

Studies on Hyperbranched Polyurethane by Multidetector Size Exclusion Chromatography

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ABSTRACT: Hyperbranched polyurethane (HP) and its linear analog (LPU) were studied by size exclusion chromatography (SEC), utilizing a combination of refractive index (RI), right angle light scattering (RALLS), and differential viscosity (DV) detectors. The relationships between retention volume (V_e), intrinsic viscosity (η), radius of gyration (R_g), and the molecular structure were investigated. It was shown that the hyperbranched polyurethane had lower V_e , η , and R_g than its linear analog when they had the same molecular weight. The branching parameter g and g' were calculated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2445–2450, 2002

Key words: multidetector size exclusion chromatography; hyperbranched polyurethane; branching parameters

INTRODUCTION

Highly branched polymer structure has been given much attention in recent decades.^{1–5} The interest in such macromolecules stems from the possibility that, owing to their novel, highly branched, globular and unentangled structure, they may be expected to show new and helpful behavior both in solution and in bulk. Two distinct synthetic approaches to such highly branched structures have been developed. One approach is a stepwise growth process, involving a protection–deprotection strategy at every step of the growth process. The other is a single-step process, where an AB_x type monomer ($x \geq 2$) undergoes self-condensation polymerization. Although the former approach yields monodisperse polymers with well-defined structure, it often requires chromatographic purification of the products at every step of the growth process and therefore may be unsuitable for large-scale prepara-

tion. The latter approach, while being more suitable for scale-up, gives polymers with varying degrees of branching and also less precise molecular structure. The advantage of this one-pot AB_x approach, of course, lies in its potential for greater general applicability, should this class of polymers exhibit some potentially useful properties.

A more thorough investigation of a hyperbranched polymer reveals three different types of repeat units as illustrated in Figure 1. The constituents are dendritic units (D), fully incorporated AB_x monomers, terminal units (T) having the two B-groups unreacted, and linear units (L) having one B group unreacted. The linear segments are generally described as defects. The degree of branching (DB) in AB_2 systems according to the definition of Frey et al.⁶ was given by $DB = (2D + L)/(2D + L)$.

To date, two different techniques had been used to determine the degree of branching. The first technique was presented by Frechet et al.⁷ and involved the synthesis of low molecular weight model compounds resembling the repeat units to be found in the hyperbranched skeleton.

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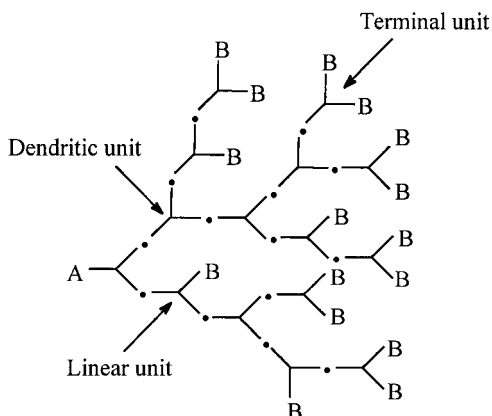


Figure 1 Different segment types present in hyperbranched polymer (AB_2 type).

The model compounds were characterized with NMR. From the spectra of the model compounds, the different peaks of the hyperbranched polymers could be assigned. The degree of branching was calculated from the integrals of the corresponding peaks in the spectrum of the polymer. This method was limited to polymers exhibiting differences in NMR for different building blocks. The other method, based on the degradation of the hyperbranched backbone, was presented by Kambouris and Hawker.⁸ The chain ends were chemically modified and the hyperbranched skeleton was fully degraded by hydrolysis. The degradation products were identified with capillary chromatography. Two chemical requirements had to be fulfilled to use in this technique. First, degradation must not affect chain ends, and second, the conversion into elementary submits must be complete.

Size exclusion chromatography (SEC) is a powerful method for determining molecular weight and molecular weight distribution of polymers. However, it is difficult to gauge the true molecular weight of the hyperbranched polymer due to its three-dimensional shape. The conventional SEC (with refractive index detection, or RI) was combined with a right angle laser light scattering photometer (RALLS) and a four-capillary bridge design differential viscometer (DV). The DV detector was used to monitor polymer solution viscosity, the RALLS detector was used to acquire the polymer molecular weight across the SEC chromatogram accurately, and the RI detector measures polymer concentration.

In this paper, the hyperbranched polyurethane and its linear analog were characterized by triple-detector SEC³. The properties of these two polymers were compared to try to get branching information about hyperbranched polyurethane.

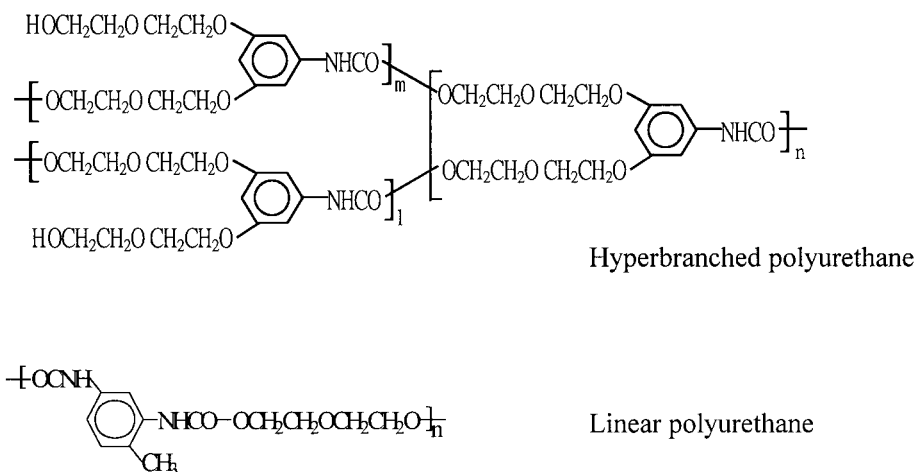
EXPERIMENT

Samples

The synthesis procedure of the hyperbranched polyurethane (HPU) has been described in detail in our previous report.⁹ The linear polyurethane was synthesis from toluene-2,4-diisocyanate (TDI) and diethylene glycol (DEG). The molar ratio of TDI: DEG was 1:1. Their structural formulas were showed in Scheme 1.

Size Exclusion Chromatography

A dual SEC detector (Model T60, Viscotek Corp.), with RALLS and DV detectors in series, was com-



Scheme 1 The structure of hyperbranched and linear polyurethane.

Table I Characterization Data of HPU and LPU Obtained via SEC¹, and SEC³

Samples	Method	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PD	$[\eta]_n$ (dL/g)	$[\eta]_w$ (dL/g)	R_{g_n} (nm)	R_{g_w} (nm)
HPU	SEC ¹	7800	21000	2.69	—	—	—	—
	SEC ³	28600	89900	3.14	0.0655	0.0835	4.43	5.84
LPU	SEC ¹	31900	93300	2.92	—	—	—	—
	SEC ³	32100	98400	3.06	0.289	0.380	7.47	10.00

bined on-line with a differential refractometer (RI, Model 410, Waters Corp.) coupled to a programmable high performance liquid chromatography (HPLC) pump (Model 590, Waters Corp.). Two chromatographic columns (American Polymer Standards Corp., Mentor, Ohio), measuring 30 cm in length and packed with 5 μm diameter polystyrene (PS) gel, were used in series. Tetrahydrofuran (THF) was degassed ultrasonically and used as the mobile phase at a flow rate of 1.0 mL/min. The samples were dissolved in THF at a concentration of 3.000 mg/mL and were filtered through 0.2 μm pore size membrane filters. Measurements were performed at 25°C, and injection volumes of the sample solutions were 100 μL . TriSEC software (Viscotek) was used to treat the data obtained.

RESULTS AND DISCUSSION

Characterization via SEC/RI (SEC¹) and SEC/RI/RALLS/DV (SEC³)

Characterization data of hyperbranched polyurethane and linear polyurethane obtained via SEC¹ and SEC³ were listed in Table I. The RALLS detector in SEC³ was a useful method to obtain the true molecular weight of polymers. Good agreement was observed between the molecular weights of LPU (linear analog of HPU) obtained via SEC¹ and SEC³. It meant that SEC¹ was a useful method for determining molecular weight of linear polyurethane. However, it can be found that SEC¹ can only give values of M_n and M_w relative to PS standards for the hyperbranched polyurethane, not the true average molecular weights.

Characterization data of PS standards, HPU, and LPU obtained via SEC³ were listed in Table II. M_i , $[\eta]_i$, R_{g_i} were molecular weight, intrinsic viscosity, and radius of gyration of each individual slice.

Figure 2 showed that the retention volumes of LPU were fit well on the PS calibration curve. The retention volumes of HPU were larger than those of PS standards and LPU with the same molecular. The LPU had a linear structure, while HPU had a highly branched structure. HPU had a smaller R_g than LPU with the same molecular due to its spherical shape (Table II). This meant that the retention volumes of HPU were larger than those of LPU. This also explained the reason that the molecular weight of HPU obtained via SEC¹ was smaller than the true molecular weights obtained via SEC³.

Figure 3 showed that HPU had lower intrinsic viscosity than LPU with the same retention volume. This meant HPU had a compact structure and had no chain entanglements. Figure 4 showed the plot of $\log M[\eta]$ vs V_e . It was interesting to note that the data points for LPU fit well on the PS calibration curve. However, the universal calibration concept was not applicable to HPU.

Mark–Houwink–Sakurada Equation Constants

Solution behaviors differed for hyperbranched polymers compared to linear polymers. Figure 5 showed the intrinsic viscosity as function of molar mass for LPU and HPU. The relationship between the two polymers was

$$\text{LPU: } [\eta] = 0.00198 \times M^{0.47} \quad (1)$$

$$\text{HPU: } [\eta] = 0.00083 \times M^{0.41} \quad (2)$$

Hyperbranched polyurethane exhibited a relatively low α value in Mark–Houwink–Sakurada equation and low intrinsic viscosities. This was consistent with highly branched and compact structures. Turner et al.^{10,11} also found the Mark–Houwink plots of hyperbranched polyester actually passed through an inflexion when the value of $\log M$ was about 3.5.

Table II Characterization Data of PS, HPU, and LPU Obtained via SEC³

V_e (mL)	PS			LPU			HPU			
	$M_i \times 10^{-4}$	$[\eta]_i$ (dL/g)	V_e (mL)	$M_i \times 10^{-4}$	$[\eta]_i$ (dL/g)	R_{g_i} (nm)	V_e (mL)	$M_i \times 10^{-4}$	$[\eta]_i$ (dL/g)	R_{g_i} (nm)
13.59	26.0	1.034	13.62	28.5	0.672	18.90	13.60	140.3	0.288	24.24
13.88	17.0	0.708	13.97	16.1	0.546	14.57	13.80	101.2	0.246	20.63
14.18	11.5	0.527	14.14	12.3	0.493	12.91	14.18	56.32	0.192	15.62
14.94	4.65	0.276	15.00	4.13	0.294	7.55	14.95	20.11	0.131	9.76
15.60	2.06	0.160	15.69	2.16	0.204	5.39	15.71	7.22	0.088	6.09
16.94	0.36	0.061	16.90	0.42	0.10	2.47	16.86	2.17	0.055	3.48
17.38	0.18	0.047	17.42	0.22	0.075	1.80	17.44	1.34	0.045	2.82

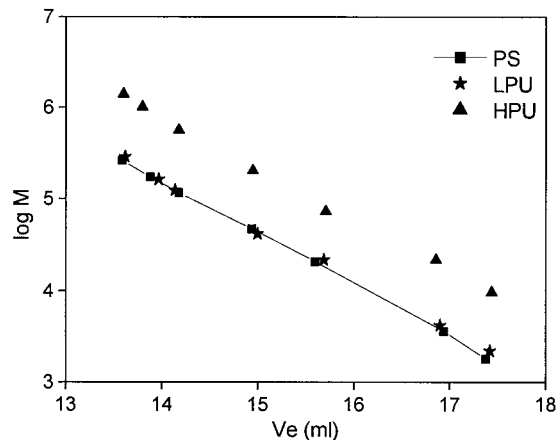


Figure 2 Correlation of V_e with $\log M$.

Branching Parameters g and g'

Branching changed the relationship between hydrodynamic volume and molecular mass because a branched molecule was smaller than a linear molecule of the same molecular mass. This decrease in size was described by the branching index, g , which was the ratio of the mean square radius of gyration R_{gb}^2 of the branched molecule to that of R_{gl}^2 of the linear molecular with the same molecular mass (M),¹²

$$g = (R_{gb}^2/R_{gl}^2)_M \tag{3}$$

The decrease in the hydrodynamic volume was described by g' , which was defined as the decrease in intrinsic viscosity $[\eta]$ at a given molecular mass due to branching,

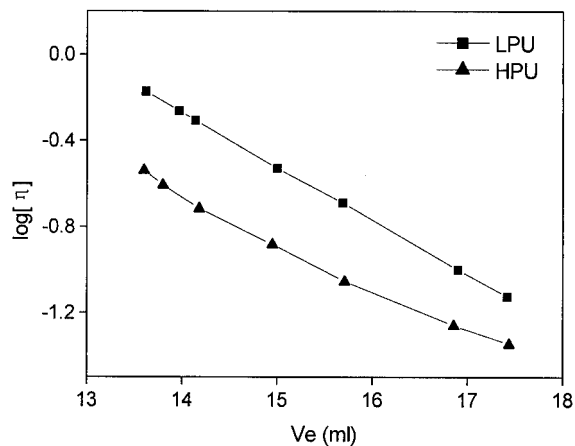


Figure 3 Correlation of V_e with $\log[\eta]$.

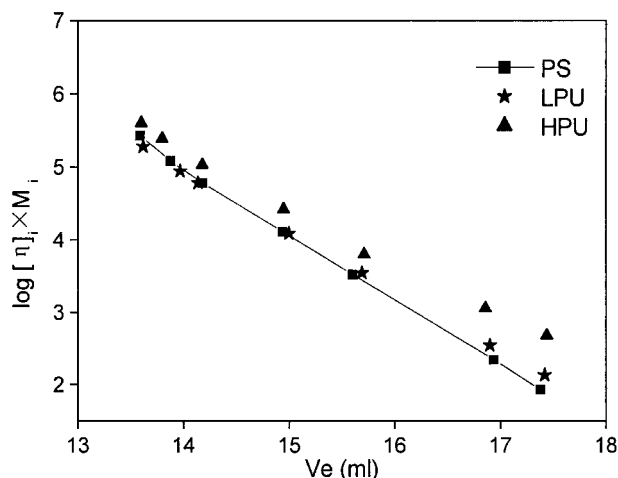


Figure 4 Correlation of V_e with $\log M[\eta]$.

$$g' = ([\eta]_b/[\eta]_i)_M \quad (4)$$

This was expected to be proportional to the decrease in the radius of gyration:

$$g' = g^\epsilon \quad (5)$$

Experimental ϵ was found to vary from 1/2 to 3/2. One point: $\epsilon = 1/2$ for lightly branched polymers, $\epsilon = 3/2$ for highly branched polymers. Another point: $\epsilon = 1/2$ for random and star branched polymers, $\epsilon = 3/2$ for comb polymers.

Figure 6 showed the radius of gyration as function of molar mass for LPU and HPU. The relationship between the two was

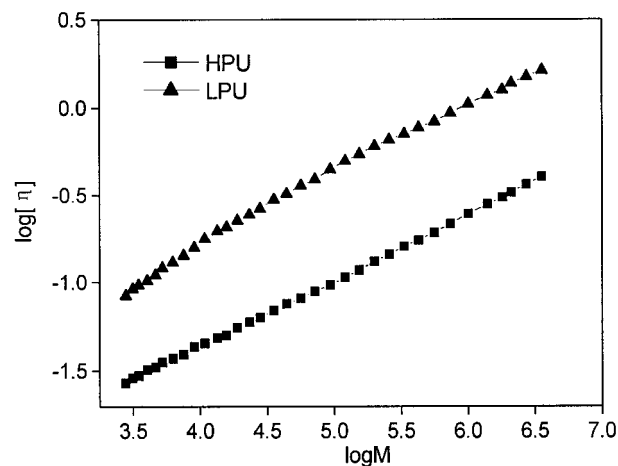


Figure 5 plot of $\log[\eta]$ as a function of $\log M$ for LPU and HPU.

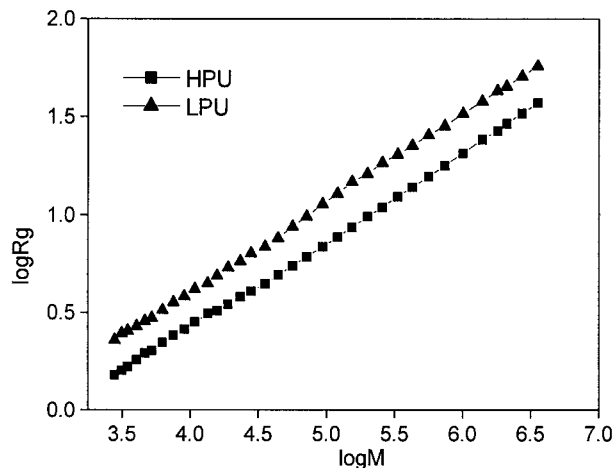


Figure 6 plot of $\log R_g$ as a function of $\log M$ for LPU and HPU.

$$\text{LPU: } R_{gl} = 0.061 \times M^{0.45} \quad (6)$$

$$\text{HPU: } R_{gb} = 0.045 \times M^{0.44} \quad (7)$$

In order to compare HPU to LPU with the same molecular weight and molecular weight distribution, the molecular weight and concentration of each individual slice of LPU was supposed to be the same value of those of HPU. The number-average and weight-average intrinsic viscosity and the radius of gyration were recalculated. Then the g , g' , and ϵ could be calculated (Table III). It could be found that $\epsilon = 1.41$ reached the value 3/2. This supported the point that ϵ was equal to 3/2 for highly branched polymers.

The g can be directly related to the number of branched points if the radius of gyration was measured under θ conditions, where the effect of excluded volume on the radius of gyration was apparently canceled by Van der Waals attractions between segments of the chain. With the assumption of long chain, a randomly branched polydisperse polymer with trifunctional branch points the weight-average value of g was given by¹²

$$g_w = \frac{6}{n_w} \left\{ \frac{1}{2} \left[\frac{2 + n_w}{n_w} \right]^{1/2} \ln \left[\frac{(2 + n_w)^{1/2} + (n_w)^{1/2}}{(2 + n_w)^{1/2} - (n_w)^{1/2}} \right] - 1 \right\} \quad (8)$$

where n_w was the number of trifunctional branch points per weight-average molecule.

In this study, the SEC experiment was carried out using a thermodynamically good solvent, and

Table III Calculation of Branching Parameters for HPU

Samples	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$[\eta]_n$ (dL/g)	$[\eta]_w$ (dL/g)	R_{gn} (nm)	R_{gw} (nm)	g_w	w	ϵ
HPU	28600	89900	0.066	0.084	4.43	5.84			
LPU	28600	89900	0.286	0.365	7.46	9.95	0.344	0.225	1.41

so it was assumed that the radii of gyration of branched and linear polymers had the same expansion factors. This assumed that the results based on eqs. (3) and (8) were still valid.

Equation (8) was so sophisticated. It was not possible to solve for n_w directly. However, it was easy to get $g_w - n_w$ curve when various values of n_w were given. Moreover, $g_w - \ln(n_w)$ curve could be obtained (Figure 7). Then n_w could be obtained from the curve when the value of g_w was given. In this study the following result was obtained: $n_w = 16$ ($g_w = 0.346$). It was obvious that the branching index was an unspecified lower average because only long branch chains were considered.

CONCLUSION

SEC, utilizing a combination of RI, RALLS, and DV detectors was used to study the relationship

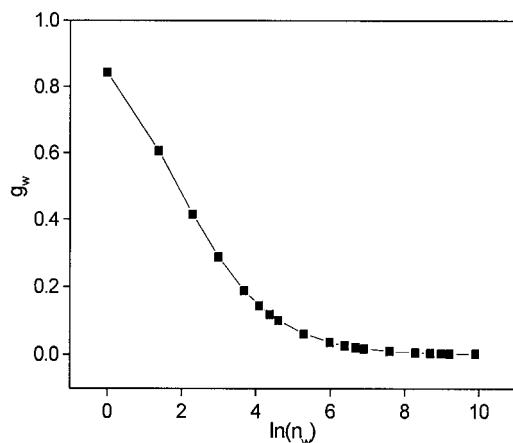


Figure 7 The $g_w - \ln(n_w)$ curve calculated from eq. (8)

between the decrease in intrinsic viscosity and radius of gyration caused by branching. It could be found that the intrinsic viscosity and the radius of gyration of HPU were much lower than that of its linear analog with the same molecular weight. Branching parameter g and structure parameter ϵ showed that HPU had a highly branched structure.

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