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Characterization and Synthesis of Pentafluorophenyl-terminated Hyperbranched Benzyl Ether Polymer

Benjamin A. Arce

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Benjamin A. Arce

Department of Chemistry and Biochemistry, The University of Texas at Tyler, Tyler, Tx 75799

Introduction

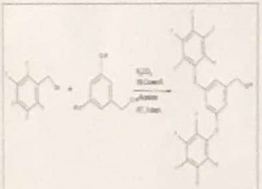
Hyperbranched polymers are polymers with three-dimensional dendritic structure. Their significance can be seen in their use as surface coatings or drug delivery transports. Recent studies have shown an increase in using polyfluorinated hyperbranched polymer systems due to the relative inertness of the compounds. It is because of its high temperature resistance, chemical resistance and low solubility that polyfluorinated polymers have numerous applications in chemical research and industrial settings.

One difficulty of hyperbranched polymer synthesis is the random branching that occurs, making the outcome of the desired product usually less than 100%. Synthesis and characterization of pentafluorophenyl-terminated hyper-branched benzyl ether polymer allowed for analysis of polymer mechanism.

Synthesis

The synthesis of monomer 1 (78% yield) was prepared by the reaction of α-bromopentafluorotoluene and 3,5-dihydrooxybenzyl alcohol with the reagents K_2CO_3 18-crown-6 ether, and acetone.

Initial formation of pentafluorophenyl for polymerization (1)



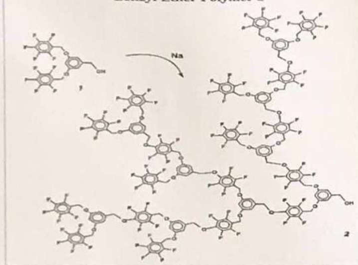
The synthesized monomer was treated with two different reactants For study polymerization.

Potassium bis(trimethylsilyl)amide yielded a desired product. A study of sodium metal pieces in suspended toluene were shown to produce polymers. There was shown to be a noticeable effect on polymer size and sodium pellet size.

Synthesis

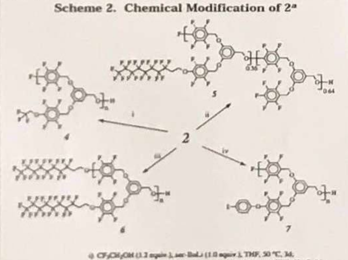
Temperature and monomer concentration were evaluated for their effect on polymerization. Increased temperature and concentration yielded larger molecular weights than at lower temperatures. The product (2), was then modified to increase fluorocarbon character and decrease reactivity by use of perfluoroalkoxy moieties as seen in scheme 2.

Scheme 1. Synthesis of the Pentafluorophenyl-terminated Hyperbranched Benzyl Ether Polymer 2



Scheme 1. Polymerization of pentafluorophenyl-terminated hyperbranched benzyl ether.

Scheme 2. Chemical Modification of 2ᵃ



Scheme 2. Modification of polyfluorophenyl-terminated hyperbranched benzyl ether.

Results/Discussion

The modified polymers were measured through gel permeation chromatography (GPC) using polystyrene standards. Number average molecular weights were determined using H^1 NMR and F^{19} NMR as can be seen in table 1.

sample	PS equiv M_w	PS equiv M_n	^1H NMR $M_n{}^b$	^{19}F NMR $M_n{}^c$
I	1000	700	600	600
II	1600	1000	800	1000
III	above calibration	6000	4000	5000
IV	above calibration	123 000		

Table 1. Molecular weight comparison obtained by two oligomers (I, II) and two modified polymers (I, II).

Both methods of molecular weight determination were not capable of measuring the molecular weights of the samples. Hyper-branched polymers typically give inaccurate lower molecular weight characterization. The likely reason for similar molecular weights determined from the NMR spectra was because the polyfluorinated systems did not have the degree of branching that was expected (~50%).

Thermogravimetric analysis was used to measure thermal stability of compounds. There was no loss of mass for the polymers under 300 °C. Compound (2) showed loss of 25% mass at 310-370 °C, and 15% more mass loss at temperatures from 370-500 °C. Polymer 6 showed mass loss similar to compound (2).

Contact angle were measured using the sessile drop method to determine the hydrophobic and lipophobic character of the sample polymer films as seen in table 2.

Table 2. Contact Angles Measured with the Sessile Drop Method,[17] after 30 s and 4 min with Water and after 30 s with Hexadecane

	contact angle (deg)		
	water		hexadecane
	30 s	4 min	30 s
1	69 ± 1.7	30 ± 0.6	18 ± 2.0
2	96 ± 2.3	91 ± 2.2	21 ± 2.2
4	99 ± 1.1	95 ± 1.7	14 ± 1.1
5	120 ± 1.1	120 ± 1.6	62 ± 2.0
6	120 ± 1.8	120 ± 2.1	67 ± 3.0

Table 2. Contact angles measured for polymer samples.

Sample 1 exhibited a small hydrophobicity in comparison to the other samples. As the polymerization and modification of the samples occurred, the samples exhibited a larger hydrophobic character. Samples 1, 2, and 4 displayed low lipophobic character. In contrast, samples 5 and 6 had considerably higher lipophobicity.

Conclusion

Modification of these compounds provided various products with similar characteristics. As the compounds increased in size, there was an increase in hydrophobic and lipophobic character and thermal stabilities greater than 300 °C. As the study of polyfluorinated hyper-branched polymers increases, researchers have found usage as industrial lubricants, electrolyte membranes, organic semiconductors, and coatings for minimal adhesive materials. This underscores the significance of proper characterization and study of these compounds.

References

[1] Mueller, A., Kowalewski, T., & Wooley, K. L. (1998). Synthesis, characterization, and derivatization of hyperbranched polyfluorinated polymers. *Macromolecules*, *31*(3), 776-786.

[2] Quast, M. J., & Mueller, A. (2014). Hyperbranched Polyfluorinated benzyl ether polymers: Mechanism, kinetics, and optimization. *Journal of Polymer Science Part A: Polymer Chemistry*, *52*(7), 985-994.

[3] Gao, C., & Yan, D. (2004). Hyperbranched polymers: from synthesis to applications. *Progress in Polymer Science*, *29*(3), 183-275.

Contact:

Department of Chemistry and Biochemistry
University of Texas at Tyler

Phone: (903)-539-0051
Email: barce@patriots.uttyler.edu
Web: http://uttyler.edu

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