

Characterization of hyperbranched polyols by multiple detection SEC

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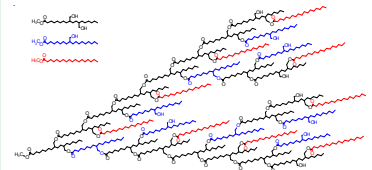
Introduction

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 biobased 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 relatively narrow M_w/M_n of 2.6-3.2 was attributed to the AB₂-type monomers. We studied the power relationship of radius of gyration and molecular weight, and viscometric radius and molecular weight.

Experimental

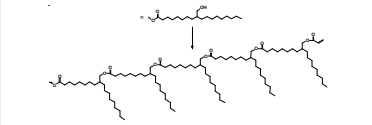
Synthesis of hyperbranched polyols

- Hydroxyl groups were introduced into fatty acid methyl esters of soybean oil by the hydroformylation/hydrogenation 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 (AB), 54% of hydroformylated methyl linoleate (AB₂) and 3% of hydroformylated methyl linolenate (AB₃).
- Hyperbranched polyols were made by transesterification reaction.



Structure of an HB polyester polyol with an M_n of 10,976 g/mol and 10 OH groups. Three major components of fatty acid methyl esters are also displayed

- A linear reference was made by self-condensation of hydroformylated methyl oleate (AB).
- A characteristic property of prepared AB₂ monomers and consequently HB polyols was the presence of dangling side chains (length from 3 to 18 carbons).



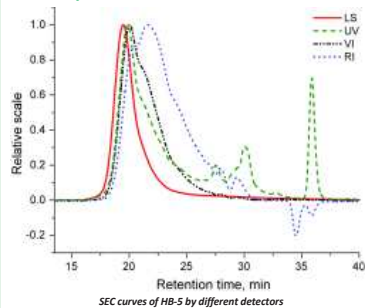
Synthesis of the linear reference: polyhydroformylated methyl oleate (PHFMO)

Solution properties – multiple detection SEC

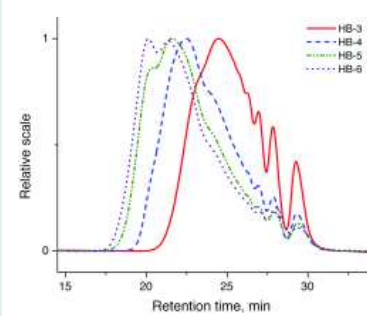
- The SEC system consisted of:
 - Pump 515 (Waters Corp., Milford, MA);
 - Manual 200 μ l injector (Rheodyne, Rohnert Park, CA);
 - Three Phenogel 5 μ m columns (100, 1000, and 10000 Å) plus a Phenogel guard column from Phenomenex (Torrance, CA) covering a MW range of 10^2 - 10^6 ;
 - Multiangular LS detector, Dawn EOS (Wyatt Technology Corp., Santa Barbara, CA);
 - Differential refractometer, Optilab rEX (Wyatt); and
 - Viscosity detector, ViscoStar (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

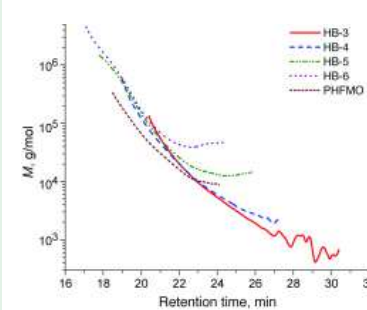


MW and MW distribution of HB polyols



Chromatograms of HB-3 to HB-6 obtained with the RI detector

- Multimodal distribution is a consequence of mainly transesterification but also interesterification.



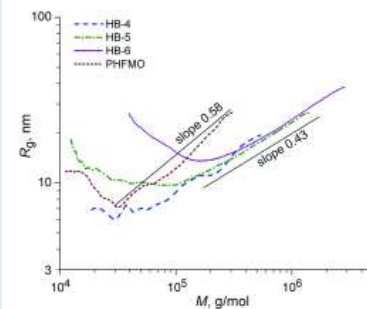
M_w plotted as a function of the retention time for the HB polyols and PHFMO

- MW vs. RT curves are not straight and do not overlap indicating diverse molecular structure that changed throughout the polymerization.
- Turning point - adsorption onto the pore surface or trapping by the tortuous pore structure.

Average Molecular Weights and Refractive Indices of the HB Polyols and PHFMO

Sample	M_n , g/mol	M_w , g/mol	M_w/M_n	dn/dc , ml/g	n_D at 25°C
HB-3	2.1×10^3	5.5×10^3	2.6	0.079	1.472
HB-4	6.1×10^3	1.9×10^4	3.2	0.081	1.474
HB-5	2.3×10^4	6.9×10^4	2.9	0.081	1.475
HB-6	4.2×10^4	1.3×10^5	3.2	0.081	1.475
PHFMO	2.1×10^4	3.2×10^4	1.6	0.080	—

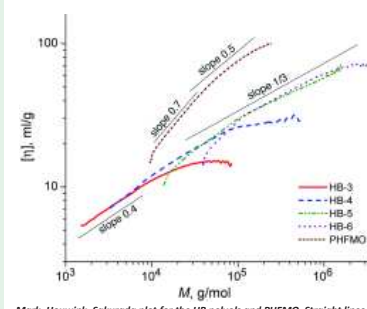
Radius of gyration



Dependence of R_g on MW for HB-4, HB-5, HB-6, and PHFMO

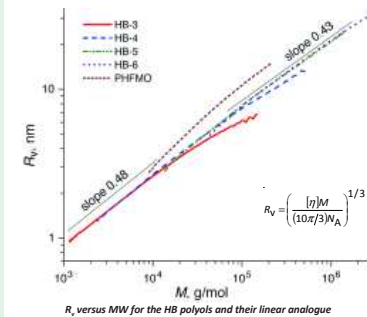
- $v = 0.43$ indicates polymer conformation between globular and linear.

Rheological properties of the HB polyols

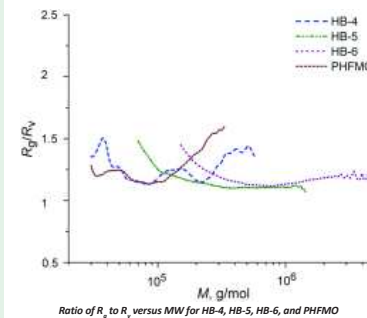


Mark-Houwink-Sakurada plot for the HB polyols and PHFMO. Straight lines are drawn to indicate the Mark-Houwink-Sakurada equations with specific slopes.

- The downward deviation indicates the presence of high-MW components.
- The small value of the slope confirms that polymer is compact and close to globular.
- The high-MW components may have had linear-chain portions like antennas stemming from the dense core, and they were vulnerable to local side-chain alignment.

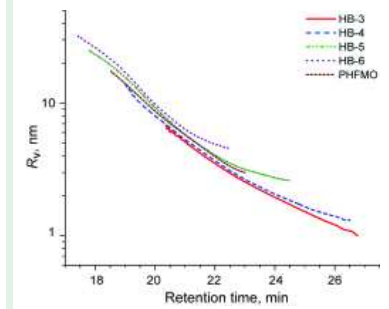


R_g versus MW for the HB polyols and their linear analogue



Ratio of R_g to R_v versus MW for HB-4, HB-5, HB-6, and PHFMO

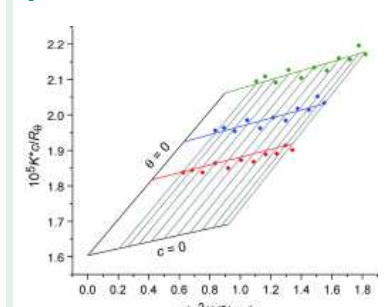
Universal calibration



R_v as a function of the retention time for the HB polyols and their linear analogue

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

A₂ values of the HB polyols



Zimm plot of HB-5 (scaling factor, $k = 171.3$ ml/g; $c = 2.45, 3.68$, and 5.25 mg/ml; and optical constant, $K^* = 3.72 \times 10^4$ ml²cm³/g²)

- The A_2 values of HB-polyols and their linear reference were on the order of 10^{-4} ml²-ml/g.
- The large values of $A_2 M_w / [\eta]$ despite a small A_2 indicates that HB-polyols and high-MW fraction of PHFMO have a dense core with extended antennas.

M_w, R_g, A_2 and $A_2 M_w / [\eta]$ of the HB polyols and PHFMO (highest MW fraction)

Sample	M_w , g/mol	R_g , nm	A_2 , ml ² -ml/g ²	$A_2 M_w / [\eta]$
HB-5	$6.2 \pm 0.1 \times 10^4$	17 ± 3	$4.3 \pm 0.2 \times 10^{-4}$	1.6
HB-6	$1.8 \pm 0.3 \times 10^5$	26 ± 2	$8.0 \pm 2 \times 10^{-5}$	0.5
PHFMO	$4.0 \pm 0.6 \times 10^5$	42 ± 4	$1.7 \pm 0.3 \times 10^{-4}$	1.4

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 R_g - MW plots was assigned to either adsorption onto or trapping by the gel pores.
- The MW, size, and $[\eta]$ of HB 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 $[\eta]$ at high MW coupled with large geometric volume suggests the presence of linear-chain portions extended from the dense core.
- The exponent α in the Mark-Houwink equation was around 0.4 for $M < 10^4$ g/mol and decreased to around $1/3$ 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

- Petrovic, Z. S., Cvetkovic, I., Milic, J., Hong, D. and Javni, I. (2012), Hyperbranched polyols from hydroformylated methyl soyate. J. Appl. Polym. Sci., 125: 2920–2928. doi: 10.1002/app.36232
- Milic, J., Teraoka, I. and Petrovic, Z. S. (2012), Solution properties of biobased hyperbranched polyols investigated by multiple-detection size exclusion chromatography. J. Appl. Polym. Sci., 125: E586–E594. doi: 10.1002/app.36800