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Synthesis and Characterization of New Hyperbranched Polymers with Only Inner Functional Groups Modified

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ABSTRACT: The novel core-shell polymers were synthesized based on the perfluoroalkyls grafting onto the inner hydroxyl groups of hyperbranched polyglycidol while the outer hydroxyl groups remained unaffected. The samples were characterized with FTIR, NMR, element analysis, and liquid chromatography/mass spectrometry. The various results obtained by different measurements are in good agreements. The conversion ratio of inner hydroxyl groups is about 0.3 and most functionalizations took place in linear 1,4-units (L_{1-4}). Differential Scanning Calorimetry results suggest the samples are amorphous within the experiment range. Their inner lipophilicity and outer hydrophilism resulted from their unique structures are expected to gain promising applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 317–322, 2006

Key words: hyperbranched; polyglycidol; perfluoroalkyl; protection; amphiphile; esterification

INTRODUCTION

In recent years, polymers with a treelike structure (cascade-type polymers) have gained widespread attention due to their unique properties, which differ significantly from their linear counterparts. Such cascade-type polymers, which are noncrosslinked and possess a large number of branching points and numerous pendant endgroups, include the structurally perfect dendrimers and less structurally perfect hyperbranched polymers. Whereas the tedious multistep synthesis of dendrimers limits their application, hyperbranched polymers are eliciting rapidly increasing interest as potential alternatives for dendrimers in some fields where structural perfection is not a strict prerequisite or structural imperfection may be needed.[1–3]

In hyperbranched polymers, the structural units include terminal (T), dendritic (D) and linear (L) units. According to the statistical model provided by Gennes and Hervet, all the terminal units reside on the surface of the hyperbranched polymer and form the most dense layer in periphery.[4] Therefore, compared with the outer functional groups in terminal (T) units, in most functionalization reactions, the inner functional groups in linear (L) units show much lower activities, because of steric effect. The structure of hyperbranched polyglycidol is shown as an example in Scheme 1.

In general modification of hyperbranched polymers, the outer functional groups take the priority to react because of steric effect, and the resulting arms further hinder the inner functional groups from reaction. To explore the properties of inner functional groups and the hyperbranched polymers with arms in interior, in the current study, we selected perfluoroalkyls to modify the inner hydroxyl groups of hyperbranched polyglycidol. To avoid the effects of outer hydroxyl groups, we used 2,2-dimethoxypropane to protect them in the first step. The resulting polymers were characterized with FTIR, NMR, element analysis (EA), and liquid chromatography/mass spectrometry (LC/MS).

EXPERIMENTAL

Materials

Glycidol (AR) was from ACROS (Geel, Belgium), perfluoro-octanoic acid and perfluoro-acetic anhydride (AR) were from Shanghai 3F New Materials Co. (Shanghai, China), 2,2-dimethoxypropane (AR), and all other reagents (AR) were from Shanghai Chemical Reagent Co. (Shanghai, China). HPG was prepared precisely according to the procedure published by Tokar et al., by solution cationic ring-opening polymerization of the AB_2 monomer glycidol with $SnCl_4$ as initiator.[5] Perfluoro-octanoyl chloride was prepared by the reaction of perfluoro-octanoic acid and $SoCl_2$ with DMF as catalyst.

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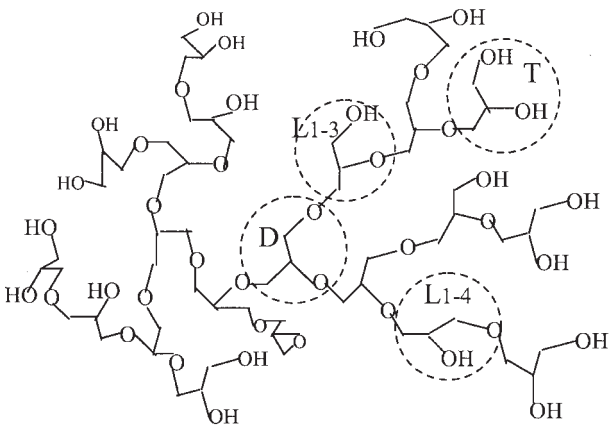


Scheme 1 Schematic structure of hyperbranched polyglycidol (HPG). D, L_{1-3}, L_{1-4}, and T refer to dendritic units, linear (1–3) units, linear (1–4) units, and terminal units, respectively.

Synthesis

In a typical approach, the reactions were performed according to the following procedures.

Protection of outer hydroxyl groups

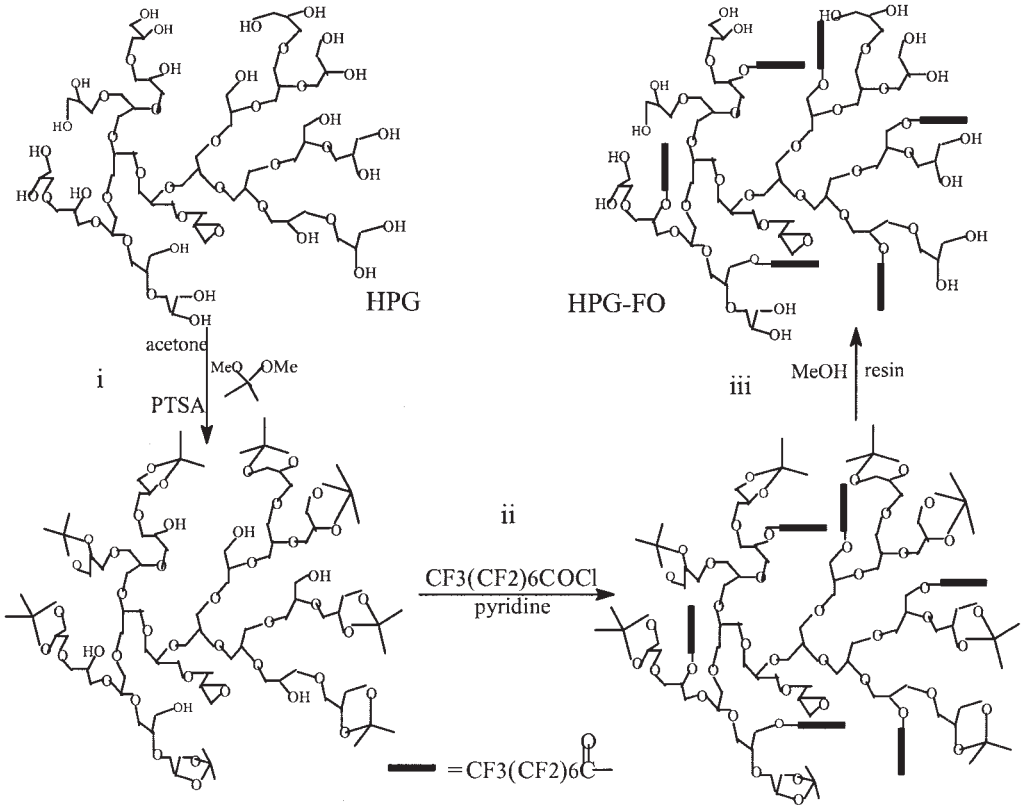
p-toluenesulfonic acid (PTSA) was added to the mixture of HPG and excessive 2,2-dimethoxypropane, and the reaction was carried out under ultrasonication over 3 h at 25–40°C. The crude product was diluted in chloroform, extracted with saturated Na_2CO_3 solution, dried over $MgSO_4$, and then under vacuum at 80°C for 15 h. The resulting polyketal HPG1 was obtained as a viscous, slightly yellow, transparent oil. In ^{13}C NMR spectra, the appearance of the ketal's characteristic resonance (δ = 26.3 (C—CH_3), 27.6 (C—CH_3), 110.3 (C—CH_3)), confirmed the success of protection.

Esterification of inner hydroxyl groups

Perfluoro-octanoyl chloride was dropwise added in the solution of HPG1 dissolved in anhydrous pyridine under nitrogen, and then the mixture was stirred at room temperature for 3 h and refluxed for 0.5 h. In the solution some deposit appeared. After cooling to room temperature, the mixture was filtrated. The deposit was washed by deionized water and dried under vacuum at 80°C for 15 h. The remaining polymer HPG2 was viscous, yellow, and transparent.

Deprotection of outer hydroxyl groups

HPG2 was dissolved in methanol. Sulfoacid polystyrene resin was added to the solution, stirred and re-



Scheme 2 Synthesis route of HPG-FO.

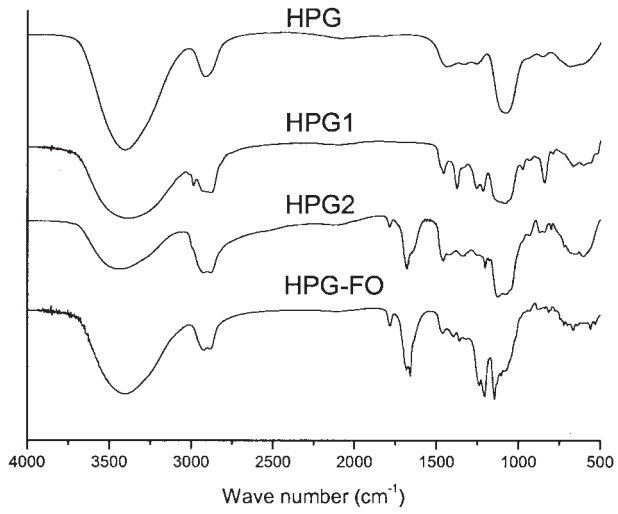


Figure 1 IR spectrum of HPG, HPG1, HPG2, and HPG-FO.

fluxed for 15 h. After filtering and concentrating the solution, and drying under vacuum at 80°C for 15 h, the yellow, viscous polymer, HPG-FO, was obtained.

Synthesis route of HPG-FO is shown in Scheme 2.

HPG-FA was obtained through above procedures when perfluoro-octanoyl chloride is replaced by perfluoro-acetic anhydride, except that esterification was conducted at room temperature.

Characterization

FTIR was performed with a Bruker Equinox 55 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with DMSO-d_6 as a solvent with a Varian DRX 500 NMR spectrometer operating at 500 and 125 MHz, respectively. EA was conducted with a Perkin-Elmer 240 Element Analysis meter. Liquid chromatography (LC) spectra were obtained with an Eclipse XDB-C18 LC column at a flow speed of 0.7 mL/min with water/methanol (80/20) as an eluent at 25°C. Mass spectra were obtained with an HP 1100 LC/MS detector with an air pressure ion-electronic spray mass spectrometry ion source at 10 L/min at fragmentor voltage of 50 V. gel permeation chromatography (GPC) measurement

TABLE I
Assignment of the IR Spectra

Band/cm^{-1}	Assignment	Intensity
3050~3700	$\nu_{O—H}$ (association)	s
2750~3050	$\nu_{C—H}$ (CH, CH2)	m
1550~1850	$\nu_{C—O}$ (CF_2—COO—CH)	s
1200~1300	$\nu_{C—F}$	s
1000~1200	$\nu_{C—O—C}$	s

was carried out on PerkinElmer series 200 with DMF as solvent at a concentration of 10 mg/mL. Differential Scanning Calorimetry (DSC) measurements were carried out with a PerkinElmer thermal analysis system, from −70 to 80°C at a heating rate of 20 K/min. Viscosity measurements were carried out using an Ubbelohde viscosimeter with a capillary diameter of 0.53 mm in pyridine at room temperature.

RESULTS AND DISCUSSION

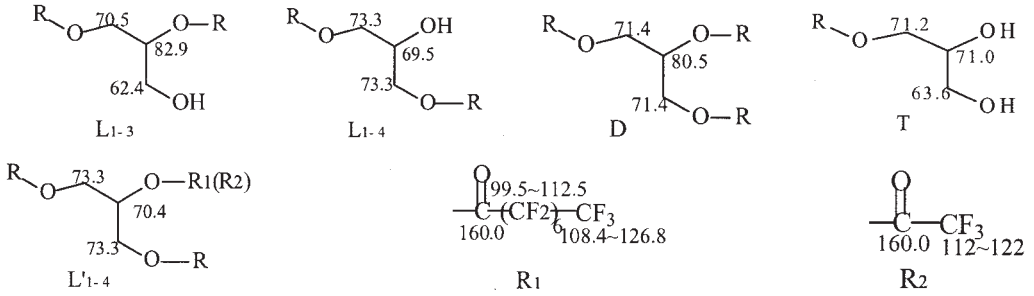
FTIR

We can see from Figure 1 that after protection step, OH stretch reduced, which indicates some hydroxyl groups were converted into ketal. After esterification step, OH stretch reduced further and carbonyl stretch appeared, which proves that esterification took place. After deprotection, OH stretch was enlarged, which shows that some hydroxyl groups were produced. All these phenomena went parallel with the route of synthesis.

NMR

NMR spectroscopy is an important and precise tool for the characterization of hyperbranched polymers since detailed analysis of the spectra could deduce the most prominent features, such as the degree of polymerization (DP_n) and the degree of branching (DB). Therefore, it is appropriate to discuss the results of this method in detail.

The assignments of the signals in the ^{13}C NMR spectra of HPG, HPG-FO, and HPG-FA are listed in



Scheme 3 structural units and corresponding chemical shifts of HPG, HPG-FO, and HPG-FA.

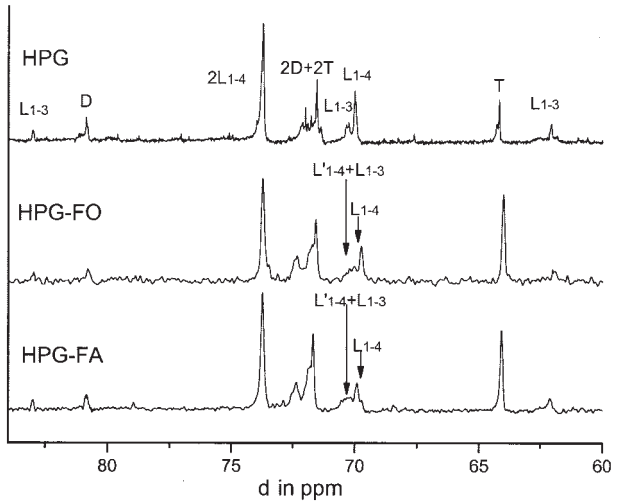


Figure 2 ^{13}C NMR spectra of HPG, HPG-FO, and HPG-FA.

Table I, based on reports by Tokar et al.,[5] Dworak,[6] Sun et al.,[7] and Sunder.[8] All structural units and corresponding chemical shifts are displayed in Scheme 3.

While comparing HPG and resulting polymers, the resonance of methylene connected to hydroxyl group in L_{1-3} unit appeared at 62.4 ppm, with neither shift nor change in area (Fig. 2). We deduce that few hydroxyl groups in L_{1-3} units participated in the reactions. The resonance of methine in L_{1-4} (69.5–70.0 ppm) reduced, which indicates that the esterification took place. Since the next hydroxyl group was esterified, the chemical shift of the methine moved left, appearing at (70.5 ppm) and overlapping with the methylene (70.4 ppm). And so the area from 70.0 to 71.0 ppm enlarged. No other areas showed significant changes. The reason why the hydroxyl groups in L'_{1-4} units accounted for most esterifications is probably that methine made the next hydroxyl group more active compared with methylene. Moreover, lower sterical hindrance and the higher stability of the primary ester is helpful to enhance the reactivity of hydroxyl groups.

TABLE II
Interpretation of ^{13}C NMR Spectra of HPG, HPG-FO, and HPG-FA

Structure units	Chemical shift (ppm)	Relative integral		
		HPG	HPG-FO	HPG-FA
L_{1-3}	82.8	0.8	0.7	0.7
D	80.2	0.9	1.4	1.0
$2L_{1-4}$	73.1	5.4	6.4	4.5
2D+2T	71.5~72.0	4.4	8.0	5.5
$L'_{1-4} + L_{1-3}$	70.0~71.0	0.7	1.7	1.5
L_{1-4}	69.5~70.0	2.5	1.7	1.4
T	63.5	1.1	2.1	1.2
L_{1-3}	62.4	1.0	1.0	1.0
R_1	99.5~160.0		9.56	
R_2	112.1~160.0			1.66

TABLE III
Relative Abundance of Structural Units of HPG, HPG-FO, and HPG-FA

Structure units	Relative abundance (%)		
	HPG	HPG-FO	HPG-FA
T	21.4	24.3	23.1
L_{1-3}	14.3	12.2	15.4
L_{1-4}	46.4	27.0	26.9
L'_{1-4}		16.2	15.4
D	17.8	20.2	19.2

The results of the interpretation of the ^{13}C NMR spectra are summarized in Table II, showing the signal intensities and assignments for the three different samples studied. Using the relative integrals from ^{13}C NMR spectra, it is possible to calculate the relative abundance of each structural unit (Table III). The conversion ratios of inner hydroxyl groups in HPG-FO and HPG-FA are 29.2% and 26.7%, respectively.

DB, which measures the suitability of a hyperbranching reaction to create dendritic structures, and DP_n were calculated on the basis of the intensity of the NMR signals, according to eqs (1) and (2), respectively[7]:

$$DB = \frac{2D}{2D + L_{1-3} + L_{1-4}} \quad (1)$$

$$DP_n = \frac{T + L_{1-3} + L_{1-4} + D}{T - D} f_c \quad (2)$$

f_c represents the functionality of the core molecule. Here $f_c = 1$. When the above equations are applied to HPG-FO and HPG-FA, L_{1-4} includes L'_{1-4}.

We can also deduce M_n from DP_n. The results are shown in Tables IV and V. Despite imperfect measurements, the DB values are still satisfactorily similar. They are somewhat low. We assume that this was caused by the absence of By type molecule as core units in the synthesis process. After esterification, samples' molecular mass correspondingly increased

TABLE IV
NMR and Element Analysis Results of HPG, HPG-FO, and HPG-FA

	NMR			Element analysis	
	DB	DPn	OH (consumed)	F (wt %)	OH (consumed)
HPG	37.0%	27.5			
HPG-FO	40.0%	26.0	15.6%	30.9%	14.1%
HPG-FA	42.3%	24.7	14.8%	8.3%	12.5%

TABLE V
Molecular Mass, T_g, and η of HPG, HPG-FO, and HPG-FA

	NMR	LC-MS	GPC		T_g	η
	M_n	M_n	M_n	M_w/M_n	(°C)	(mL/g)
HPG	2040	1960	18000	1.34	-54.2	6.4
HPG-FO	3540	3340	30700	1.72	-32.1	16.4
HPG-FA	2180	2140	10100	1.46	-47.4	15.4

according to the mass and number of the introduced perfluoroalkyls.

^{1}H NMR spectra of polyglycidol are less informative than the ^{13}C NMR spectra. In some articles, it was used to determine the molar content of the functional groups incorporated, or to analyze primary and secondary hydroxyl groups.[9,10] In this article, it confirmed reduction of the hydroxyl groups. The four methylene and one methine proton of polyglycidol appear as a broad, irregularly shaped resonance between 3.2 and 3.8 ppm; hydroxyl protons give a signal at 4.4 ppm in DMSO.

Element analysis

Through EA measurements, the contents of F in HPG-FO and HPG-FA were achieved, and moreover, we deduced the equations (3) and (4) about the content of F (F%, wt) and the percent of consumed OH groups (OH_c%, mol), on the basis of the important features of their structures. In HPG, the number of all structure units almost equals to that of hydroxyl groups. In HPG-FO and HPG-FA, the number of consumed OH groups is equal to that of introduced perfluoroalkyls.

$$F\% = \frac{M_2 b}{M_0(a+b) + M_1 b} \quad (3)$$

$$OHc\% = \frac{\text{OH consumed}}{\text{OH total}} = \frac{b}{a+b} \quad (4)$$

Here, a and b refer to remained and consumed hydroxyl groups respectively. M_0, M_1, and M_2 represent molecular weights of monomer, grafting unit, and total F atoms in each grafting unit, respectively. So, M_0 = 74; for HPG-FO, M_1 = 397, M_2 = 285; and for HPG-FA, M_1 = 97, M_2 = 57. The results about the content of F show that the resulting polymers have a good abundance of F. About 14% of total hydroxyl groups were grafted by perfluoroalkyls, and the results are close to that computed from NMR.

LC/MS

In the LC spectra (Fig. 3), each sample had one sharp peak, and this indicated that the sample was successfully synthesized through the design approach. The signal peaks in this mass spectrum are attributed to all fragments of HPG-FA. The possible fragments corresponding to peaks 103.2 and 203.1 are shown in Scheme 4. The mass differences between the other peaks and the peaks 103.2 or 203.1 are multiples of 74.1 which is exactly the molar mass of glycidol monomer. So, all the peaks in the spectrum could find reasonable fragments of HPG-FA. Moreover, if the largest value (713.2) in the spectrum is an ionic peak with three charges, M_n of HPG-FA is calculated to be 2140 which is very close to the value resulting from NMR (2180). HPG and HPG-FO were handled in the same way.

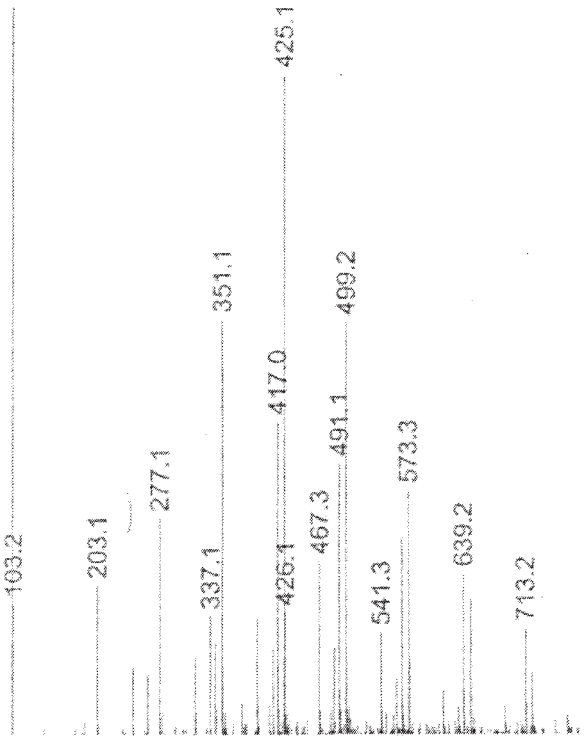
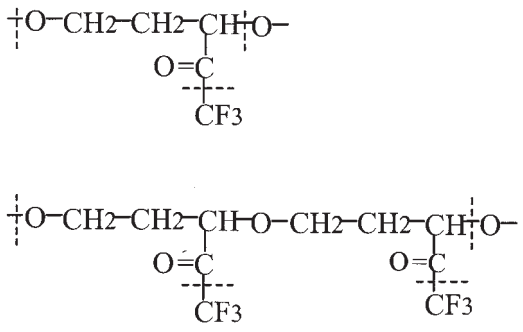


Figure 3 Mass spectrum of HPG-FA.



Scheme 4 Possible structures of fragments corresponding to peaks at 103.2 and 203.1, respectively.

GPC

Due to high DB, unique sphere shape, solvent/polymer interactions, and aggregation or interaction with the GPC columns, results from GPC are incredible, far beyond those from other instruments. But polydispersities measured by GPC is acceptable according to Sunder's reports.[8] The dispersities of three samples are satisfactorily low, ranging from 1.3 to 1.7.

DSC

Thermal properties of all the samples have also been studied, using DSC with respect to the T_g. The solid-state properties of all the samples were similar, despite their different structures. There was no crystalline reflection in the curve; this indicated that the core-shell polymer was amorphous within the experimental range. In the last column of Table V the respective data are given: The T_g of HPG, HPG-FA, and HPG-FO are about -54, -47.4, and -32.1°C, respectively. This is reasonable, since the molecular weights of the three samples vary a lot, they could enhance T_g accordingly. Besides, because of introduction of F atoms, the polarity of endgroups is enhanced and molecules become more compact, which accelerates the movement of T_g toward higher temperature. This phenomenon is also in accordance with reports by Stutz et al.,[11,12] Kim and Beckerbauer,[13] and Tande et al.[14]

Viscosity

Determination of the concentration-dependent specific viscosity is an important method to investigate the solution conformation of macromolecules. Lots of research has been well conducted to explore the viscosity of hyperbranched polymers.[15–17] And it is well proved that they have lower viscosity than their linear counterparts. In this study, HPG-FO and HPG-FA exhibit greater viscosities compared with HPG. This is acceptable because the polarity of F atoms strengthened the interaction between macromolecules and the interaction between macromolecules and solvent. Molecular mass also account for this. The resulting values for η are summarized in Table V.

CONCLUSIONS

Two novel hyperbranched polymers, using HPG as a framework, and with perfluoroalkyl arms in interior were synthesized and characterized, while the outer hydroxyl groups were successfully retained. Through protection of outer hydroxyl groups, only inner hydroxyl groups reacted with perfluoroalkyls; their conversion ratio is 0.3 and most esterifications take place in linear 1,4-units (L_{1-4}). After esterification, the polymers' T_g and η were enhanced. Besides, their inner lipophilicity and outer hydrophilism resulted from their unique structures are expected to gain promising applications.

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