TOSOH

INSTRUMENTATION

Application Note

GPC: A TOOL TO DETERMINE THE PROCESS PROPERTY RELATIONS IN POLYVINYL CHLORIDE

INTRODUCTION

Polyvinyl chloride (PVC) is a thermoplastic polymer that has the property of softening under temperature and hardening when it is cooled. The temperature at which the softening or hardening occurrs is called the glass transition temperature (Tg). Researches have shown that the major part of the PVC structure is amorphous (~90 %) which indicates that the polymer molecules are randomly arranged. Due to the amorphous structure, PVC shows characteristic mechanical properties of a polymer such as creep resistance, low shrinkage, impact resistance and good transparency up to the Tg.

PVC is beeing used in a wide range of short and long term applications. In recent years, PVC has been replacing traditional building materials such as wood and concrete in many areas. In addition, PVC is beeing used in the production of pipes, electric wires, toys, bottles, doors and window components, film and fabric coatings. Among these, the largest area of PVC application is in the field of construction (>60%). PVC is extremely cost effective in comparison to other plastics and has a high level of versatility in end-use and processing applications.

The properties of PVC are extensively influenced by its average molecular weight and its molar mass distribution (MMD). The molecular weight of PVC is generally controlled by the reaction time and temperature during synthesis. The higher the polymerization temperature, the lower the molecular weight because the rate of chain transfer dominates over the chain propagation rate with increasing reaction temperature.

The number of monomer units in a polymer chain is referred to as the degree of polymerization (DP). The DP of a polymer can provide indications on the molecular weight of a polymer. Synthetic polymers always comprise a set of macromolecules of varying DP and respectively varying molecular weight. Polymers with identical composition but different molecular weights may exhibit different physical properties. In general, increasing DP values correlate with higher melting temperature and higher mechanical strength. With this application note, we show the variation in MMD with increasing the DP of PVC samples.

EXPERIMENTAL CONDITIONS

Sample analysis was performed on an EcoSEC Ambient Temperature GPC System equipped with a RI detector. Separation of 30 μL injections occurred over a bank of one TSKgel SuperH4000 (P/N 0017994) and one SuperH3000 column (P/N 0017993) with 6.0 mm ID x 15 cm L, 3 μm particle size and the corresponding guard column. The mobile phase and solvent were THF at a flow rate of 0.4 mL/min. Detector, pump oven and column oven were maintained at 40 °C.

Two PVC samples (PVC 6 and PVC 13) which vary in their DP were provided by Tosoh Corp. Japan. The DP for PVC 6 and PVC 13 varies from 620-660 and 1270-1370, respectively. The polymer samples were dissolved in THF. The final sample concentrations were approximately 5.0 mg/mL. Data was processed with the EcoSEC GPC Workstation software. Molar mass averages were determined for each polymer sample using a calibration curve. A calibration curve for the column according to the experimental conditions was created using Tosoh polystyrene standards at 40 °C. Calibration curve data for polystyrene standards in THF at a flow rate of 0.4 mL/min was fitted with a cubic function and error values were less than 5%.

RESULTS AND DISCUSSION

The GPC chromatograms of the two PVC samples are shown in Figure 1. This graph shows that the MMD of PVC 6 is shifted to the lower molar mass region compared to that of PVC 13. Due to the lower DP, PVC 6 shows lower MMD and the higher DP caused the higher MMD of PVC 13. This result shows that the DP is directly related to molar mass of PVC.

RI CHROMATOGRAMS OF PVC 6 AND PVC 13 GPC RUN

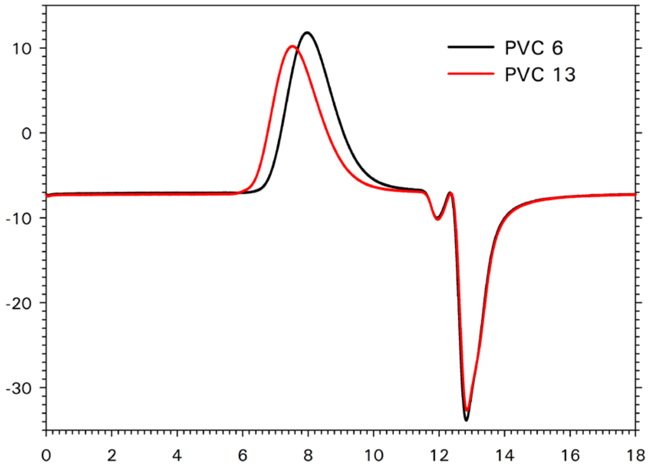

Figure 1

EcoSEC workstation was used for the calculations. The dedicated data analysis tab was used to calculate a calibration curve and determine the MMD and the average molecular weights. Each sample was injected three times to determine the coefficient of variation. The analytical procedure validation tab was used to determine the coefficient of variation (CV) of retention time, peak area, peak height, average molar masses and the polydispersity index (PDI). The obtained results are summarized in Table 1. From the CV values, it can be seen that the reproducibility of the measurements is excellent. Differential and cumulative distributions of molar masses are depicted in Figure 2.

DIFFERENTIAL AND CUMULATIVE DISTRIBUTIONS OF PVC 6 AND PVC 13

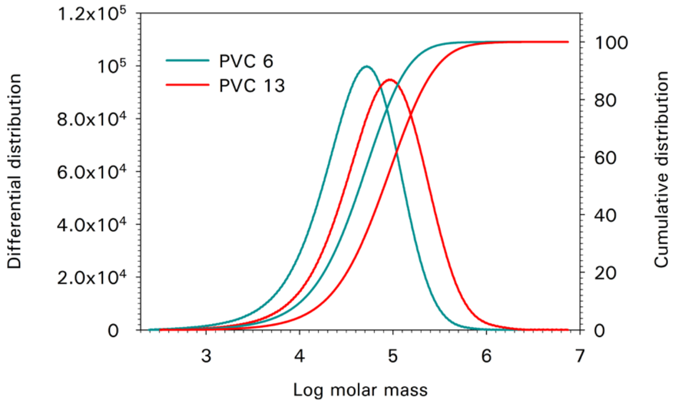

Figure 2

Even though the amount of crystalline regions of PVC is very low, many researchers study the crystallization behavior. It has been shown that the crystallinity of PVC is inversely proportional to the molar mass. In this study, PVC 6 showed a low molar mass from which we can conclude a higher crystallinity. With an increase of crystallinity, the polymer tends to show higher tensile strength. These reasons make PVC 6 attractive for applications like the production of rigid plates, extruded sheets, draw films, blowbottles, injection molding etc.

However, the tensile strength decreases with increasing molar mass, but due to longer polymer chains, the tensile strain or the elongation of the polymer increases. Due to these reasons, PVC 13 can be used for agricultural films, general flexible films, sheets, artificial leathers, wires and cables, food films, tape etc.

CONCLUSION

The molar mass averages and molar mass distributions of two PVC samples, PVC 6 and PVC 13, were determined via a dual flow RI detector using the EcoSEC GPC System and semi-micro GPC columns in THF. The GPC analysis shows that PVC 13 has a higher MMD compared to PVC 6. The molar mass averages, Mn, Mw, and Mz, as determined via PS relative calibration curves were found to be greater for PVC 13 than for PVC 6. It can be now concluded that the GPC analysis revels the direct relation between the DP and molar mass of PVC. This study shows that GPC is a great tool to investigate the process property relations in polymers.

MOLAR MASS AVERAGES AND CV OF DIFFERENT PARAMETERS

	Sample	Retention time (min)	Peak area (mV.sec)	Peak height (mV)	Molecular weight averages			PDI
					Mn	Mw	Mz	
Average of three injections	PVC 6	7.9	1923	18.7	19625	65115	137063	3.3
	PVC 13	7.5	1789	17.2	34472	124155	276431	3.6
CV %	PVC 6	0.2	0.9	1.2	1.1	0.8	1.8	
	PVC 13	0.1	0.9	0.9	2.7	0.15	1.7	

Table 1