Going Green: Analysis of Virgin and Recycled Nylon 11 in HFIP Using the EcoSEC® GPC System and Semi-Micro Gel Permeation Chromatography Columns

EcoSEC GPC System
APPLICATION NOTE

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Introduction

Over the past several decades green initiatives have been approaching the polymer science discipline from all sides. Companies are not only interested in greener products and additives but greener and more cost effective synthesis and characterization methods. One class of polymers that is of high interest is polyamides, more specifically nylons, as these plastics are common materials in everyday life which produce large quantities of scraps and wastes that contaminate the environment. The not so simple solution for decreasing nylon waste is plastic recycling, because recycling can decrease the cost and environmental contamination related to everyday use of nylons. The major caveats of recycling nylon are the reduction of physical-mechanical properties and changes in morphology which result from polymer degradation that occurs during the recycling processes.[1-2]

Due to the aforementioned caveats, the ability to accurately and precisely characterize virgin and recycled nylon materials is essential. One common method used for nylon characterization is the determination of molar mass averages and distributions by gel permeation chromatography (GPC). The use of GPC for the analysis of nylons has its own challenges, namely the poor solubility in common organic solvents and strong adsorptive interactions.[3] To solve the problems related to GPC analysis of nylons, the analysis is typically performed at extremely high temperatures using *m*-cresol or temperatures closer to ambient using very costly solvents such as hexafluoroisopropanol (HFIP).

The necessity to use HFIP for the analysis of nylons by GPC to determine the similarities and differences between the molar mass averages and distributions of virgin and recycled nylon materials results in very costly experiments. Here we report on the use of a low dead volume all-in-one GPC system, the EcoSEC GPC System, with semi-micro (6 mm ID × 15 cm) GPC columns for the analysis of virgin and recycled nylon material in HFIP. The combination of the low dead volume of the EcoSEC GPC System and semi-micro GPC columns provides significant solvent related cost savings while doubling sample throughput without compromising resolution.

Experimental Conditions

Sample analysis was performed on a system consisting of an EcoSEC GPC System (HLC-8320) equipped with a RI detector. Separation of unfiltered 20 µL injections occurred over a column bank consisting of two 6 mm ID × 15 cm, 9 µm particle size TSKgel® SuperAWM-H columns (exclusion limit ~1 × 10^7 g/mol) (Tosoh Bioscience LLC). The mobile phase and solvent were hexafluoroisopropanol (Oakwood Chemical) with 5 mmol/L sodium trifluoroacetate (Alfa Aesar) at a flow rate of 0.35 mL/min. Detector, pump oven, and column oven were maintained at 40 °C. Two Nylon 11 samples, which produce successful final products, were analyzed: virgin nylon 11 and recycled nylon 11. Sample solutions were prepared by diluting the samples in hexafluoroisopropanol with 5 mmol/L sodium trifluoroacetate for a final sample concentration of 1.0 mg/mL. Samples were shaken manually for a minute and allowed to sit overnight before analysis was performed. For all chromatographic determinations, results are averages of six injections from two separate sample dissolutions. Data was processed with the EcoSEC GPC Workstation software, version 1.08.

A calibration curve was created for the RI at 40 °C using poly(methyl methacrylate) (PMMA) standards (Polymer Standard Services) ranging in molar mass from 6,270 to 1.1 × 10^6 g/mol. PMMA standards were prepared by diluting nine individual PMMA standards in hexafluoroisopropanol with 5 mmol/L sodium trifluoroacetate, in separate vials, for a final sample concentration of 1.0 mg/mL. PMMA standards were analyzed under the same conditions as those used for sample analysis as described above. Calibration curve data for 0.35 mL/min was fitted with a linear function and error values were less than 5%.

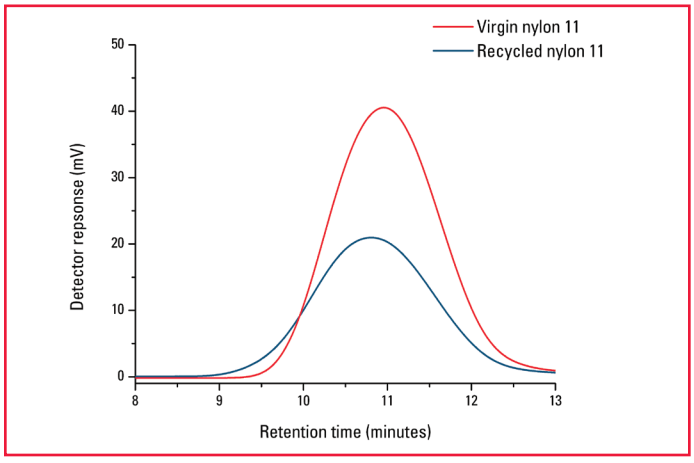
Results and Discussion

A greener and more cost effective method for the characterization of nylon 11 in hexafluoroisopropanol (HFIP) was employed by using an EcoSEC GPC System encompassing a dual flow refractive index detector and semi-micro gel permeation chromatography (GPC) columns. The combination of the low dead volume of the EcoSEC GPC System and semi-micro GPC columns provides significant solvent related costs. For example, for solvents such as HFIP the use of the EcoSEC GPC System and semi-micro GPC columns results in yearly savings in solvent related costs of more than $80,000.

Two nylon 11 samples, which produced successful final products: virgin nylon 11 and recycled nylon 11, were analyzed in HFIP. The GPC experiments provided two forms of comparison between the virgin and recycled nylon 11 samples: GPC chromatograms and poly(methyl methacrylate) relative molar mass averages and molar mass distributions.

The GPC elution profiles of the virgin and recycled nylon 11 as monitored by the dual flow RI detector are shown in *Figure 1*. The virgin nylon 11 elutes after the recycled nylon 11. The longer retention time of the virgin nylon 11 indicates that the virgin material is slightly smaller in polymeric size compared to the recycled material: as elution order in GPC is that of an "inverse-sieving" technique, smaller analytes elute after the larger analysts. The GPC elution profiles of the two samples also vary in broadness, with the elution profile of the recycled nylon 11 extended further in the shorter retention time, larger polymeric size, direction than its virgin counterpart.

Figure 1. GPC elution profile of virgin nylon 11 (red), and recycled nylon 11 (blue) as monitored by RI.



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The molar mass averages and polydispersity index, *PDI*, as determined via a poly(methyl methacrylate) RI calibration curve are given in *Table 1*. A comparison of the molar mass averages of the virgin nylon 11 material with the recycled nylon 11 material reveals higher number-, weight-, and *z*-average molar mass values for the recycled nylon 11 compared to the virgin nylon 11. In general, an increase in the molar mass averages of the recycled nylon 11 compared to the molar mass averages of the virgin nylon 11 is expected, as the rate of increase between the molar mass values is dictated by probability of main-chain scission and crosslinking during the recycling process.[2]

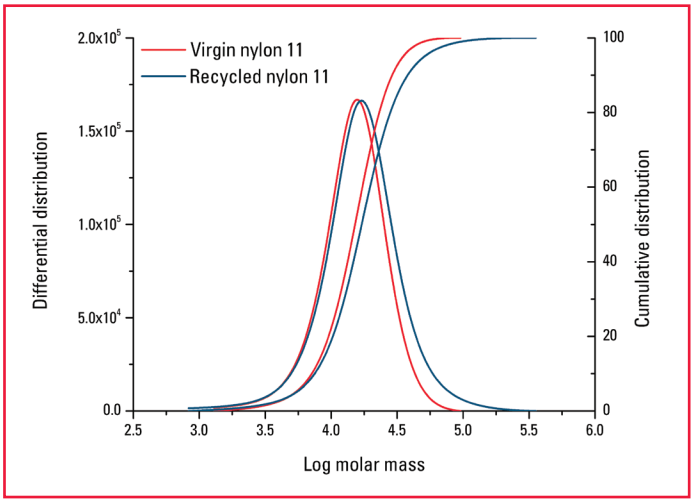
Table 1. Molar mass averages and polydispersity index of nylon 11 samples via RI

Sample	Retention time (minutes)	M_w (g/mol)	M_n (g/mol)	M_z (g/mol)	*PDI*[a]
Virgin nylon 11	10.959	$1.21^5 \times 10^4$ ± 46[b]	1.713×10^4 ± 75	2.293×10^4 ± 346	1.41 ± 0.01
Recycled nylon 11	10.802	1.334×10^4 ± 438	2.169×10^4 ± 210	3.932×10^4 ± 1,105	1.62 ± 0.05

[a] $PDI = M_w/M_n$
[b] Standard deviations from six injections

The differences between the virgin and recycled nylon 11 can also be observed by comparing the *PDI* values, *Table 1*, and the differential and cumulative distributions, *Figure 2*. The recycling process of nylon 11 results in an increase in the polydispersity index, virgin material PDI=1.41 and recycled material PDI=1.62, thus a corresponding increase in the breadth of the distribution curves and molar mass range for the recycled nylon 11, *Figure 2*. The molar mass averages and distributions of the virgin and recycled nylon 11 samples obtained by GPC are different enough to distinguish the two products from one another but similar enough to create successful products with the same end-use properties.

Figure 2. Differential and cumulative distributions of nylon 11 (red) and recycled nylon 11 (blue).



Conclusions

The molar mass averages and molar mass distributions of two nylon 11 samples, which produced successful final products: virgin nylon 11 and recycled nylon 11, were determined via a dual flow RI detector using the EcoSEC GPC System and semi-micro GPC columns in HFIP. The GPC elution profile for the virgin nylon 11 was determined to be narrower and elute later than the recycled nylon 11. The molar mass averages, M_n, M_w, and M_z, as determined via poly(methyl methacrylate) relative calibration curves were found to be greater for recycled nylon 11 than for virgin nylon 11. Additional differences between virgin and recycled nylon 11 were observed by comparing the *PDI* values of the samples. The recycling process of nylon 11 results in an increase in the polydispersity index. The molar mass averages and distributions of the virgin and recycled nylon 11 samples obtained by GPC in this case were determined to be distinguishable from one another even though both nylon 11 samples can be used to create successful products with the same end-use properties. Additionally, the use of the EcoSEC GPC System with semi-micro GPC columns decreases the consumption of HFIP by ~85%. This equates to savings of over $80,000 in solvent costs for a time period of one year. The end result is a greener and more cost effective method for the characterization of nylon 11.

References

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