

Synthesis, Properties and Molecular Modeling of Functional Hyperbranched Polymers and Dendrimers

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Summary: The design, synthesis, properties and molecular modeling of fully conjugated dendritic molecules and conjugated hyperbranched polymers are described. It has been shown that conjugated hyperbranched molecules are much more soluble than their linear analogues while maintaining all the properties characteristic of conjugated polymers. It was found that the use of polymeric solid support in hyperbranched polymerization allows to control molecular weight and degree of branching (DB). The molecular modeling of hyperbranched conjugated molecules reveals that hyperbranched structure of conjugated molecules affects significantly neither their stability nor the conjugation. On the other hand the terminal groups affect appreciably the electronic structure of conjugated hyperbranched molecules

Introduction

In the last decade much attention has been paid to the synthesis and detailed characterization of macromolecules with the architectures differed from conventional linear and comb-like structures.

Among others are calixarenes^[1], fullerene-containing polymers^[2,3] and, highly branched structures: dendrimers and hyperbranched polymers^[4]. The interest in those types of macromolecules is due to the unique properties imparting to the polymeric materials derived from unusual molecular shape.

Hyperbranched macromolecules can be conveniently divided into two major groups. The first is the perfect dendritic macromolecules prepared by stepwise synthetic approaches^[5,6,7]. Their properties are easy to control but they are obtained only in limited quantities and after much efforts. The second is hyperbranched polymers obtained by direct polymerization of AB_n monomers^[8,9]. Hyperbranched polymers generally have less perfect branching, show polydispersity and their properties are not so easy tailored; however, they are readily available by simply one-step polymerization. The most attractive features of hyperbranched structures are their excellent solubility, low solution viscosity and high concentration of terminal groups even for high polymers.

It is also well known that the conjugated polymers, which show conductivity and non-linear properties, are mostly insoluble unless they contain long aliphatic spacers. Those spacers deteriorate the polymer properties related with conjugation and interchain interactions. Fully and partially conjugated hyperbranched polymers could be interesting alternative to conventional conjugated polymers combining good tractability of hyperbranched structure with high concentration of conjugated units.

Although the chemistry of hyperbranched molecules in general is experiencing now explosive development, the conjugated dendritic molecules have been paid little attention and only a few papers have been published to date, probably due to rather sophisticated chemistry involved in the preparation of conjugated dendrimers. Among them is the synthesis of a conjugated monodendron having a smooth gradient in electronic excitation energy from the periphery to the core reported by Moore^[10]. Miller and Neenan^[11] published their efforts on all-hydrocarbon polyphenylene dendrimers. Recently the synthesis of dendrimers up to third generation with stilbenoid chromophores into dendritic structure has been described^[12], considered as potential materials for light-emitting diodes, non linear optics (NLO) and optical imaging storage. A simple orthogonal approach to poly(phenylenevinylene) has been developed^[13]. Other interesting synthetic approach was reported by Klaus Müllen et al. to obtain spherical polyphenylene dendrimer via Diels-Alder reactions. Important result was that all dendrimers prepared were soluble in common organic solvents^[14].

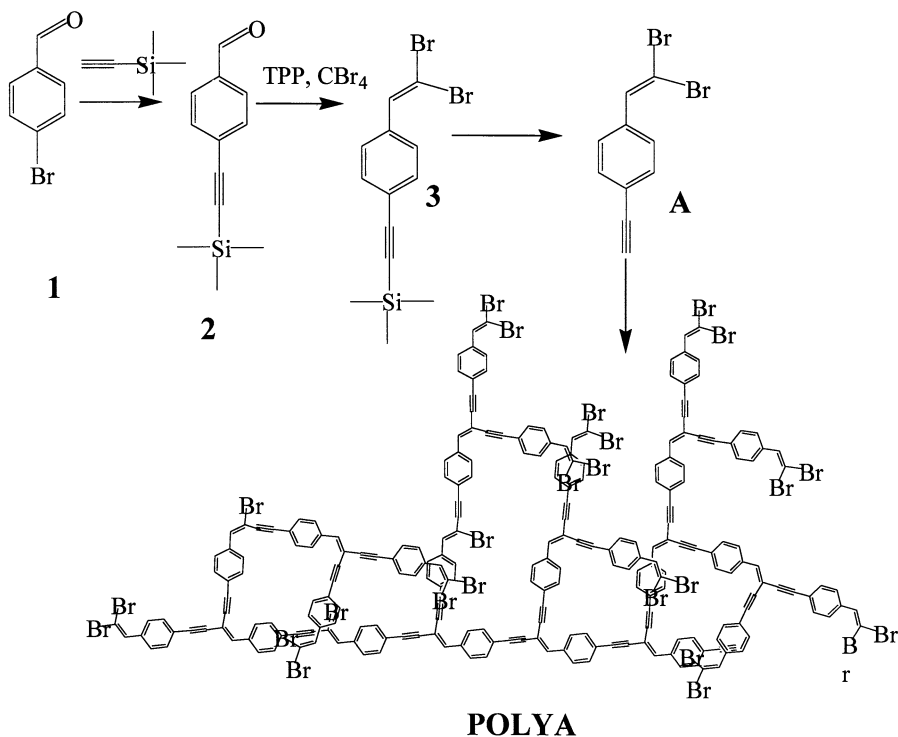
In general, a clear understanding of the structure-properties relationship is crucial for the directional design of hyperbranched conjugated structures. The appropriate way to get this kind of information deals with the comparative analysis of the electronic structure of linear and hyperbranched conjugated structures, however, little has been published date.

This paper is an attempt to fill this gap. It briefly describes the advances in design, synthesis, characterization and electronic structure modeling made in our group in the last several years.

Design, Synthesis and Molecular Modeling of Fully Conjugated Dendritic Molecules

For the synthesis of fully conjugated hyperbranched polymers and dendrimers β,β -diethynylphenyl building block has been chosen for two reasons^[15]: easiness of preparation and possibility of functionalization. The synthetic route to the monomer and its polymerization is shown in Scheme 1. A simple Pd catalyzed polymerization of AB_2 monomer **A** produced hyperbranched polymer **POLYA**. During the polymerization of

monomer **A** the reaction solution turned yellow and then orange, indicative of the formation



Scheme 1 Synthetic route to **POLYA**

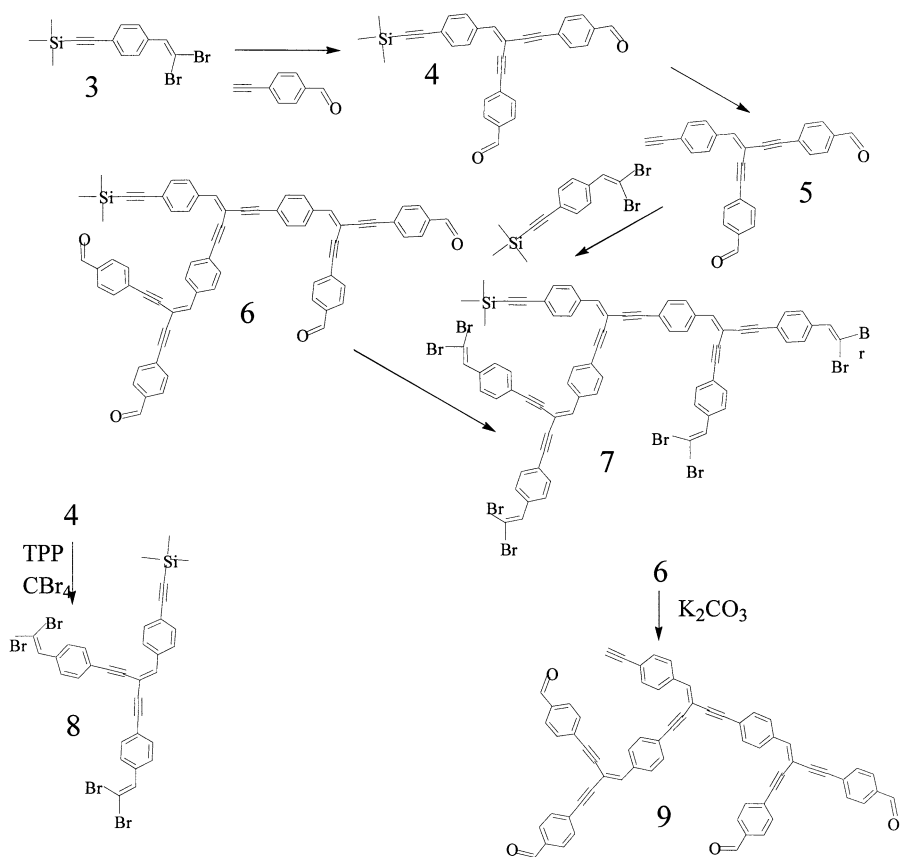
of a polyconjugated structure. The resulting polymer was partially soluble in chloroform and toluene. The M_w of **POLYA** reached 70000 with polydispersity of 1.76. The bromine contents found by elemental analysis also suggested high molecular weight of the polymer. FTIR and NMR analysis confirmed the chemical structure of **POLYA**, however, the degree of branching could not be measured. Thus, absorption bands at 2108 and 3275 cm^{-1} corresponding to $\text{HC}\equiv\text{C}$ and $\text{H}-\text{C}\equiv$ stretches in monomer **A** are completely disappeared in polymer and a new peak at 2190 cm^{-1} appeared in polymer due to stretching of conjugated internal triple bonds. It is interesting to note that while the long wave absorption maximum of monomer **A** is located at 286 nm (CHCl_3), a significant bathochromic shift of long wave absorption maximum observed for **POLYA** (90 nm) was attributed to the formation of conjugated hyperbranched structure.

Similar to linear polyphenylenevinylenes^[16], hyperbranched polymer **POLYA** showed intense photoluminescence in the visible region. Thus, the luminescence spectrum of **POLYA** presents two maxims (at 500 and 460 nm) when excited at 420 nm.

To gain better insight in structure – properties relationship of fully conjugated hyperbranched polymers, several well defined oligomers of different generations of **POLYA** have been synthesized and characterized^[17]. Convergent approach to the oligomer synthesis was applied (Scheme 2). The synthesis consisted of two repeating steps: The Pd-catalyzed cross-coupling of β,β -dibromovinylstyrene derivative (**1**) with 4-ethynylbenzaldehyde to generate formyl-terminated oligomers followed by the Wittig reaction of formyl-terminated oligomer with triphenyldibromomethylphosphorane generated from triphenylphosphine and carbon tetrabromide. After removing the protective trimethylsilyl group under mild basic conditions the prepared building block is reacted with **3** to produce next generation conjugated dendritic molecule. Similar to hyperbranched polymer **POLYA** the chemical structure of synthesized dendritic oligomers was proved by FTIR and NMR spectroscopy. Important information about conjugation in unsaturated dendritic structures can be obtained from comparison of long wave absorption in **POLYA** and well-defined oligomers of **POLYA**. Thus, the first generation oligomers **4** and **8** absorb at 377 and 367 nm which is very close to that of **POLYA** (367 nm). The second generation dendrimers (molecules **6,7**) showed their long wave absorption maxims at 399 and 383 nm, respectively.

This means that either steric hindrances in **POLYA** causes that the effective conjugation length does not exceed a repeating unit or **POLYA** has rather defective structure with low DB affecting the conjugation. It is seen that long wave absorption maxims of Br-terminated oligomers (**7,8**) are blue shifted compared to those of formyl terminated ones probably due to bulky bromine terminal atoms disturbing conjugation of Br-terminated oligomers.

Theoretical approaches have been used to understand the effect of steric hindrances and terminal groups on conjugation and electronic structure in general in hyperbranched conjugated molecules. Although a few theoretical studies of dendritic molecules have recently appeared^[18,19,20,21] little is known about electronic structure of conjugated polymers. As simplest representative of conjugated hyperbranched polymers: 1→2 hyperbranched polyacetylene (PA) was used for this study^[22]. Five generations of acetylenic dendrimers shown in Fig. 1 were modeled as idealized hyperbranched PA molecules at different stages of growth.



Scheme 2 Synthetic route well defined hyperbranched oligomers

The respective bromine-terminated acetylenic dendrimers up to fourth generation were also studied to clarify the effect of bulky and polarizable bromine terminal groups on geometry and electronic properties of hyperbranched PA. For comparison proposes linear trans-PA oligomers with the same number of atoms were also modeled. PM3^[23] semiempirical hamiltonian was used for geometry optimization while Becke three parameter hybrid (B3) exchange functional in combination with the Lee-Yang-Parr (LYP) correlation functional (B3LYP) with split valence basis set (3-21G) was used for single point energy calculations to achieve the electron correlation. The vertical ionization potentials (IP_v) was taken as negative HOMO energy from RHF/3-21G single point calculations according to Koopman's theorem^[24]. Good agreement was found between calculated and experimentally observed IP_v and energy gap (E_g) available for **Lin1**, **Lin2** and trans-PA, showing that the level of theory

chosen for modeling was adequate.

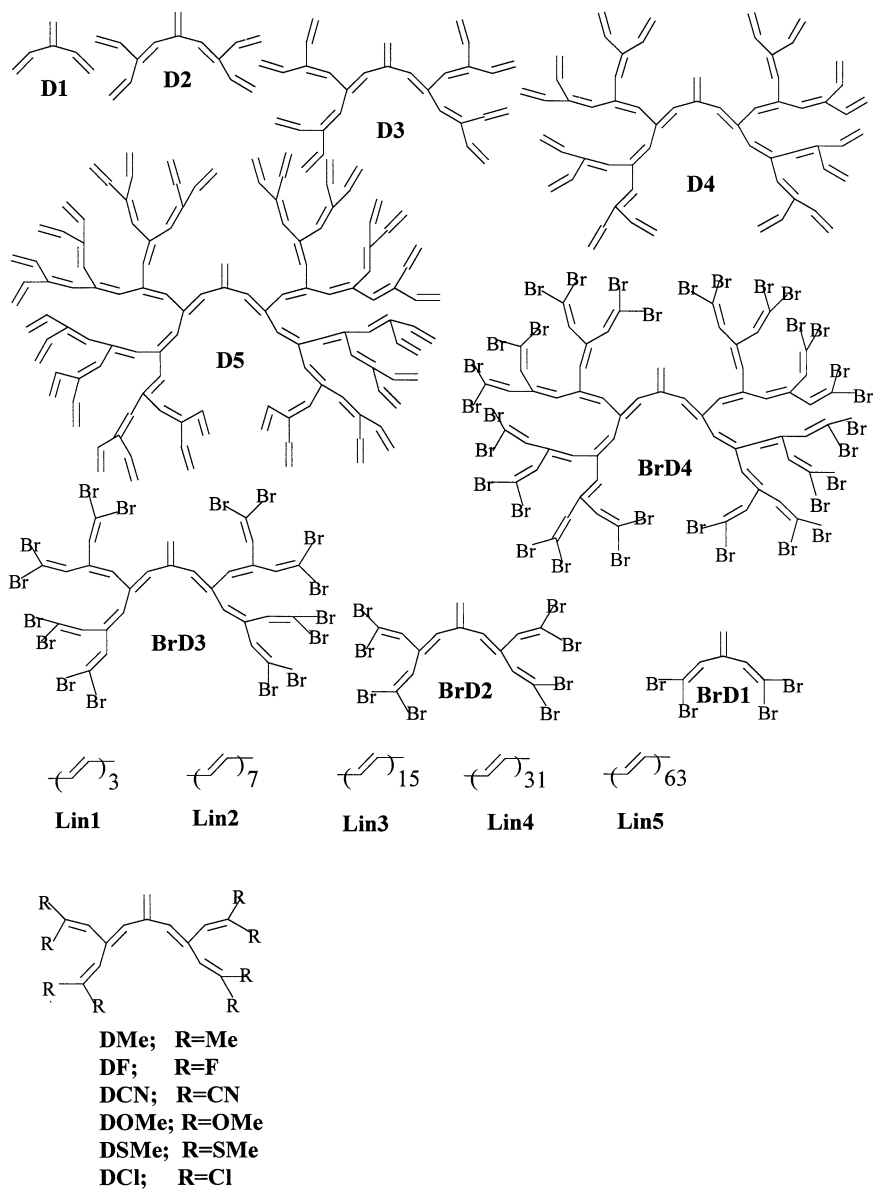


Fig.1 Idealized hyperbranched PA molecules at different stages of growth.

The relative stability of dendritic PA compared to linear trans-PA was estimated at B3LYP/3-

21G//PM3 and HF/3-21G//PM3 levels of theory as the total energy difference between dendrimer and the respective linear oligomer normalized by number of carbons in molecule. Both models present similar trends. Hyperbranched structure is less stable than linear one due to steric hindrances and destabilization increases with molecular weight. The destabilization of hyperbranched structure is, however, rather small. Both models gave the energy difference not to exceed 3.5 kcal/mol atom. Moreover, this difference seems tends to a limit with molecular weight being almost the same for **D3**, **D4** and **D5** molecules.

Both oligomer series, **D1-D5** and **BrD1-BrD4** follow the same trends as linear trans-PA oligomers (**Lin1-Lin5**). Both IP_v 's and E_g 's decrease with molecular weight due to expanding the conjugated system tending to a limit for high molecular weight dendrimers. Experimentally found E_g for trans PA (1.9 eV)^[25] agrees well with that calculated for **Lin5** (1.94 eV) allowing us to extrapolate E_g 's for dendrimers of **D** and **BrD** series with infinite molecular weight to 3.30-3.25 and 3.55-3.50 eV, respectively. Calculated E_g 's and IP_v 's of **D** and especially **BrD** series dendrimers are constantly higher than those of trans-PA oligomers. This reflects the twisting of conjugated double bonds in dendrimers especially notable for BrD series due to bulky Br terminal groups. Twisting of the double bonds decreases the conjugation in hyperbranched PA compared to linear trans-PA. However, the conjugation though less effective than in trans-PA is extended up to fourth or fifth generation.

While in linear polymers the numbers of terminal groups per repeat unit tends to zero with molecular weight not affecting properties of high polymers, the situation is completely different for hyperbranched polymers. The polymerization of AB₂ type monomer leads to a hyperbranched polymer similar to dendrimers of **BrD** series where the number of terminal group per repeat unit approaches 1 not 0 with molecular weight. Bromine terminal groups strongly affect the electronic structure of hyperbranched PA. On the one hand the bulky bromine atoms decrease even more the conjugation in bromine-terminated acetylene dendrimers due to steric hindrances as followed from calculated E_g 's and IP_v constantly higher for **BrD** series. On the other hand highly polarizable bromine atoms reduces significantly the adiabatic PI_v 's to be very close to that for trans-PA oligomers. Such a strong impact of terminal groups on the electronic structure of hyperbranched polymers is a particular feature of hyperbranched architecture and very unusual for linear polymers. Therefore, the correct choice of terminal groups is extremely important to impart desirable properties to a conjugated hyperbranched polymer.

To clarify the impact of the terminal groups on such important properties of hyperbranched

polyacetylene as IP, E_g and electron affinity (EA) second generation dendritic PA oligomer (**D2**) bearing different terminal groups was modeled^[26]. The end groups have been chosen in such a way to cover all possible combination of electronic effects. The results were compared with the corresponding linear oligomer **Lin2**. Higher level of theory was used in this study: all geometry's were minimized at HF/3-21G (d) level of theory while for single point energy calculations B3LYP hybrid functional was applied with 6-31G (d) basis set. The calculation showed that the geometry of dendrimer is strongly affected by the nature of terminal group. There can be considered two main factors affecting the molecular geometry, steric and electronic. While the steric hindrances caused by terminal groups tend to deteriorate conjugation, the lonely pairs and vacant orbitals of terminal groups involved in conjugation with the rest of the molecule lead to flattening of molecule. Similar effect of planarization of molecular geometry produces ionization or addition of an electron to dendritic molecule. This effect is easy to understand taking into account energy gain produced by delocalization of excessive charge on planarization. It is noteworthy that the lone electron pairs and π -electrons of terminal groups participate in the stabilization of positive charge in dendrimers as followed from the shortening R-C bond in cation radicals compared to neutral molecules in the case of R bearing lone pairs or π -electrons.

Table 1. Calculated ionization potentials (IP), electron affinity (EA) and band-gap (E_g) for the dendrimers with different terminal groups (in eV)

Compound	Formula	IP _v ^{a)}	IP _a ^{b)}	IP _v -IP _a	EA ^{c)}	E_{g1} ^{d)}	E_{g2} ^{e)}	σ_{para} ^{f)}
D_{OMe}	C ₂₂ H ₃₂ O ₈	5.47	5.09	0.41	0.17	3.93	3.90	-0.28
D_{SMe}	C ₂₂ H ₃₂ S ₈	6.61	5.74	0.87	-1.30	4.31	4.63	-
D_{Me}	C ₂₂ H ₃₂	6.76	5.91	0.85	-0.39	4.55	4.66	-0.14
D_H	C ₁₄ H ₁₆	7.24	6.73	0.51	-0.63	4.41	4.51	0.00
D_F	C ₁₄ H ₈ F ₈	7.30	6.92	0.38	-0.70	4.13	4.20	0.15
D_{Cl}	C ₁₄ H ₈ Cl ₈	7.63	7.07	0.56	-1.59	4.14	2.74	0.24
D_{CN}	C ₂₂ H ₈ N ₈	9.16	8.74	0.42	-3.70	3.66	3.90	0.70
Lin2	C ₁₄ H ₁₆	6.39	5.89	0.50	-1.15	3.20 (3.18) ^{g)}	3.62	-

a). Adiabatic ionization potentials were calculated as the total energy difference between the neutral molecule and the corresponding cation-radical with molecular geometry optimized at HF/3-21G (d) level and single point energy calculations at B3LYP/6-31G (d) level.

b). Vertical ionization potentials were obtained as B3LYP/6-31G (d) energies difference between cation-radical and neutral molecule calculated on HF/3-21G (d) optimized geometries.

c). Electron affinities were calculated as the total energy difference between the neutral molecule and the corresponding anion-radical with molecular geometry optimized at HF/3-21G (d) level and single point energy calculations at B3LYP/6-31G (d) level.

d). Band gap calculated as HOMO-LUMO energy difference taken from a single point energy calculations at B3LYP/6-31G (d)//HF/3-21G (d) level.

e). Band gap taken from ZINDO calculations as the first singled excited state.

f). Hammett constants of the corresponding terminal groups

g) Experimental band gap for **Lin2** (Ref. 30)

The Table 1 shows calculated IP's, EA's and E_g 's of the dendrimers. As seen the electronic structure of hyperbranched polyacetylene is strongly affected by the nature of the terminal groups unlike linear conjugated polymers. IP's show clear correlation with Hammett constants (σ_{para}) of the corresponding terminal groups^[27]. Thus, the lowest IP's showing by **DOMe** molecule correspond to the lowest negative σ_{para} value and the highest IP's (**DCN**) are in agreement with the highest positive σ_{para} for CN group. This is a clear indication of the participation of terminal groups in the stabilization of excessive positive charge. The lower σ_{para} the better electron donating properties of terminal groups, are and therefore, the lower the IP's of the corresponding dendrimer. The dendrimers bearing strong electron donor terminal groups such as OMe and SMe show IP_a even lower than that of linear oligomer **Lin2**. A similar correlation holds also for EA's. The larger σ_{para} the greater the EA's. However, **DSMe** is eventually dropped out of the correlation. Even though σ_{para} is not available for SMe, the second lowest IP's among all dendrimers showed by **DSMe** would suggest strong electron donating properties for this group and, therefore, low EA for **DSMe** molecule. Nevertheless, EA of **DSMe** is rather high reaching -1.30 eV. This apparent inconsistency is due to the participation of 3d orbitals of sulfur atom in the stabilization of the negative charge. Similar effect contributes to the higher EA of **DCI** molecule compared to **DF** one.

All other things being equal the IP_v reflects the conjugation in neutral molecule while the IP_a also accounts for the relaxation of molecular geometry and electron density distribution following the ionization process. Fast ionization produced by a photon impact when nucleus and electrons have no time to relax follows the vertical mechanism, whereas the ionization related with slow electron transfer (chemical oxidation) is adiabatic process and the difference between PI_v and PI_a reflects the energy gain due to the relaxation of molecular geometry. Generalizing the data presented in the Tables it can be said that the more voluminous the terminal group is the larger IP_v - IP_a difference. This trend is broken, however, when strong interaction between lonely pairs of a terminal groups and the rest of conjugated molecule takes place similar to that of **DF** and **DOMe** molecules.

As seen from the Table 1 the E_g 's calculated by two different methods show similar trends. However, the LUMO-HOMO energy difference taken from a single point energy calculations at B3LYP/6-31G(d)//HF/3-21d(d) level reproduces best experimental E_g for **Lin2** molecule. Although there is no rigorous correlation between the volume of the terminal group and E_g 's, the larger the terminal group the wider E_g . This reflects the twisting of conjugated double

bonds in dendrimers, which is especially notable for large terminal groups. At the same time the electronic properties of the terminal groups strongly affected E_g values. Thus, all other things being equal the dendrimers bearing terminal groups with their electrons involved in conjugation show lower E_g 's (**DF** compared to **DH**, **DOMe** and **DCN** compared to **DMe**).

To gain better insight in properties-structure relationship of synthesized dendritic oligomers of β,β -dibromo-4-ethynyl styrene those oligomers were modeled using quantum chemistry tools. In order to evaluate the accuracy of HF/3-21G and PM3 model chemistries in the geometry optimization, NMR shielding tensors of dendritic molecules were computed at HF/3-21G //HF/3-21G level of theory and the simulated ^1H -NMR spectra were compared with experimental data^[28]. Computed NMR shielding tensors are known to be very sensitive to the molecular geometry^[29,30]. The results of the calculations are presented in Fig. 2. As can be seen from the picture, the calculated proton chemical shifts agree reasonably well with experimentally observed. Only for aldehyde protons the difference is about 0.7 ppm while for all other protons the deviations from experimental values are not to exceed 0.35 ppm.

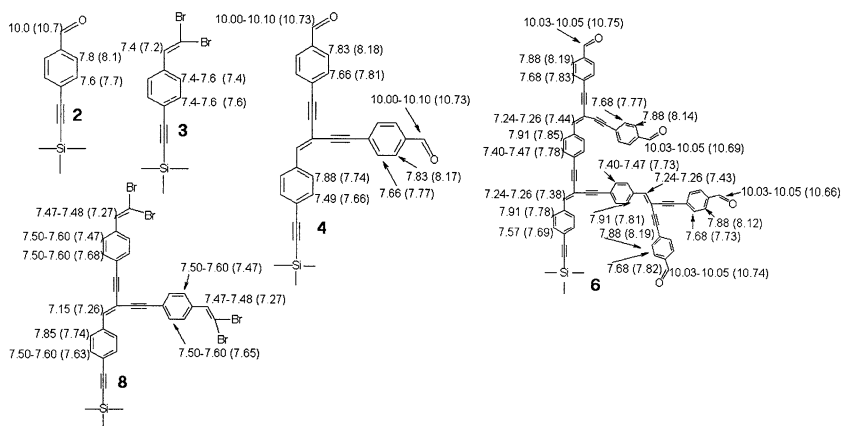


Fig. 2 Experimentally observed and theoretically calculated chemical shifts of some dendrimers.

Taking into account the above, HF/3-21G (d) level of theory is reliable enough for accurate geometry prediction of synthesized molecules. On the other hand when comparing HF/3-21G (d) Fig 2 and PM3 optimized structures the bond lengths and bond angles differed very little in the conjugated hydrocarbon part of molecules (0.01-0.02 Å and 1-2° respectively).

However, C-Si and C-Br bonds lengths in PM3 optimized structures differed by 0.04-0.09 Å and Br-C-Br angles even by 10° from these in HF/3-21G (d) optimized structures thus revealing certain deficiencies of PM3 method in the accurate treating of the atoms heavier than second row elements. Fortunately, both HF/3-21G (d) and PM3 optimized geometry produced similar molecular properties when using B3LYP/3-21G single point energy calculations as seen from the Table 1. Therefore, the most computationally demanding adiabatic ionization potential (IP_a) calculations were run at PM3-optimized geometries.

As a rule IP_a's is lower than IP_v's, the energy difference accounts for the relaxation of molecular geometry and electron density distribution following the ionization process. This is also the case for the studied dendrimers. The difference between IP_v and IP_a is larger for bromine terminated molecules and tends to increase with generation number. Fig. 3 shows PM3 optimized molecular structures of the dendritic oligomers and the respective cation-radicals. As seen there is a significant difference in shape between neutral molecules and cation-radicals. Ionization causes flattening of molecular geometry. This behavior is similar to that observed for hyperbranched polyacetylene cation-radicals^[22] and the explanation is that flattening of the molecule allows better stabilization of excessive positive charge by its delocalization. The larger the conjugated system the better stabilization of excessive charge can be achieved by the geometry adjusting which agrees with the increase of the difference between IP_v and IP_a with generation number. It is noteworthy that while **8+** is almost completely plane in **4+** molecule one of the benzene rings is almost perpendicular (at 81°) to the rest of the molecule. From our point of view this difference in molecular geometry is due to the influence of Br atoms. While in plane **8+** molecule the energy gain due to charge delocalization overcompensates the strain induced by the molecule flattening for polarizable bromine atoms participating in charge delocalization, a completely flat conformation for **4+** is not so favorable and the energy minimum is reached when one benzene ring is out of plane to decrease the steric hindrances with the rest of the molecule completely flat to achieve better delocalization of excessive positive charge.

Loose dendritic architecture of β,β -dibromo-4-ethynyl styrene oligomers contributes little to the instability and conjugation disruption compared to 1→2 branched polyacetylene. However, Br terminal atoms of dendrimers affect strongly the electronic structure of studied dendrimers. On the one hand the bulky bromine atoms decrease the conjugation in bromine-terminated dendrimers due to steric hindrances as followed from measured and calculated Eg's. On the other hand highly polarizable bromine atoms reduced significantly IP_a's to be up

to 1.5 eV lower than corresponding IPv.

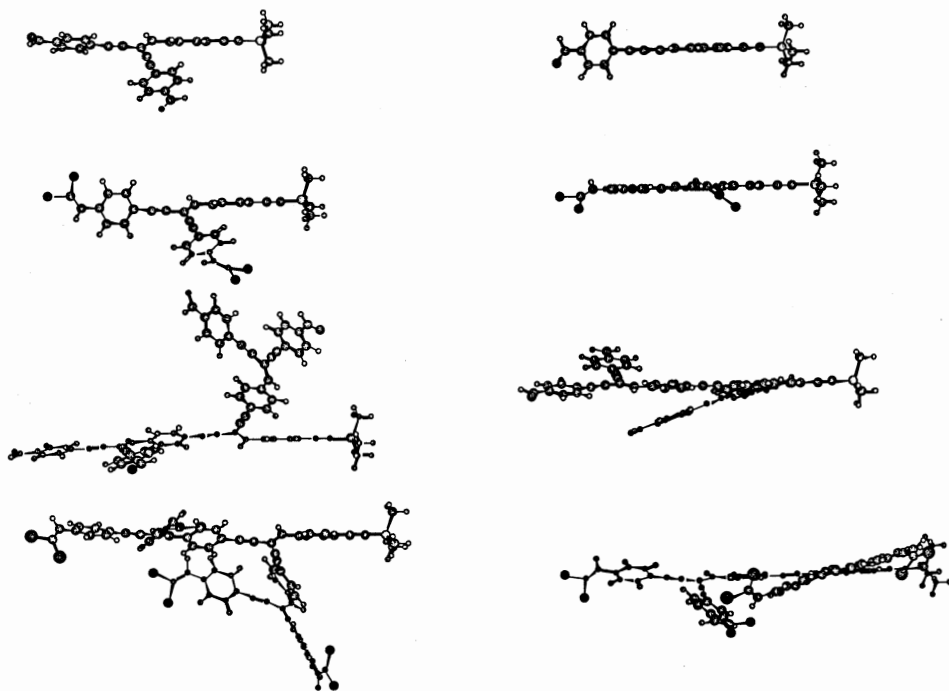


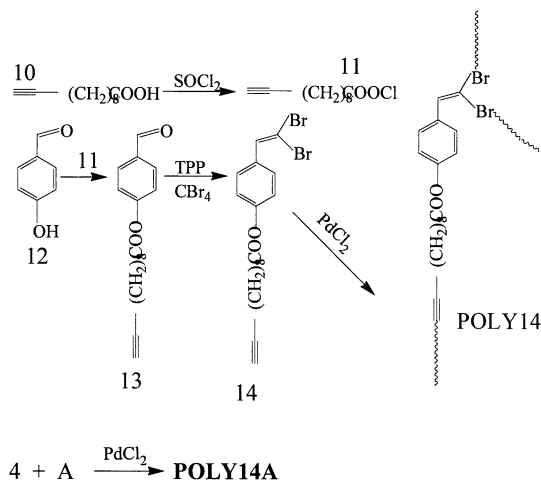
Fig. 3. PM3 optimized geometries of some conjugated dendrimers

Design, Synthesis and Molecular Modeling of Dendritic Molecules Containing Discrete Conjugated Units

In spite of much better solubility of hyperbranched fully conjugated polymers compared to their linear analogs they are still not soluble enough in low boiling solvents to form good quality films essentials for optical applications. Moreover, as it follows from electronic absorption spectra of **POLYA** and the results of molecular modeling of **POLYA** oligomers, the conjugation does not exceed a repeating unit in those types of hyperbranched polymers due to steric hindrances. On the other hand for many applications there is no need for very large conjugation system due to the fact that non-linear optical susceptibility and energy gap tends to a limit with effective conjugation length.

Therefore, a hyperbranched polymer having discrete conjugated groups connected by flexible spacers would combine the desirable electronic properties of fully conjugated polymer with

improving tractability and film forming properties. Two approaches to hyperbranched polymers with discrete conjugated units have been studied; polymerization of AB₂ type monomer when discrete conjugated unit is formed during the polymerization and polymerization of AB₂ monomer where conjugated unit is part of monomer.

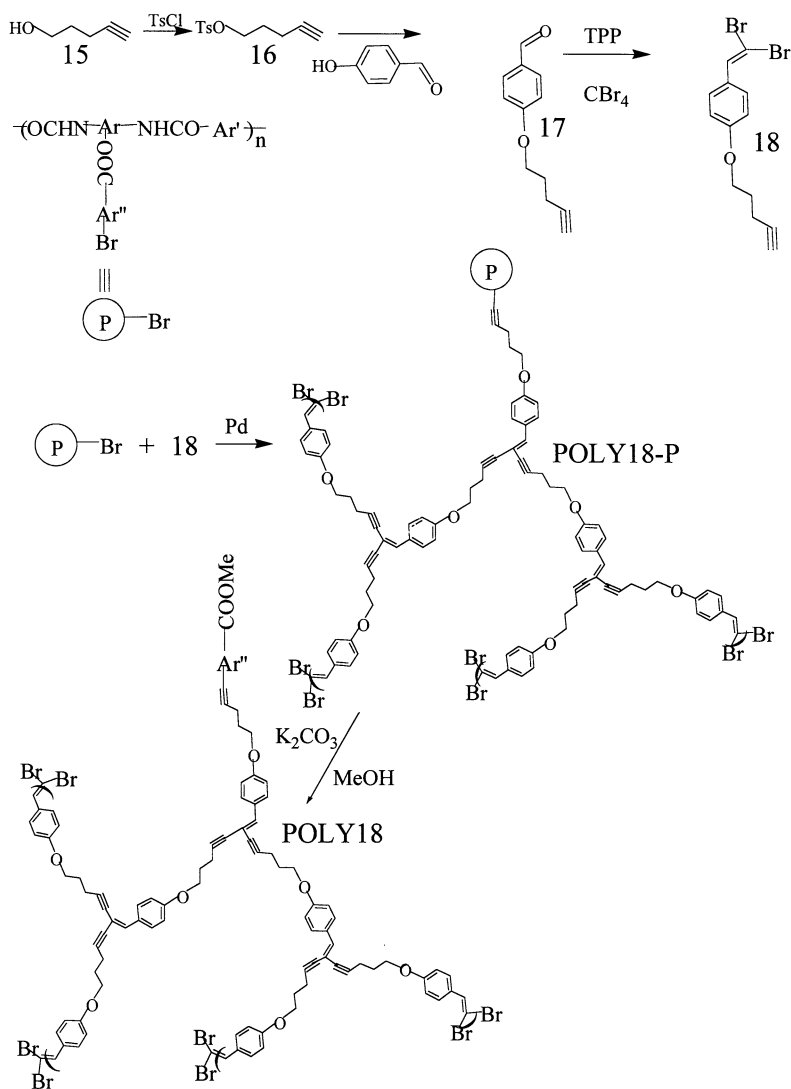


Scheme 3 Synthetic route to a hyperbranched polymer containing discrete conjugated units

The first approach is shown in Scheme 3. Monomer **14** having octamethylene spacer produces polymer **POLY14** under conditions similar to formation of **POLYA**. During the polymerization β,β -diethynylstyryl conjugated group is formed^[31]. Hyperbranched polymer **POLY14** was completely soluble in aliphatic chlorinated hydrocarbons at room temperature and gave transparent and flexible films on casting from chloroform. GPC gave M_w of 11500 for **POLY14**. Although, the DB of **POLY14** could not be exactly determined, the data of ¹³C-NMR spectroscopy suggest the presence of linear fragments of $C\equiv CBrC=CH$ type where only one bromine reacts with terminal acetylenic group. UV-visible absorption spectra of **POLY14** clearly show the formation of discrete conjugated groups during the hyperbranched polymerization reflecting in bathochromic shift of long wave absorption maxim in **POLY14** compared to monomer **14** (from 226 to 300 nm). The relative amount of conjugated units in hyperbranched polymer can be increased by copolymerization of monomers **A** and **14** resulted in hyperbranched polymer **POLY14A**. When molar ratio of monomers is 1:1 **POLY14A** was almost completely soluble in hot chlorinated solvents like chlorobenzene and *o*-dichlorobenzene and showed MW of 11800. It is noteworthy that long wave absorption

maxim of **POLY14A** (360 nm) is significantly red shifted compared to **POLY14** reflecting longer average conjugation in the former. Both hyperbranched polymers **POLY14** and **POLY14A** present intense photoluminescence in visible region. While **POLY14** emits blue light (maximum at 468 nm) **POLY14A** shows fluorescence in green region (maximum at 524 nm) when excited at 350 nm. Therefore, just by changing monomer ratio in copolymer it is possible to tune the emission spectrum of conjugated hyperbranched copolymer.

An undesirable feature of one-step AB₂ polymerization is loss of control over molecular weight accompanied by a broad molecular weight distribution. Recently it has been found that hyperbranched polymerization on an insoluble solid support allows better control over the structure of hyperbranched polymers^[32]. Therefore this method was tested for the synthesis of hyperbranched polymers with discrete conjugated units^[33]. Novel monomer and novel polymer supports have been synthesized (Scheme 4). AB₂ type monomer **18** was synthesized starting from 4-hydroxybenzaldehyde and 5-hexyne-1-ol (**15**) in three steps. The tosylation of **15** with TsCl produced tosylate **16**. The alkylation of 4-hydroxybenzaldehyde gave **16**, which is converted in monomer **18** by the Wittig reaction with dibromotriphenylphosphorane. Several new aromatic polyamides bearing aromatic bromine have been prepared and used as solid supports in hyperbranched polymerization. When monomer **18** is polymerized in the presence of a solid support **POLY18** is formed both in solution and on the support due to the Pd catalyzed cross-coupling reaction of terminal acetylene with aromatic bromine thus formed sp-sp² link. The polymer formed in solution is soluble in the reaction mixture and is separated from insoluble solid support by simple filtration. The support bounded hyperbranched polymer **POLY18-P** is cleaved by K₂CO₃ catalyzed transesterification in MeOH followed by the extraction with chloroform as shown in Scheme 4. The M_w found for **POLY18** formed in solution was of 17500 with polydispersity of 3.5 according to GPC. The DB, determined from ¹H-NMR spectra of protons *ortho* to vinyl group for this polymer was 30-35 %. Another part of polymer **POLY18** obtained after the detaching from the insoluble polymer support differed in properties from the polymer obtained in solution. **POLY18** synthesized using solid support showed lower molecular weight (M_n between 7300 and 12000) depending on polymeric support nature and lower polydispersity (about 1.8). It should be mentioned two important observations made for this type of hyperbranched polymerization. The first is that only the supports bearing bromine very active in Pd catalyzed cross-coupling reaction caused the formation of bounded hyperbranched polymer. Thus, dibromovinyl group is active enough to



Scheme 4 Polymer supported hyperbranched polymer synthesis

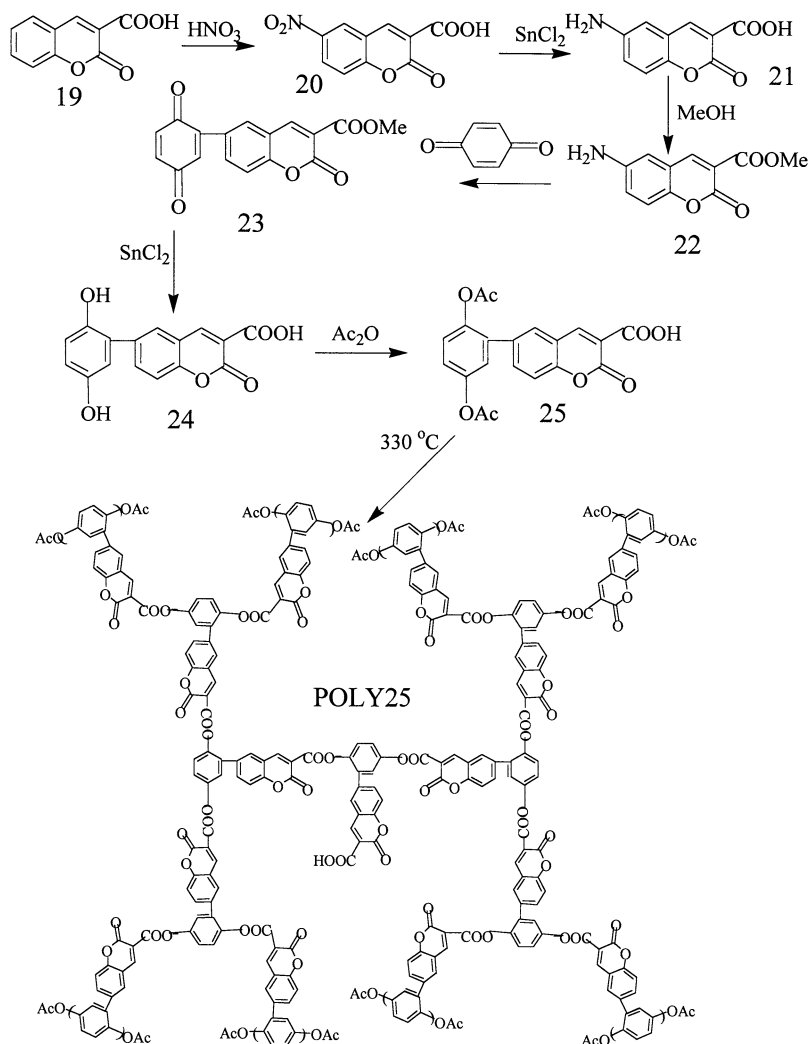
cause the formation of bounded polymer while aromatic bromine of 4-bromo benzoyloxy group is not. Another interesting feature is that the molecular weight of detached polymer increased with the distance between active sites polymeric support. To gain better understanding of the nature of this phenomenon the process of solid supported hyperbranched polymerization was modeled using MM2 force field^[34]. The polymeric supports were

represented by oligomers of 7 and 14 repeating units while the hyperbranched polymer at different stages of growth were modeled by perfect dendritic molecules from first to sixth generation. The results showed that the decrease in molecular weight of detached polymer with decrease of the distance between active sites of polymeric support is due to steric hindrances between hyperbranched molecules attached to adjacent active sites of polymeric supports. It is noteworthy, that it has not been found any steric hindrances between the support and hyperbranched molecule attached to the support molecule.

Another approach to the synthesis of hyperbranched polymers with discrete conjugated units is shown in Scheme 5^[35].

Coumarins have been recently paid attention for their fluorescent properties and they are widely used as laser dyes due to their excellent photostability and quantum yield of luminescence^[36,37]. Coumarin-containing AB₂ monomer **25** was synthesized starting from 3-carboxycoumarin **19** in 6 steps. The nitration of coumarin **21** followed by the reduction of formed 6-nitrocoumarin-3-carboxylic acid **20** produced 6-aminocoumarin-3-carboxylic acid **21**. After esterification of carboxylic group of **21** the diazonium salt of **22** was reacted with benzoquinone to give substituted benzoquinone **23**. The reduction of quinone **23** with simultaneous hydrolysis of carbomethoxy group and acetylation of formed hydroquinone **24** with acetic anhydride leads directly to AB₂ coumarin containing monomer **25**.

High temperature transesterification of monomer **25** in melt results in hyperbranched coumarin containing polymer **POLY25** which is completely soluble in chloroform. The DB was found to be 1 using the ratio of the inner to outer protons in ¹H-NMR spectra which was also confirmed by the analysis of NMR signals of CH₃ protons of acetyl groups. The number average molecular weight calculated from ¹H-NMR spectrum by the end group analysis was of 27000, corresponding to degree of polymerization of 60. A series of copolymers of monomer **25** with AB monomer m-acetoxybenzoic acid have been prepared to correlate the polymer properties with the density of branching. Among all described here hyperbranched polymers **POLY25** and the respective copolymers were most thermostable which is even reflected by the method of preparation. The 10% weight loss temperatures were in the range of 370-400 °C. As a result of the presence of 6-phenylcoumarines chromophores in **POLY25** and copolymers were blue emitters, emitting in the range of 450-490 nm when excited at 400 nm. Single layer electroluminescent devices on the basis of **POLY25** have been made showing turn on voltage from 3 to 8 V.



Scheme 5 Synthesis of coumarin containing hyperbranched polymer

Conclusions

Hyperbranched conjugated molecules have been synthesized both by polymerization of AB₂ type of monomers and stepwise synthesis. Fully conjugated hyperbranched polymers were found to be much more soluble than the respective linear polymers while maintaining all other properties characteristic of conjugated polymer. The introduction of flexible spacer between

conjugated fragments increases even more the processability of hyperbranched polymers. In the case of hyperbranched polymerization of coumarin-containing monomer of AB₂ type novel hyperbranched coumarin-containing polymers and copolymers were prepared with DB close to 1. Those polymers combined excellent solubility and film forming properties with intense photo and electro-luminescence properties. To improve the control over the structure of hyperbranched molecules solid-supported synthesis has been tested. It was found that choosing appropriate solid support it was possible to control the molecular weight and DB of a hyperbranched polymer. The theoretical analysis of the model hyperbranched polyacetylene showed that although hyperbranched structures were less stable than the respective linear analogs the difference is not excessively large and tends to a limit with molecular weight of hyperbranched molecule while the conjugation in conjugated dendritic molecule extends up to fourth or fifth generation. It was shown that the electronic properties of terminal groups were of importance and allow to tailor the electronic properties of hyperbranched molecule.

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