Characterization of hyperbranched polyols by multiple detection SEC

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Introduction
Polymerization of fatty acids with multiple hydroxyl groups inadvertently leads to hyperbranched polymers with molecular weights, degree of branching and macromolecular shape dependent on the degree of polymerization. Characterization of hyperbranched polymers as a function of the extent of reaction is of practical and theoretical interest. We have investigated the solution properties of novel bio-based hyperbranched polyols from hydroformylated methyl esters of soybean oil. A range of hyperbranched polyols with acceptable viscosities and hydroxyl values, suitable for application in PU foams, was obtained by ceasing the reaction at different polymerization degrees. We used multiple-detection size exclusion chromatography and batch-mode light scattering to follow structure development during reaction. A relative MW/Mn of 2.6±1.2 was attributed to the AB type monomers. We studied the power relationship of radius of gyration and molecular weight, and viscometric radius and molecular weight.

Experimental
Synthesis of hyperbranched polyols
- Hydroxyl groups were introduced into fatty acid methyl esters of soybean oil by the hydroformylation/reduction process.
- With the ester groups designated as A and the hydroxyls designated as B, the monomer mixture contained 15% of hydroformylated methyl esters of palmitic and stearic acids (monomer type A), 28% of hydroformylated methyl oleate (AB1), 54% of hydroformylated methyl linoleate (AB2) and 3% of hydroformylated methyl linolenate (AB3).
- Hyperbranched polyols were made by transesterification reaction.

Solution properties – multiple detection SEC
- The SEC system consisted of:
  - Pump 530 (Waters Corp., Milford, MA);
  - Manual 200 µl injection (Rheodyne, Rohnert Park, CA);
  - Three Phenogel g.lc. columns (500, 1000, and 1000 Å plus a Phenogel guard column from Phenomenex (Torrance, CA)) covering a MW range of 10^2–10^7;
  - Multisize LD detector; Dawn EOS (Wyatt Technology Corp., Santa Barbara, CA);
  - Differential refractometer, Optilab EX (Wyatt), and Viscosity detector, Viscotek (Wyatt).
- Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.00 ml/min.
- The concentration of the injected solutions varied from 29 to 13 mg/ml and were higher for lower MW samples.
- Astra V 5.3.4.20 software (Wyatt) was used for data processing.

Results
Sensitivity of the detectors

MW and MW distribution of HB polyols
- Multimodal distribution is a consequence of mainly transesterification but also intersterification.

Rheological properties of the HB polyols
- MW vs. RT curves are not straight and do not overlap indicating the exponent of radius of gyration and molecular weight, and viscometric radius and molecular weight.

Universal calibration
- Even in the early elution, the fractions of the four polyol samples and their linear analogue that eluted at the same time had different Rg’s.
- The curves do not lie along a master curves.

Conclusions
- Multiple detection SEC is a powerful technique for studying solution properties of complex macromolecules such as hyperbranched polymers.
- Sensitivity of the LS detector was low at low molecular weights. Additional complications were due to the refractive index changes in this region.
- The upturn on the MW - retention time and Rg - MW plots was assigned to either adsorption onto or trapping by the gel pores.
- The MW, size, and [η] of AB polyols were, as expected, smaller than that of their linear analogues of the same molecular weight.
- Conformational analysis showed that HB polyols were roughly spherical in shape. Small MW-dependence of [η] at high MW coupled with large geometric volume suggests the presence of linear-chain portions extended from the dense core.
- The exponent n in the Mark-Houwink equation was around 0.4 for M > 10^5 g/mol and decreased to around 1.6 for M < 10^5 g/mol.
- The second virial coefficient, determined in the batch-mode, had positive but small values.
- The samples did not follow the universal calibration curve. Separation in SEC was not based purely on the hydrodynamic volume due to the heterogeneity in branching density and molecular structure.

References