtained using Online micro Reaction Sampler

Table 1 Reproducibility of monomer formation ratios

| n | M1/M2 |
|---------|-------|
| 1 | 0.410 |
| 2 | 0.422 |
| 3 | 0.405 |
| Average | 0.412 |
| RSD (%) | 2.1 |

Reaction time: 300°C (1 hr), sample wt.: 50 µg
 Separation column: Ultra ALLOY*-5 (5% phenyl 95% dimethyl polysiloxane, L=30 m, id.= 0.25 mm, df.= 0.25 µm)
 Column flow rate: 1 mL/min, split ratio: 1/50
 Detector: quadrupole MS

Ref. 1) A. Hosaka, et al., Journal of Analytical and Applied Pyrolysis, 106, 160-163 (2014)

Keyword : Nylon, Reactive pyrolysis GC/MS, Online micro reaction sampler, Chemolysis

Applications : General polymer analysis, Forensic differentiation, fabric, textile, analysis

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