TOSOH

APPLICATION NOTE

DETERMINATION OF THE MOLAR MASS DISTRIBUTION OF PHENOL-FORMALDEHYDE RESINS USING GPC

INTRODUCTION

Phenol formaldehyde resins (PFRs) are condensation polymers and are obtained by condensing phenol with formaldehyde in the presence of an acidic or alkaline catalyst. The class of PFRs having a low degree of polymerization are soft and those having a high degree of polymerization are hard, rigid, infusible and resistant to scratches. The soft PFRs possess excellent adhesive properties which makes them attractive as binding glue for laminated wooden planks and in varnishes. PFRs with high degree of polymerization and a higher molar mass are resistant to non-oxidizing acids, salts and many organic solvents. In addition, PFRs can withstand high temperatures, have poor electric conductivity and can be used as excellent electrical insulators. The electrical insulation property of PFRs makes them applicable to household electrical appliances. Furthermore, PFRs have been used for a variety of applications which includes making molded articles such as radio and TV parts, combs or fountain pen barrels.

The ratio between the monomer units and the pH of the catalysts plays a crucial role for the chemical properties of PFRs. Depending on the monomer unit ratio and the pH of the catalysts used for the synthesis, two classes of PFRs namely Novolac or Resol resins can be formed. Resol type PFRs are condensation products synthesized in presence of basic catalysts. During the synthesis of resols, the hydroxyl group of the phenol gets deprotonated and the resonance stabilization of the resulted phenoxide ion allows the hydroxymethylation at the ortho or para position of the phenol. There are one para and two ortho sites in a phenol molecule. The para position is more reactive than the ortho position. Condensation of these hydroxymethylated phenols form a methylene bridge between them yields the formation of Resol type PFRs. Novolac resins are amorphous thermoplastic polymers produced by reacting formaldehyde with phenol under acidic conditions. The reaction between phenol and formaldehyde in the acidic pH range occurs as an electrophilic substitution of hydroxymethylene carbonium ion formed from the methylene glycol at acidic pH. Curing of both types of resins yields the formation of three dimensional network structures in PFRs. In this study, we compare the development of molar mass distribution (MMD) in a thermos-reactive Resol (PFR 1) and a thermoplastic Novolac (PFR 2) resin by utilizing the gel permeation chromatography (GPC) technique.

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 SuperH2500 (P/N 0017992) and one SuperH2000 column (P/N 0017991) with 6.0 mm ID x 15 cm L, 3 µm particle size and the corresponding guard column (P/N 0018002). The mobile phase and solvent were THF at a flow rate of 0.35 mL/ min. Detector, pump oven and column oven were maintained at 40 °C.

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. MMDs 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 0.35 mL/min was fitted with a cubic function and error values were less than 5%.

RESULTS AND DISCUSSION

GPC elution curves obtained for PFR 1 and PFR 2 are depicted in Figure 1. Multiple MMDs can be clearly seen from Figure 1. The use of two TSKgel columns in series with different exclusion limits and pore size distribution delivered the best resolution for different molar mass distributions within each sample even at the very low molar mass range. The conventional use of GPC analysis requires 3 columns in series with an analysis flow rate of 1 mL/min.

GPC ELUTION CURVES OF PFR 1 AND PFR 2

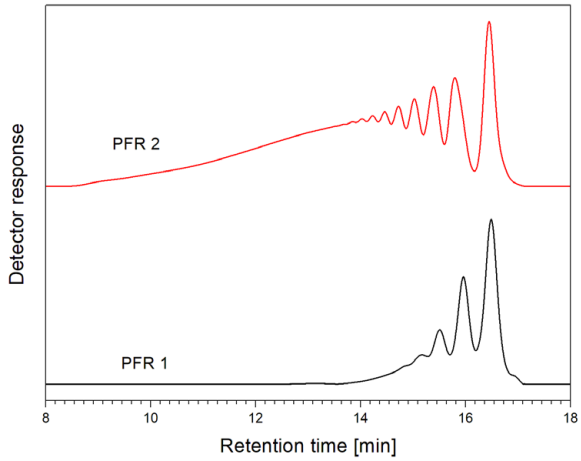

Figure 1

However, by using semi-micro columns with smaller dimensions as mentioned in the experimental section and using only two columns in series provided the great advantage of saving analysis time and solvent by 60% compared to a conventional GPC analysis. Molecules of PFR 1 elutes later with higher retention times than those of the molecules of PFR 2. This indicates that the hydrodynamic volume of PFR 1 molecules in THF is much smaller because the elution order in GPC is that of an "inverse-sieving" technique: large molecules access a smaller pore volume than smaller molecules resulting in larger molecules eluting from the GPC column prior to the smaller molecules.

MMDs were calculated using PS standards as described in the experimental section using the dedicated EcoSEC workstation software. The results obtained are presented in Figure 2.

PFR 1 shows a lower molar mass distribution than the PFR 2. One of the key properties of phenolic resins is their ability to change from the liquid state to the solid state by forming covalent bonds. Resols which completed their synthesis stages including the curing phase will be completely thermoset, unmeltable and unsoluble. During the synthesis of resols, methylol groups are attached to the benzene ring which makes it reactive for cross linking even in the absence of curing agents. Curing of resols therefore can occur at room temperature with time which can be accelerated by heating or adding crosslinking agents resulting an increase in molar mass. The PFR 1 used for the analysis was a thermoreactive one step resin where the curing was not completed. From the low MMDs of the PFR 1 determined by EcoSEC GPC systems, it can be confirmed that the samples were not cured.

In phenols, the para position is more reactive than the ortho or meta positions. This is because, the electron releasing hzdroxyl group in phenols donates electrons to the benzene ring. Due to the excess electrons, the benzene ring tends to form resonance structures and induce negative charges at para and ortho positions in which the substitution at the ortho positions has a steric hindrance by the hydroxyl groups. In order to make the curing of PFR resins faster, highly active para positions of the benzene rings have to be preserved during the formation of methylene linkages in the pre-polymer formation step which can be achieved by the additions of catalysts. Catalysts which promote ortho-ortho methylene linkages tend to preserve the more reactive para positions. Novolac resins synthesized in presence of these catalysts favour the curing more rapidly than the randomly linked resins. Therefore, novolac resins are commonly refered to as two step products because of the addition of the cross linking agents during curing.

Both PFR 1 and PFR 2 show multiple MMDs in the GPC chromatogram. This can be caused by the different possibilities for the formation of branches because the reaction can occur at any of the three sites (one para and two ortho positions) on each benzene ring. As the reaction continues, the random orientations and branching quickly result in an extremely complex mixture of polymers of different sizes and structures.

CONCLUSION

The MMDs of two PFR resins, PFR 1 and PFR 2, were determined via a dual flow RI detector using the EcoSEC GPC system and semi-micro GPC columns in THF. The GPC analysis show that the single step resol type PFR 1 resins has low MMDs compared to the cured thermoplastic PFR 2 resins. Highly resolved multiple MMDs were observed for PFR 1 and PFR 2 resins. This study shows that GPC is a powerful tool to study the molar mass variations of PFR resins developed during the different stages of synthesis to curing. In addition, the semi-micro design of the EcoSEC GPC system allows the usage of semi-micro columns without affecting the quality of the chromatogram. This study proved that one of the great advantages of using the semi-micro columns is that the resolution of the MMDs was retained while the solvent consumption and analysis time were reduced by 60 % compared to a conventional GPC analysis.

GPC ELUTION CURVES OF PFR 1 AND PFR 2

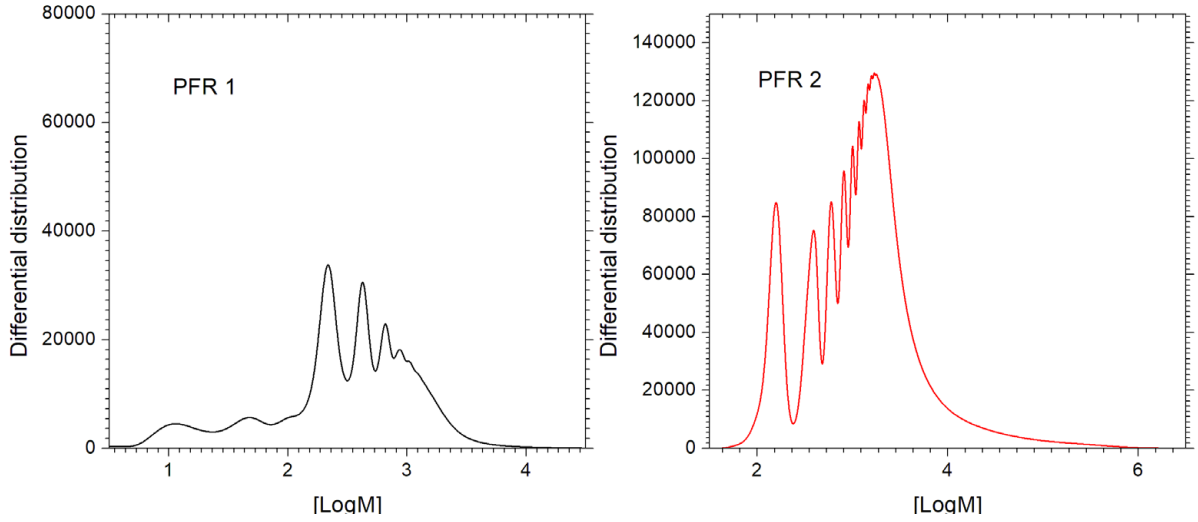

Figure 2