

Rapid Determination of the MW of a PF Resin by HPSEC Using a Bondagel Column

INTRODUCTION

Phenol-formaldehyde (PF) resins intended for use as wood adhesives are synthesized by reacting phenol and formaldehyde in the presence of a catalyst.¹ The phenol is methylolated and subsequently condenses to form a higher molecular weight (MW) polymer. The molecular weight distribution (MWD) of PF resins is critical because it affects their viscosity, reactivity, and wood permeability.² Currently, the growth in resin MW during synthesis is followed using dynamic viscosity, gel time, or turbidity point.¹ However, these measurements only give an average estimate of the MW and are affected by the solids content and temperature of the resin. Measurement of the MWD with high pressure steric exclusion chromatography (HPSEC) would be a better method for monitoring the progress of the reaction.

In HPSEC a dilute polymer solution is pumped through a column packed with porous particles which separates the polymer molecules according to size.³ Two approaches have been used in determining the MWD of PF resins by HPSEC. The first approach uses a column with a large number of theoretical plates (up to 100,000) which is capable of separating a PF resin into monomers, dimers, or trimers in the early stages of polymerization.⁴⁻⁶ As these columns have such a large number of plates, the analysis can take up to 2 h per run. The second method is to use a column with about 20,000 plates to determine the MWD of the resin after synthesis.⁷ With this method, analysis times are shorter (30 min), but only relatively large molecules can be separated.

This paper describes the rapid determination of the MWD of a PF resin using Bondagel E-125, a silica-based column packing. Bondagel columns are available with a nominal upper exclusion limit of 2,000,000 daltons³ and can tolerate the polar solvents required to dissolve higher MW PF resins. HPSEC columns previously used for analyzing PF resins have been limited to nonpolar solvents such as tetrahydrofuran (THF), which is a poor solvent for higher MW PF resins.⁴⁻⁷

EXPERIMENTAL

Resin Preparation. A PF resin was synthesized according to the procedure of Adams and Schoenher⁸ by combining 55.5 g of phenol, 64.8 g of 37% formaldehyde, 2.6 g of NaOH, and 59.5 g of H₂O in a 500 mL, three-necked flask equipped with a thermometer, stirbar, and heating mantle. The flask was heated to reflux (95°C) over a 70-min period. The heating mantle was removed during the initial exotherm. The mixture was refluxed for 70 min, and then cooled to 70°C. After addition of 6 more grams of 50% NaOH, the flask was heated at 80°C for 60 min. Then, 4 g of 50% NaOH was added, and the mixture was heated for an additional 130 min at 80°C.

High Pressure Steric Exclusion Chromatography. Five PF samples (0.05 g) were removed from the reaction flask at representative times, and dissolved in 5 mL of 0.1M LiCl/dimethylformamide (DMF). The DMF was distilled and deaerated prior to use. LiCl was added to the mobile phase in order to reduce PF molecular associations.^{7,9}

The PF samples were stored at room temperature for up to 6.5 h, and then analyzed with a Waters modular HPLC. This system consisted of the Model 510 pump, an automatic gradient controller, and a Model 441 UV absorbance detector set at 280 nm. The column was 3.9 mm (ID) × 30 cm and packed with Bondagel E-125 (Waters Assoc.). The column has approximately 200 theoretical plates and a void volume of 1.5 mL. Analysis times were less than 5 min, at a flow rate of 1.0 mL/min and an injection volume of 15 μL. The column was calibrated with polystyrene standards (Supelco) using HPLC grade THF (Aldrich) as solvent.

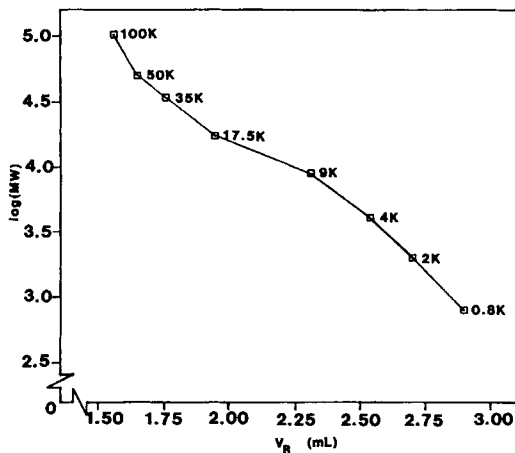


Fig. 1. The relationship between $\log(MW)$ and retention volume (V_R) for polystyrene MW standards on Bondagel E-125 with THF as the solvent.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between $\log(MW)$ and retention volume (V_R) for polystyrene MW standards chromatographed on the Bondagel E-125 column. This curve approximates the upper and lower MW limits of the column but cannot be used for an absolute PF MW calibration since the hydrodynamic volumes of PF and polystyrene molecules of the same MW are different.⁹

Figure 1 exhibits the typical S-shape of calibration curves⁹ in which the 100K polystyrene standard approaches the column exclusion limit and the 0.8K standard approaches the total permeation limit. The nonlinear relationship does not detract from the accuracy of the column for determining the average MW of a polymer.⁹ Based on the MW of the polystyrene standards, the Bondagel E-125 is able to accommodate the MW range of a normal PF resin.

Figure 2 shows the changing molecular weight distribution of a PF resin as a function of reaction time. As the MW of the resin increases, the peaks shift toward smaller retention volumes. As shown in Figure 2, the PF resin synthesized in this study did not reach the MW of a commercial PF resin.

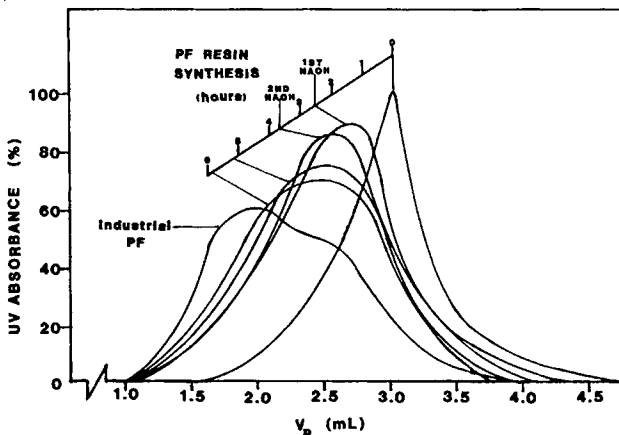


Fig. 2. Chromatographs of a PF resin at time intervals during synthesis as analyzed by HPSEC on Bondagel E-125 with 0.1M LiCl/DMF as solvent at a flow rate of 1.0 mL/min.

CONCLUSIONS

This study shows that the MW increase of a PF resin during synthesis can be rapidly monitored in under 5 min with the Bondagel E-125 column. HPSEC analyses with a Bondagel column could be a valuable tool for monitoring and optimizing the MW distribution of a PF resin during commercial synthesis or in research laboratory studies. This method would be faster and more accurate than those currently used.

References

1. A. Pizzi, in *Wood Adhesives: Chemistry and Technology*, A. Pizzi, Ed., Dekker, New York, 1984, Chap. 3.
2. L. Gollob, R. L. Krahner, J. D. Wellons, and A. W. Christiansen, *For. Prod. J.*, **35**(3), 42 (1985).
3. W. W. Yau, J. J. Kirkland, and D. D. Bly, *Modern Size Exclusion Liquid Chromatography*, Wiley, New York, 1979.
4. A. Sebenik, *J. Chromatr.*, **160**(1), 205 (1978).
5. T. Takeuchi and D. Ishii, *J. Chromatr.*, **257**(2), 327 (1983).
6. M. Duval, B. Bloch, and S. Kohn, *J. Appl. Polym. Sci.*, **16**(7), 1585 (1972).
7. J. D. Wellons and L. Gollob, *Wood Sci.*, **13**(2), 68 (1980).
8. J. W. Adams, and M. W. Schoenherr, U.S. Pat. 4,306,999 (1981).
9. J. V. Dawkins, in *Steric Exclusion Liquid Chromatography of Polymers*, J. Janca, Ed., Dekker, New York, 1984, Chap. 2.

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