

Hyperbranched Polyols from Hydroformylated Methyl Soyate

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ABSTRACT: Hydroformylation of methyl soyate produces a mixture of fatty acid methyl esters with zero, one, two, and three hydroxyl groups, the major component being with two hydroxyls (around 50%). Polymerization of methyl esters of hydroxy fatty acids gives a hyperbranched product with a different content of hydroxyl groups depending on the degree of conversion. Molecular weights can be controlled by controlling the degree of conversion but also using monofunctional components. A range of hyperbranched polyols with acceptable viscosities and functionalities, suitable for flexible applications, was obtained by stopping the reaction at varying degrees of conversion. Monte-Carlo simulation of the polymerization of hydroxylated methyl soyate gave molecular weights and polydispersity which were compared with experimental values. Although hydroxy-

lated methyl soyate contains considerable amounts of mono- and difunctional fatty acids, the system produces a physical gel at the highest conversions. This is due to very high molecular weights and was confirmed by experiments and the simulation. The simulation unexpectedly gave lower molecular weights but wider distribution than the experiments. This discrepancy was explained by the combination of experimental difficulties and possible side reactions leading to higher molecular weights. Functionality of polyols determined from gel points at critical NCO/OH ratios was reasonably close to predictions. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2920–2928, 2012

Key words: hyperbranched; renewable resources; structure-property relations; polyesters; synthesis

INTRODUCTION

Properties of flexible polyurethanes are determined to a large extent by the polyol component, having typically molecular weights above 3000 and functionality greater than 2. Currently, vegetable oil polyols usually have lower molecular weights and functionality that varies from molecule to molecule.^{1,2} Increasing the molecular weight of vegetable polyols significantly increases viscosity. One way to obtain polyols of higher molecular weight and controlled functionality is to use the concept of hyperbranching.³ Branched polymers are known to have lower viscosities than their linear analogues. Polyester polyols prepared from fatty acids (FA) are of special interest due to the availability of fatty acid methyl esters (bio-diesel). Methyl esters must be functionalized by introducing hydroxyl groups in order to create polymerizable fatty acids. In this work we have prepared hydroformylated soybean oil fatty acid methyl esters by introducing methylol groups at the position of double bonds. Major components of the FA mixture were two saturated fatty acids, palmitic and stearic,

and three hydroformylated FA, oleic, linoleic, and linolenic, having one, two, and three hydroxyls, respectively. Hydroformylation is a process where double bonds react with hydrogen and carbon monoxide to give an aldehyde, which is then reduced to a hydroxyl by hydrogenation.⁴ The process is illustrated in Figure 1.

The structure of hydroformylated methyl esters of soybean oil (SBO) is given in Figure 2. It should be noted that oleic acid gives two isomers with methylol groups attached either to the 9th or 10th carbon, while linoleic acid gives four and linolenic eight isomers (three methylol groups could be attached to the 9th, 10th, 12th, 13th, 15th, or 16th carbons). The starting mixture consists of monomers of the type A, A-B, A-BB, and ABBB, where A is an acid or methyl ester group, and B is the hydroxyl group. Preparation of the A-BB type hyperbranched polymers is well known.⁵

This mixture can self-polymerize to very high molecular weights forming hyperbranched polyols. The degree of polymerization (or conversion) determines the functionality of the polyol, its molecular weight, and molecular weight distribution, viscosity, hydroxyl, and acid number (if one starts from the hydroxy fatty acids rather than hydroxylated methyl esters). Three major components of the hydroformylated methyl soyate are species with two hydroxyls (~ 50%), one hydroxyl (~ 25%), and saturated fatty

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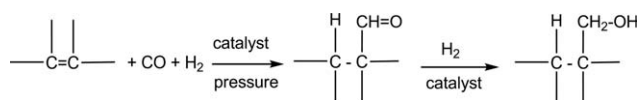


Figure 1 Hydroformylation of internal double bonds and hydrogenation reactions.

acids (15%). A schematic representation of a polyol from these three components is given in Figure 3.

In the simple case of self-condensation of dihydroxylated linoleic acid (A-BB case), which is similar to the generation of a family tree (Fig. 4), the properties are related to the generation, g , as in dendrimers, although the shape of molecules is irregular and the molecular weight distribution is wider. Thus, we can talk about a pseudo generation rather than a true generation. It is instructional to analyze the properties of polyols obtained in this simple case because linoleic acid is the major component in our real system, which is a modified model A-BB case.

The relationships between the generation (g) and functionality, taken to be the number of OH groups per molecule (f), OH number, acid number, and molecular weight (M) for the A-BB case can be calculated:

$$f = (f_0)^g \quad (1)$$

$$\text{number of monomers in the polyol, } N = f - 1 \quad (2)$$

$$\text{molecular weight, } M = NM_0 - 18^*(N - 1) \quad (3)$$

(M_0 = molecular weight of the monomer = 344.53 in our case)

$$\text{acid number} = 56,100/M \quad (4)$$

$$\text{OH number} = 56,100*f/M \quad (5)$$

Number and weight average degrees of polymerization (\bar{x}_n and \bar{x}_w , respectively) for this simple case can be calculated from the expressions⁶:

$$\bar{x}_n = 1/[1 - \alpha(f - 1)] \quad (6)$$

$$\bar{x}_w = [1 - \alpha^2(f - 1)]/[1 - \alpha(f - 1)]^2 \quad (7)$$

where f was defined earlier and α is the branching parameter, which is equal to the conversion of the hydroxyl groups, p_b :

$$\alpha = p_b = p_a/(f - 1) \quad (8)$$

Dependence of structural parameters on the generation is given in Table I for the case of 10,12-bis(hydroxymethyl) octadecanoic acid obtained by hydroformylation of linoleic acid. All properties of polyols obtained from this regular monomer can be calculated directly as shown in Table I. While the limiting acid number is zero (conversion based on acid

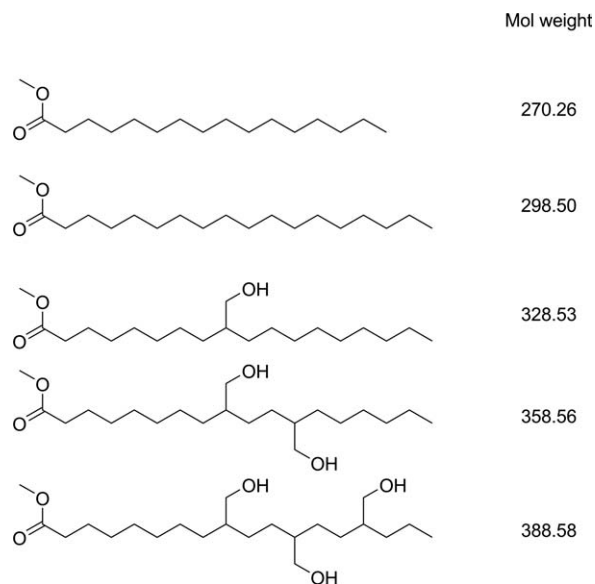


Figure 2 Schematic representation of fatty acid methyl esters from soybean oil with zero, one, two, and three hydroxyl groups obtained by hydroformylation route.

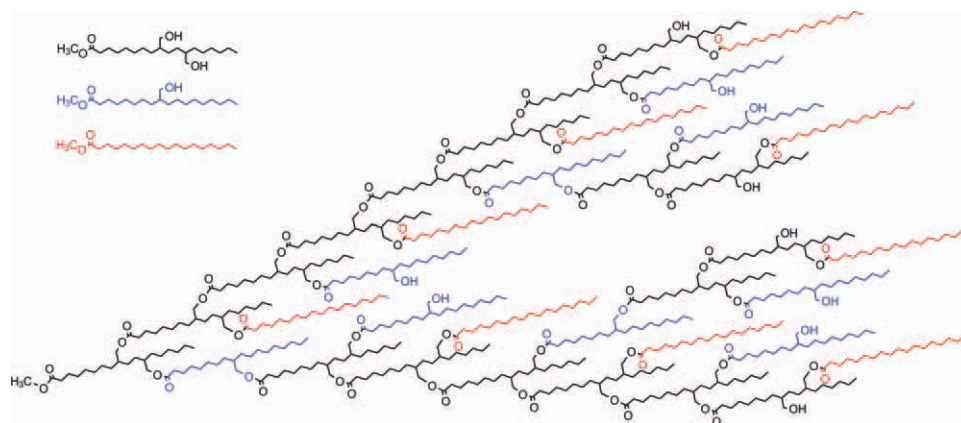


Figure 3 Hyperbranched polyol from hydroformylated methyl soyate with a molecular weight of 10,976 and 10 OH groups. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

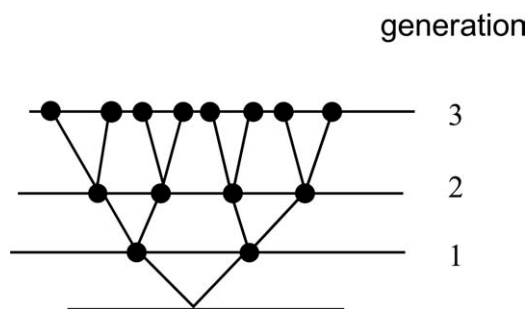


Figure 4 Growth of a branched polymer from A-BB monomers.

groups is 100%), the limiting OH number for this system is 171 and conversion based on OH groups is 50%. Table I also shows that already in the third generation the degree of polymerization is 7, functionality is 8, and M_n is 2304 (M_w is 4.4 times higher). The polydispersity index (\bar{x}_w/\bar{x}_n) increases quickly with increasing conversion. Maximal OH equivalent weight is relatively low at 328, suitable for rigid or semirigid applications. Using the OH number for the assessment of conversion is fairly difficult since changes in the OH number at high conversions are small and often within the limits of experimental error. Yet, a small increase in conversion produces a large increase in molecular weight and functionality. However, if polymerization is done with methyl esters, then the assessment of conversion from OH number is the only option. The extent of reaction (conversion) can be expressed in different ways. We calculated conversion from the amount of water (or methanol in the case of transesterification) relative to the maximum loss at 100% conversion. Weight loss at the end of reaction due to the removal of water is 5.6% and methanol 9.5% in the case of hydroformylated fatty acids from soybean oil (hydroformylated methyl soyate).

In the case of polycondensation of the hydroformylated methyl soyate, the reaction of the hydroxy-

leic component but especially the stearic and palmitic components will decrease the OH number, increase OH equivalent, and reduce functionality. Calculation of properties for such a case is more complicated and using Monte-Carlo simulation proved advantageous. Although we carried out polymerization by transesterification of methyl esters of hydroformylated soybean fatty acids, the simulations were carried out with the acid form for simplicity. The objective of this work was to study the development of the structure and properties of hyperbranched polyols obtained by transesterification of hydroxy fatty acids from soybean oil at different times and compare them with theoretical predictions. Polyols of different molecular weight and functionality were obtained by withdrawing samples at different reaction times and measuring their properties. Conversions were calculated from experimentally determined OH numbers and the simulations were carried for the same conversions. To determine functionality, the polyols were reacted with diphenylmethane diisocyanate (MDI) at different NCO/OH ratios to find the critical ratio at which gelation does not take place as shown in the Appendix.

EXPERIMENTAL

Materials

Hydroformylated fatty acid methyl esters were prepared by methanolysis of the soy oil-based polyol obtained by hydroformylation.^{7,8} The polyol had OH# (TSI) = 235.8 mg KOH/g and acid value A.V. = 1.3 mg KOH/g. Methanolysis was carried out with the excess of methanol (15 times) and in a presence of the potassium methoxide catalyst (1 wt % relative to oil) for 2 h at the reflux of methanol (65–68°C). After cooling down, the reaction mixture was diluted with diethyl ether and washed several times first with brine and later with water. The oil phase

TABLE I
Parameters of Hyperbranched Polyols of Different Generations from Hydroformylated Linoleic Acid

Generation	Functionality, f	OH#	Acid#	M_n	x_n	Conversion of OH groups (%)	OH equiv	x_w^a	\bar{x}_w/\bar{x}_n
1	2	325.6	162.8	344.5	1	0.0000	172.26	1	1.0
2	4	224.9	56.2	997.6	3	0.3333	249.4	7	2.3
3	8	194.8	24.4	2303.7	7	0.4286	288.0	31	4.4
4	16	182.6	11.4	4915.9	15	0.4667	307.2	127	8.5
5	32	177.0	5.5	10140	31	0.4839	316.9	511	16.5
6	64	174.4	2.7	20589	63	0.4921	321.7	2047	32.5
7	128	173.1	1.35	41487	127	0.4961	324.1	8191	64.5
8	256	172.4	0.67	83283	255	0.4980	325.3	32767	128.5
9	512	172.1	0.34	166875	511	0.4990	325.9	131071	256.5
10	1024	172.0	0.17	334058	1023	0.4995	326.2	524287	512.5

^a x_n and x_w were calculated for a given conversion of OH groups using eqs. (6) and (7). OH# and acid# are given in mg KOH/g.

was dried overnight with anhydrous sodium sulfate. After filtration, and vacuum evaporation of the residual solvent, methyl esters of the hydroformylated soybean oil are obtained, having OH# (TSI) = 221.4 mg KOH/g (OH# by the phthalic method was = 215.7 mg KOH/g) and acid value 1.08 mg KOH/g.

Methods

The composition of methyl esters of hydroformylated fatty acids given earlier was analyzed by a Shimadzu GC/MS Gas Chromatograph with a QP5000 Mass Spectrometer detector. Experiments were carried out with methylene chloride as solvent and with the flow rate of 0.089 MPa (13 psi) and split flow of 72.4 mL/min. Column ZB-5 (30 m, $d = 0.32$, polarity 8) with phases consisting of 5% diphenyl and 95% of dimethyl-polysiloxane was used to identify the monomer. Temperatures: injector 235°C, detector 300°C. Oven program 150°C for 4 min ramped to 250°C at 4°C/min then held for 15 min at 250°C.

Hydroxyl numbers of the polyols were determined according to the ASTM E 1899-97 using a reaction with *p*-toluenesulfonyl isocyanate (TSI) and potentiometric titration with tetrabutylammonium hydroxide as well as with phthalic anhydride method. Acid values were determined by IUPAC 2.201 method, using a 1 : 1 (V : V) toluene/isopropanol mixture as solvent.

Viscosity was determined using an AR 2000ex Rheometer (TA Instruments) at 25°C, with cone/plate geometry (truncation height 55 μm for the 40 mm diameter, 2° cone).

Swelling ratio and soluble fraction were measured according to ASTM C1247, using toluene as a solvent.

Molecular Weights (MW) and MW distribution were determined using a Waters Gel Permeation Chromatograph (Waters Corporation, Milford, MA) consisting of a 510 pump, 410 differential refractometer, and data collection system. Tetrahydrofuran (THF) was used as the eluent at 1.00 mL/min at 30°C. Four Phenogel 5 μm columns (50, 100, 1000, and 10,000 Å) and a Phenogel guard column from Phenomenex (Torrance, CA), covering MW range of 10^2 to 10^6 were used.

Synthesis of the hyperbranched polyols

Polycondensation of the M-HFSBO was carried out in a three-neck, 250 mL reaction flask with Dean Stark trap, nitrogen inlet, and magnetic stirrer. The reaction was carried out at 175°C using an oil bath, equipped with a digital thermometer. The reaction procedure involved running under nitrogen for 1 h, medium vacuum for 1 h, and finally heating under high vacuum till the end. The catalyst was titanium

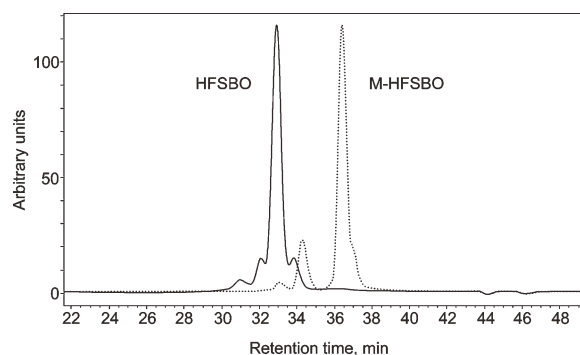


Figure 5 GPC of the hydroformylated triglyceride polyol (HFSBO) and corresponding methyl esters (M-HFSBO).

(IV) isopropoxide, 0.1 wt % of the reaction mass. Maximum reaction time was 6.25 h (until mixing was limited by the high viscosity).

RESULTS AND DISCUSSION

GC/MS analysis of the hydroformylated fatty acids polyol mixture gave us the following composition: palmitic, 10.8 wt %; stearic, 3.9 wt %; oleic, 28.4 wt %; linoleic, 53.9 wt %, and linolenic, 2.9 wt %. GPC of the methyl esters of hydroformylated fatty acids (M-HFSBO), Figure 5, showed the presence of dimers and trimers resulting from vacuum distillation at high temperature. Oligomers decreased the OH number, but the value of the hydroxyl number calculated from the composition obtained from GC/MS analysis was about 130 mg KOH/g. The presence of oligomers was not detrimental to the reaction since they participated in transesterification reactions in much the same way as the monomeric species. Figure 5 also reveals the composition of the starting hydroformylated polyol which reflects the distribution of double bond contents in individual triglycerides.¹ The most abundant species are ones with four, five, and six double bonds, which give polyols with the same number of OH groups and give the central peak at 33 min. Triglycerides with zero, one, and two OH groups give the small peak on the right hand side (the difference in molecular weights is 64 or more due to the loss of two CH_2OH groups as well as the presence of 16 carbon fatty acids). The species with higher molecular weights give a peak on the left side of the central peak.

Number average functionality, f_n , of the starting polyol (number of OH groups per molecule) was 1.37 both in the ester and acid form and weight average functionality, $f_w = 1.84$. Reacting this mixture with diisocyanate will not result in a cross-linked product because of the low polyol functionality. The functionality of the polyol increases with increasing molecular weight. Gel points correlate better with the weight average functionality.

TABLE II
Designation and Properties of Polyols Obtained after Different Reaction Times

Sample designation ^a	Reaction time (h)	OH number (mg KOH/g)	OH equiv.	Viscosity (Pa s)	Monomer content (%)
HB-0	0	230	244	<0.05	100
HB-1	2	165	340	–	25
HB-2	2.75	129	434	–	13
HB-3	3.25	115	488	1.7	7
HB-4	4.5	97	578	13	3
HB-5	5.5	86.6	648	32	2
HB-6	6.25	86.2	651	123	1.5

^aSample numbers reflect reaction times in hours.

For simulation we used the same composition of fatty acids but in the acid rather than ester form, having the following properties: $M_n = 321$, $M_w = 325$, OH number = 240 mg KOH/g, OH equivalent weight = 234 g/mol and acid number = 174 mg KOH/g. At 100% acid conversion the whole reaction mass becomes one molecule of infinite molecular weight and functionality, dependent on the size of the sample. In practice such conversion is unattainable but very high molecular weights (million range) are obtainable. At very high molecular weights this material will be impossible to handle. Thus, to control viscosity, OH number, and functionality for all practical applications the reaction must be stopped before total conversion. In this work we stopped the reaction at different conversions and measured physical properties of polyols, molecular weights, and distribution by GPC combined with light scattering (LS). Table II shows the properties of samples withdrawn from the reaction mixture at different times.

The last four samples of hyperbranched polyols were taken for a further structural analysis since

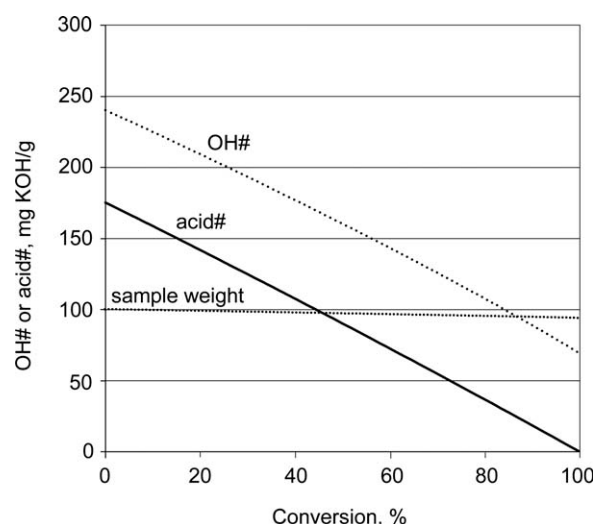


Figure 6 Change of acid number, hydroxyl number, and sample weight with conversion for the acid form of hydroxy fatty acids.

their molecular weights were sufficiently high and monomer content low. The change of acid number, hydroxyl number, and sample weight with conversion is illustrated in Figure 6. At 100% of acid conversion the sample weight is 94.4% of the initial weight and hydroxyl conversion 72.8% for the acid form of hydroxy fatty acids. The sample weight for the methyl ester form of hydroxyl fatty acids at 100% conversion is 90% of initial value but hydroxyl number is about 69 mg KOH/g as for the acid form. Dependence of acid and hydroxyl numbers on conversion is slightly nonlinear because of the water or methanol loss. A specific feature of the fatty acid-based hyperbranched polymers is the presence of side (dangling) chains varying in length from 3 to 18 carbons. Dangling chains do not affect polymerization but may lower viscosity of polyols.

Molecular weight distribution in the last four samples as obtained by GPC is given in Figure 7. It is evident that monomer content decreases and the curves shift to lower elution times (higher molecular weights) with increasing time of synthesis. M_n values determined by GPC/light scattering were 2130, 6050, 23,360, and 41,990 for the samples with OH# 115, 97, 86.6, and 86.2, respectively. Corresponding M_w values were 5485, 19,430, 68,520, 134,700. Solution properties of these polyols will be treated in a separate paper. GPC curves show a multimodal distribution at high molecular weight. Separation of hyperbranched polymers is done by hydrodynamic volume and at high molecular weights it is possible

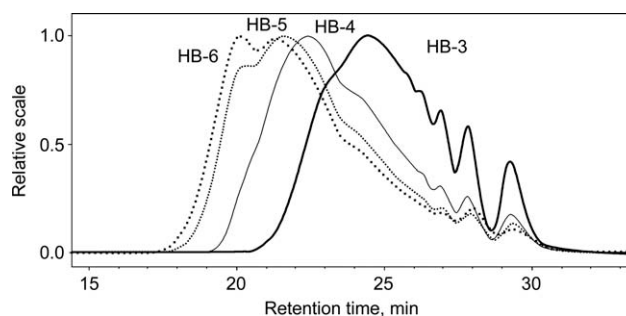


Figure 7 GPC traces of four samples.

TABLE III
Calculated Values for Self-Polymerization of Hydroxyl Fatty Acids From Soybean Oil

Sample designation	$M_{n(\text{simul})}$	$M_{w(\text{simul})}$	$M_w/M_{n(\text{simul})}$	Acid# (mg KOH/g)	OH# (mg KOH/g)	OH equivalent	Conversion ^b (%)	f_n/f_w ^c	M_n/M_w by GPC/LS
HB-0	321 (336)	324 (338)	1.01	174 (167) ^a	240 (230)	234(244)	0/0	1.37/1.38	
HB-2	886	2146	2.4	57.9 (57.3)	129 (129)	435(435)	68/49.5	2.04/-	
HB-3	1278	4113	3.2	43.6 (43.4)	114 (115)	492(488)	76/55.3	2.59/5.4	2130/5485
HB-4	2252	11,836	5.1	25.6 (25.6)	96 (97)	584(578)	86/62.3	3.70/12.4	6051/19,430
HB-5	3528	28,455	8.1	15.8 (15.8)	86 (86.6)	652 (647)	91.4/66.5	5.45/23	23,360/68,520
HB-6	3754	31,112	8.3	15.4 (15.4)	85 (86.2)	660 (651)	91.6/66.7	5.56/-	41,990/134,700
HB-100	∞	∞		0	69 (69)	801	100/72.8		

^a Values in brackets are for the methyl ester form. Acid numbers of polymerized methyl esters are equivalent values calculated from the polyacids corrected for the higher MW.

^b Conversions based on acid and hydroxyl groups are calculated.

^c f_n was calculated from simulation data and f_w was obtained experimentally from gelation theory (Appendix).

to have different molecular weights at the same hydrodynamic volume.

Conversion calculated from acid (or ester) groups, p_a , is related to the conversion of hydroxyl groups, p_b , by the initial molar ratio of the groups, r_a or r_{OH} :

$$r_a = 1/r_{OH} = p_b/p_a = [\text{COOH}]/[\text{OH}] \quad (9)$$

In our case r_{OH} was 1.374 and $r_a = 0.7277$. Number average functionality (number of OH groups per molecule) of the mixture was $f_n = 1.37$ and weight average functionality, $f_w = 1.84$. Lower than 2 functionality of the mixture is expected, since the major component is two-functional but hydroformylated oleic is monofunctional and saturated acids zero-functional. The average functionality is calculated from the expressions

$$f_n = \sum N_i f_i / \sum N_i \quad (10)$$

$$f_w = \sum N_i f_i^2 / \sum N_i f_i \quad (11)$$

where N_i is the number of moles of species with functionality f_i .

Reaction simulation

The reaction simulation was carried out using a commercial program, DryAdd+ (DryAdd, Intelligensys, UK, 2003), starting from one million molecules and ignoring cyclization reactions. The results are summarized in Table III. It shows that the values for the acid and ester form of polyols differ somewhat at low conversion. At full conversion they converge to a single value. The differences (about 10% at the start) arise from different molecular weights of ester and acid forms. OH numbers of methyl ester forms were measured and used to calculate acid numbers and OH equivalents. Conversion of acid groups is equivalent to the conversion from liberated reaction water corrected for the weight change dur-

ing reaction. Conversion of OH groups (p_b) is calculated from acid conversion and the relationship $p_a/r_{OH} = p_b/1.374$. Number and weight average molecular weights were obtained from simulated reactions.

It is evident that polydispersity (M_w/M_n) becomes wider as the reaction progresses, being 1 at the onset to about 8 (simulated) for the last sample. While f_n is calculated directly as $M_n/\text{OH equiv}$, the values for f_w were determined experimentally from the critical ratio for gelation. Approximate f_w values may be obtained by dividing M_w by OH equivalent. This procedure is correct only when functionality increases linearly with increasing molecular weight, which is only partially true in our case.

Determination of the OH number of the last sample (OH# 86.2 mg KOH/g) was difficult due to a very high viscosity and limited solubility. An error was probable as indicated by much higher viscosity for the slightly lower OH number, thus molecular parameters for this sample are questionable.

Molecular weights of the samples determined from GPC/light scattering are generally higher than simulated values especially for HB-6. Higher than calculated values may be caused by several factors: (a) overestimation of OH numbers resulting in underestimation of the conversion, (b) underestimation of the components with two and three OH groups in the initial composition, and (c) additional crosslinking reactions at elevated temperature, such as ether formation. Etherification (2%) was observed when 9-hydroxyoctadecane was heated under the same conditions for 7 h. Experimental molecular weight distributions were narrower than calculated, partly because of the overestimation of M_n by LS. The consumption of monomers, which also narrows MW distribution, was higher than predicted by simulation and the reason for this is not clear. Using GPC/light scattering for the estimation of the molecular weights of samples containing very low MW oligomers is challenging because of (a) the low

TABLE IV
Critical Ratios and Weight Average Functionality of Three Polyols

Sample designation	r (critical)	f_w
HB-3	0.225	5.4
HB-4	0.09	12.4
HB-5	0.05	23.2

HB-6 could not be mixed with MDI because of poor solubility and extremely high viscosity.

precision of LS at low molecular weights and changing refractive index; (b) the exclusion of low MW in the range selected for the analysis; (c) the complex structures of hyperbranched polymers having different molecular weights at the same hydrodynamic volume; and (d) difficulties in measuring precise OH numbers due to limited solubility.

Number average functionality increased considerably slower with conversion and increased molecular weight than in the example presented in Table I, because of the high content of saturated fatty acids and the monohydroxyl component.

Experimental determination of functionality f_w of hyperbranched polyols

Weight average functionality, f_w , can be assessed from the critical ratio (r_{acrit}) of functional groups [NCO]/[OH] to obtain a gel as shown in the Appendix. The tests were carried out by lowering the isocyanate index (ratio of [NCO]/[OH]) in an MDI/polyol system. For a system with a two-functional isocyanate and f -functional polyol critical gelation occurs at $r_{\text{acrit}} = 1/(f_{\text{aw}} - 1)$. Thus,

$$f_{\text{aw}} = (r_{\text{acrit}} + 1)/r_{\text{acrit}} \quad (12)$$

Critical ratios for three systems were measured by two ways, by reacting components at different ratios and testing the solubility of the product to find out whether or not the system gelled, and by rheological methods measuring G' and G'' with time or frequency, Table IV. The solubility method is not unambiguous since the networks close to the gel point are weak and may break due to the osmotic pressure, giving the impression that the material is soluble although small pieces of gel are present.

The high values for the f_{aw} for the lower OH# polyols indicate that these systems would gel at low conversion, which was experimentally observed. Gelation at low conversions may be useful in some applications (coatings) but it may be detrimental in others (foams). Thus, proper control of functionality is essential for specific applications. The control of functionality in our systems can be achieved by varying the ratio of components in the starting mix-

ture, for example by increasing or decreasing the amount of nonfunctional, or two- and three functional components.

CONCLUSION

A series of hyperbranched polyester polyols were prepared from hydroxy fatty acids methyl esters of soybean oil by transesterification, in order to observe the development of the molecular weights, functionality, viscosity, and chemical properties (OH number and OH equivalent) with reaction time. Polyols with workable viscosities were liquid up to 90% of ester group conversion. Compared with the simulation, larger molecular weights and lower polydispersities for the same conversion were observed. A rheological method for the determination of weight average functionality was successfully applied. Experimental weight average functionality increased to very high values despite the considerable presence of nonfunctional and monohydroxyl components in the starting mixture.

APPENDIX A

DETERMINATION OF FUNCTIONALITY OF HYPERBRANCHED POLYOLS

Functionality of polyols is important since it affects gelation properties (gel point) as well as properties of networks. Functionality of the mixture of species of different functionality is an average number. If f is a functionality of a species i then the number average functionality is:

$$f_n = \sum (N_i^* f_i) / \sum N_i \quad (A1)$$

where N_i is number of mols of species i in the mixture. Weight average functionality is defined as:

$$f_w = \sum (N_i^* f_i^2) / \sum (N_i^* f_i) \quad (A2)$$

The gel point correlates with weight average functionality, f_w , and is thus most important for the gelation process.^{5,9} Number average functionality can be easily obtained experimentally from M_n obtained by VPO or GPC and equivalent weight obtained from OH number:

$$f_n = M_n / \text{Eq.W} = M_n^* \text{OH\#} / 56110 \quad (A3)$$

Weight average cannot be easily obtained if exact composition and functionality of species are not known. True weight average functionality can be deduced using the gelation theory from the conversion at the gel point or from critical molar ratios to obtain gel. Both methods are time consuming since they

require following the gelation process and measuring the conversion close to the gel point or varying the molar ratio of components until gelation occurs.

The onset of gelation is of critical importance to processing thermoset systems. Models have been developed to predict the extent of reaction at the gel point. A commonly used example for step polymerizations is the statistical approach developed by Flory and Stockmayer¹⁰ assuming no intermolecular reactions.

Definitions

- p is the degree of conversion based on the reaction species (p_a , conversion measured by species a ; p_b , measured by species b). At the stoichiometric ratio $p_a = p_b$.
- r is the ratio of A to B groups ($r_a = p_b/p_a = [A]/[B]$, and $r_b = [B]/[A] = p_a/p_b = 1/r_a$).
- (note that while $r_a = [A]/[B]$ it is also $r_a = p_b/p_a$, i.e. p_b is in the numerator and p_a in the denominator). We can define the branching coefficient, α , as the probability that a given functional group of a branch unit at the end of a polymer chain segment leads to another branch unit.

In the absence of intramolecular reactions:

$$\alpha_c = p_a p_b = p_a^2/r_b = p_b^2/r_a = 1/[(f_{aw} - 1)(f_{bw} - 1)] \quad (\text{A4})$$

For the stoichiometric ratio of components when $r_a = r_b = 1$ and when diisocyanate with $f_{bw} = 2$ is used with the polyols of functionality f_{aw} :

$$p_a^2 = 1/(f_{aw} - 1) \quad (\text{A5})$$

$$p_a = [1/(f_{aw} - 1)]^{0.5} \quad (\text{A6})$$

$$f_{aw} = 1/p_a^2 - 1 \quad (\text{A7})$$

The problem of precision arises when $f > 1$ when the method becomes relatively insensitive. For example, differentiation between the gel points of a 10 functional ($p = 33\%$) and 9 functional ($p = 35\%$) polyol with a diisocyanate is difficult since the difference in conversion is only 2% and this is well within the experimental error.

For the non-stoichiometric ratio with $f_{bw} = 2$, gelation occurs when:

$$(f_{aw} - 1) \leq r_a \leq 1/(f_{aw} - 1) \quad (\text{A8})$$

Thus, by changing the ratio of components we can find the critical r_a when the system starts gelling. A gel is obtained when the system loses fluidity while it is above T_g .

There are two convenient methods to determine experimentally the functionality of polyols:

1. Measure the conversion with time and apply equation $f_{aw} = 1/p_a^2 - 1$ close to the gel point.
2. Vary the molar ratio of hydroxyls to isocyanates (r_a) until gelation occurs and apply equation $(f_{aw} - 1) < r_a < 1/(f_{aw} - 1)$. For the lower than stoichiometric ratio of the component a , $f_{aw} = (r_{acrit} + 1)/r_{acrit}$.

The second method is easier to carry out experimentally. In the second case the diisocyanate concentration must be less than stoichiometric, because diisocyanate in excess can enter side reactions (allophanate formation, dimerization etc).

It should be remembered that intramolecular reactions do always occur and it takes a few percent higher conversion to reach gelation, giving a somewhat lower calculated functionality. However, in practice these values are usually adequate.

Another critical aspect of the method is the determination of the gel point. Determining whether the material gelled at different component ratios by dissolution is tricky since the gel at critical r is weak and may break into pieces under osmotic pressure of the solvent. Alternatively, one may use rheological methods to find whether the material is gel or sol.^{11,12} If a material is above glass transition loss modulus is larger than storage modulus in the sol state and reverse in the gel state. One can run the reaction in a rheometer (protected from moisture) and follow evolution of G' and G'' with time at a fixed frequency. When materials gel the crossover of two moduli takes place. If one runs a frequency sweep of the finished product then the relative values of G' and G'' should show the state of the material. At the gel point $G' = G''$ at all frequencies (ω), scaling with $\omega^{1/2}$

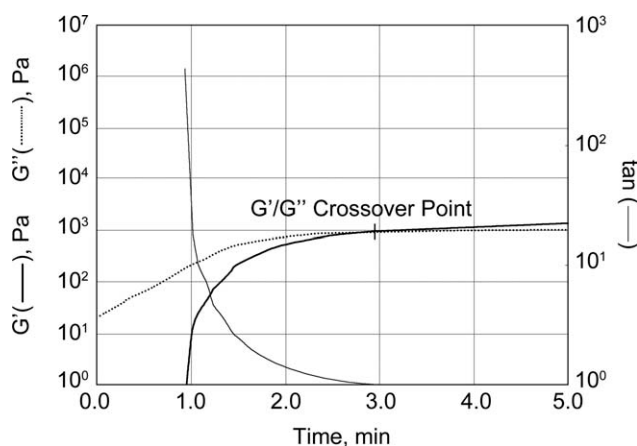


Figure 8 Change of G' and G'' in the reaction of the sample HB-3 with pure MDI at $[NCO]/[OH]$ ratio = 0.225 (the system is close to the critical ratio for gelation).

$$G'(\omega) \sim \omega^{1/2} \sim G'' \quad (\text{A9})$$

The method has been used with isocyanate cured polyols at the stoichiometric ratio of NCO/OH groups.¹³ To find whether or not a system will gel, the course of the reaction may be followed, as is shown in Figure 8. Alternatively, the reaction may be carried out to completion and the properties measured. Figure 8 shows the change of G' and G'' of a system very close to the critical ratio.

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