Hyperbranched Polymers with a Degree of Branching of 100%

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SUMMARY: 4-Methoxy-4'-(3"-N-maleimidopropoxy)benzaldazine has been prepared and used for the synthesis of hyperbranched polymers by ‚criss-cross'-cycloaddition. In this type of reaction two unsaturated groups, such as the maleic imide groups, are added to the azine function. Hence, the azine behaves as a difunctional system, and therefore 4-Methoxy-4'-(3"-N-maleimidopropoxy)benz-aldazine is an AB_2 monomer, with the maleic imide group being the A-function, and the azine group representing the B_2 part. The nature of this cycloaddition reaction ensures the coupled reaction of the two B-functions of each monomer unit. Consequently, the resulting polymer consists exclusively of branched and terminal repeating units and therefore has a degree of branching of 100%.

Introduction

Hyperbranched polymers have attracted much interest recently because of their unique set of properties. Like dendrimers, they possess e.g. an extremely large number of functional groups, a higher segment density than linear analogs, good solubility and low melt viscosity. In contrast to dendrimers, hyperbranched polymers are not spherical, they are not unimolecular, their architecture is quite uncontrolled, and the functional groups occur throughout the molecule rather than exclusively at the surface. However, hyperbranched polymers are easily prepared from monomers of the AB_x-type in a straightforward one-step synthesis.

A number of approaches have been proposed to achieve control of the degree of branching of hyperbranched polymers in order to shift the properties more closely to that of dendrimers. Examples are slow monomer addition (with or without the addition of core molecules)[1,2,3,4], the addition of core molecules in self-condensing vinyl polymerization[5,6,7,8,9], the use of monomers with preformed branch points[10,11], activation of the second B-group by reaction of the first B-group[12,13,14], and post-synthetic modification of the linear units of conventional hyperbranched polymers with monofunctional compounds into branched units[15].
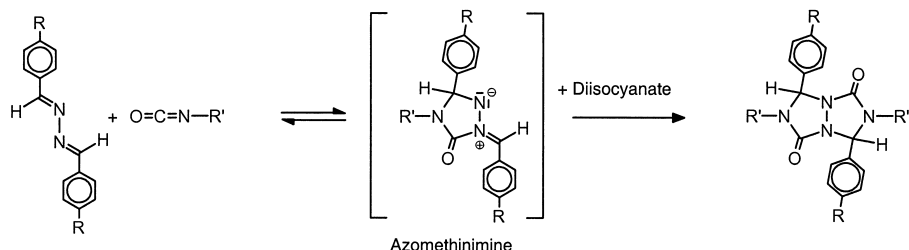
While all these methods have been shown indeed to have an influence on the degree of branching, none of them excludes the formation of linear repeating units completely, and therefore none of these methods guarantees definitely the formation of hyperbranched polymers with 100% branching. In this paper we are presenting a different approach to this problem.

Selection of a suitable type of reaction

Complete branching of an AB$_2$ monomer must occur, when both B groups are coupled in a way which prevents reaction of a single B group and enforces reaction of both B groups simultaneously. The following requirements are necessary for a reaction or reaction sequence in order to show this type of behavior:

- ✧ The reaction of the first B group with an A group must result in an *unstable* intermediate.
- ✧ The formation of the intermediate must be completely *reversible*.
- ✧ The reaction of the second B group with another A group must convert the intermediate into a *stable* final product.
- ✧ This second step must be *irreversible* under the reaction conditions.
- ✧ No other reaction or reaction sequence must occur.

The 'criss-cross'-cycloaddition reaction[16,17] between azines and unsaturated compounds meets these criteria. As Huisgen[18,19] proposed and Burger[20,21] proved, this reaction proceeds in two steps via an azomethinimine intermediate (Scheme 1). Usually, this intermediate is unstable, and unless the second step of the reaction occurs immediately after the first step to conclude the sequence under formation of the final stable product, the intermediate decomposes, reversing its formation reaction. Scheme 1 shows the mechanism using the reaction between a benzaldazine derivative and an isocyanate as an example.
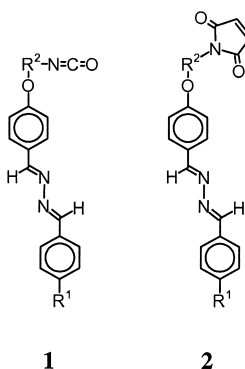

Scheme 1: Mechanism of the 'criss-cross'-cycloaddition reaction between azines and isocyanates

As we have reported previously[22,23,24,25,26,27)], the sequence shown in Scheme 1 reliably leads to telechelic polymers with two isocyanate end groups, when an azine is reacted with a diisocyanate. The functionality of these telechelics is independent of the stoichiometry of the starting materials. Thus, it is clear that the azomethinimine can follow only two reaction paths: either it adds another isocyanate group, or, if none is available, it decomposes into azine and isocyanate. Consequently, the azine group either reacts as a difunctional unit, or it does not react at all. Based on this observation, an azine which contains an unsaturated function such as an isocyanate or a CC double bond represents an AB_2 monomer according to the requirements discussed initially.
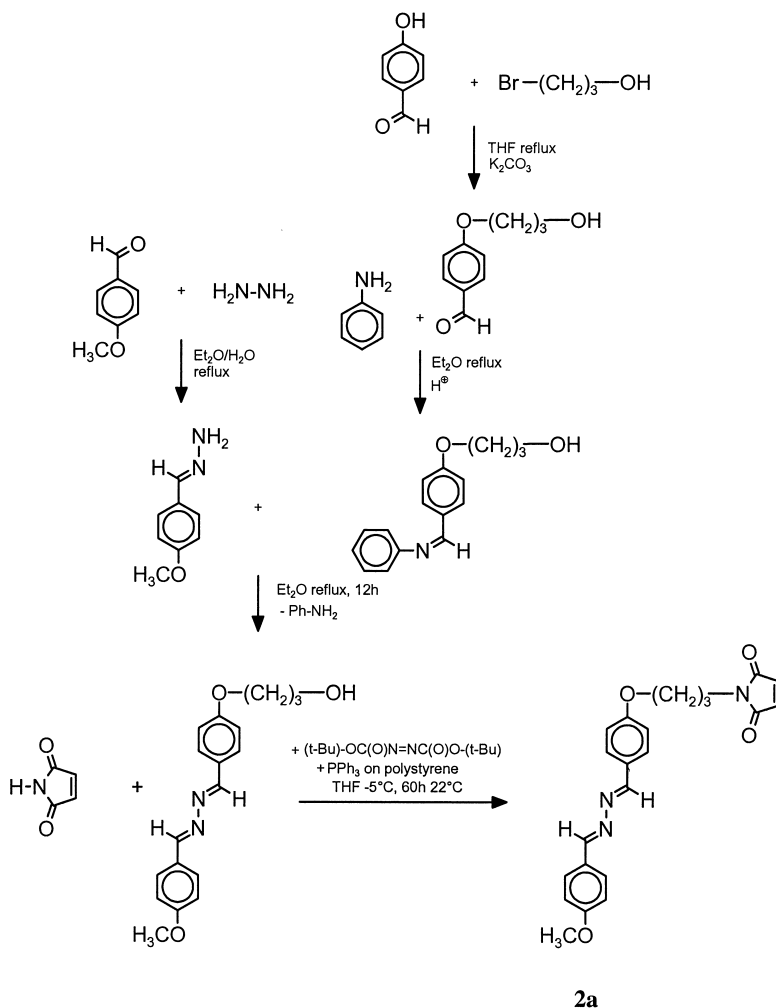
Synthesis of the monomer

Potential monomer structures are shown in Scheme 2. They are asymmetrical azines, which are not easy to synthesize in high yield and sufficient purity for polycondensation reactions..

Scheme 2: Target structures

Azines are usually prepared from carbonyl compounds and hydrazine under evolution of water. They undergo exchange reactions easily in the presence of water. Consequently, the preparation of asymmetric azines directly from different carbonyl compounds and hydrazine is often unsuccessful, since normally one of the symmetrical azines crystallizes more readily than the asymmetrical derivative and is therefore isolated first. As the most readily isolated derivative is removed from the equilibrium by crystallization, all of the asymmetrical azine is by and by converted to the symmetrical ones, if no precautions are taken. Many approaches can be found in the literature to overcome this problem. For our monomers, it proved to be most useful to prepare the hydrazone of one of the molecule halvesA and the Schiff-base with aniline of the

other ‚halve' (Scheme 3). On reaction of these two, aniline is formed rather than water, and at exact stoichiometry the desired asymmetrical azine is obtained exclusively. Scheme 3 shows the reaction sequence for monomer **2a** (R^1 = -OCH$_3$, R^2 = -(CH$_2$)$_3$-).

Scheme 3: Synthesis of monomer **2a**

From the pathway shown in Scheme 3 it is clear that rather strong nucleophiles such as amine and hydrazone groups are involved. These would react with the isocyanate function of monomers of type **1**, which demands the use of a protective group for the isocyanate. So far, our attempts to prepare the asymmetrical azine with an isocyanate group in sufficiently pure form have not been

successful.

In contrast, the maleic imide group is less readily attacked by nucleophiles, and thus seemed more promising. Finally, the pathway shown in Scheme 3 provided access to the desired monomer **2a** in pure form. A mass spectrum of the product as obtained from the last synthesis step indicated the absence of the two symmetrical azines. Even traces of these would result in undesired structures: One of the symmetrical derivatives acts as an A_2-monomer, introducing linear repeating units; the other one acts as an A_2B_2-monomer, causing crosslinking.

Polymerization

Monomer **2a** was heated to 180-185 °C to achieve polymer formation. It is interesting to note that products which were formed under vacuum or in presence of air (moisture!) were indeed partly insoluble due to crosslinking. This behavior should be expected based on the characteristic reactivity of asymmetrical azines. In the presence of traces of water, both symmetrical azines are formed from the asymmetrical azine in monomer **2a**. Since one of them is actually an A_2B_2-monomer, crosslinking is to be expected under these conditions. Also, when the reaction is conducted under vacuum, both symmetrical azines are formed, with the sublimation of 4-methoxybenzaldazine being the most probable driving force. In contrast, soluble polymers were obtained under dry nitrogen atmosphere. Table 1 summarizes the results.
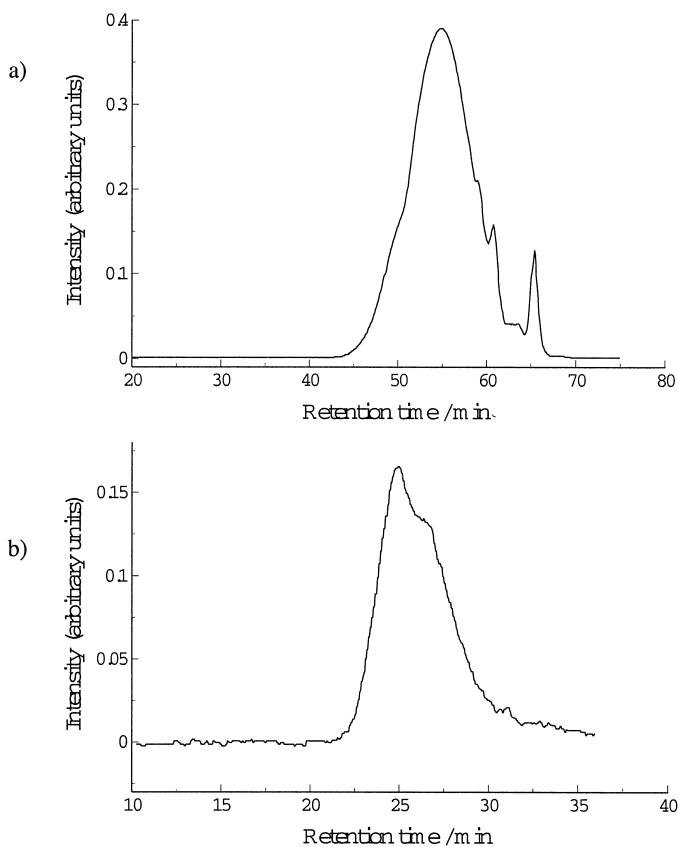
Table 1: Polymerization of monomer **2a**

No.	Reaction temperature	Reaction time	Atmosphere	$\overline{M_n}$ [a]	$\overline{M_w}$ [a]
	°C	min		$g \times mol^{-1}$	$g \times mol^{-1}$
1	185	15	dry N_2	5700	12500
2	185	30	dry N_2	4400	8600
3	180	15	air	insoluble	
4	185	15	vacuum	insoluble	

[a] GPC in $CHCl_3$, calibration with linear polystyrene

Molar Masses

The molar masses are not yet high enough to show the typical multimodal distribution of hyperbranched polymers. The reason for the limited molar masses obtained so far has to be

clarified in the future. Possibly, the reaction conditions can be improved. However, there is also the possibility of an inherent limitation due to the requirement of quasi-simultaneous reaction of both parts of the azine: as the number of maleic imide groups decreases with increasing conversion, the reaction may come to a stop because of the strongly decreasing probability of an encounter between an azine group and two maleic imide groups at the same time. It is quite obvious that the reaction is third order in functional group concentration, while conventional condensation reactions used for the preparation of hyperbranched polymers are second order in functional group concentration (provided external catalysis is used). Further work is required to shed light on this. Scheme 4 shows the GPC curves as obtained with RI-detection and polystyrene calibration (a), and a light scattering detector (b).
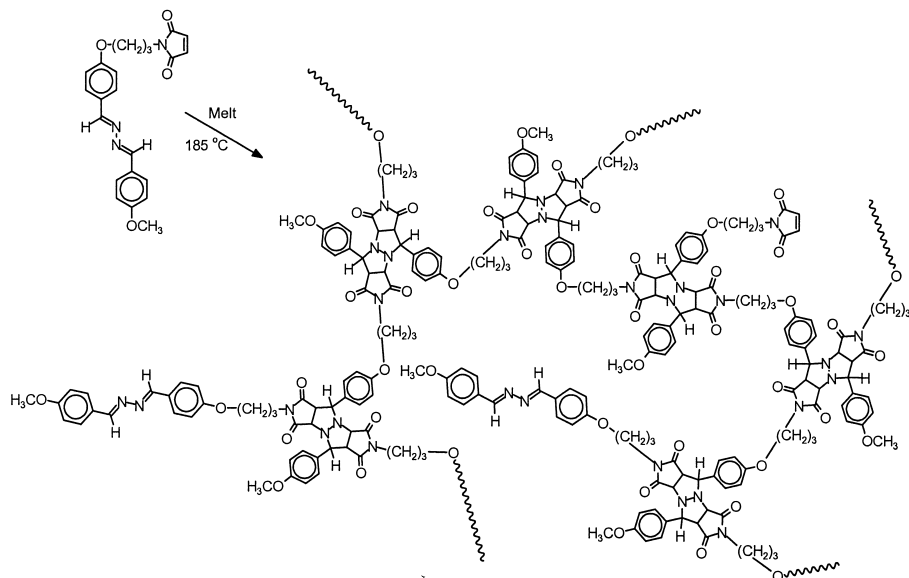

Scheme 4: GPC curves of the polymer from **2a** (entry 1, Table 1); a) in CHCl$_3$ with linear polystyrene calibration and RI detection; b) in THF with light scattering detection

DSC

DSC measurements of the soluble hyperbranched polymers exhibit a glass transition temperature of $T_g = 136$ °C. No other phase transition were observed.

Chemical structure and potential defects

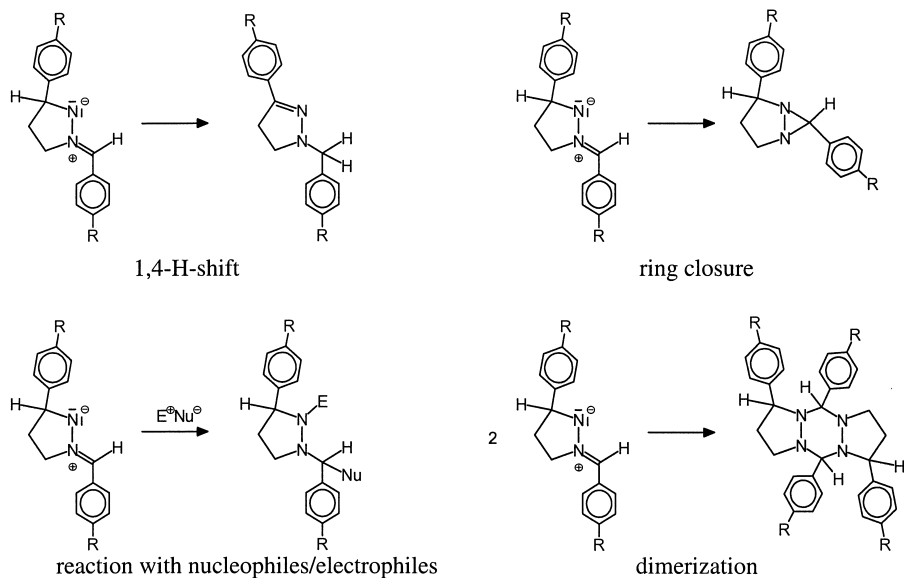Scheme 5 shows the idealized structure of the hyperbranched polymers.

Scheme 5: Structure of the hyperbranched polymers

Any defect structures which might be caused by undesired side reactions would result in incomplete branching, and hence the original idea of a perfectly branched hyperbranched polymer would be compromised. Therefore, the analysis of the chemical structure and the search for defects is important.

The most obvious method to check for the presence of defect structures is MALDI-TOF mass spectroscopy. Perfect branching requires the addition of exactly two repeating units in every addition step, and therefore the difference between the masses of the oligomers must equal twice the mass of the monomer. Defects would result in the addition of only one repeating unit, resulting in a linear, non-branched unit, and should be easily discernible because of the resulting deviation of the molar mass. However, so far we have not been able to obtain a MALDI-TOF

mass spectrum. The problem appears to be the absorption of the terminal azine units, which is close to the wavelength of the laser used for desorption, causing fragmentation.

Thus, NMR spectroscopy was used to check for defect structures. Scheme 6 shows the most probable defects.

1,4-H-shift   ring closure

reaction with nucleophiles/electrophiles   dimerization

Scheme 6: Possible defect structures

The shift of a hydrogen atom from 1-position of the 1,3-dipole to the 4-position is comparable to the 1,5-H-shift of dienes, and it is frequently observed[18,19] for various 1,3-dipoles. However, it is a concerted orbital symmetry controlled reaction, and therefore it requires a cyclic transition state. In our case, this is impossible, because the azomethinimine is fixed in a `transoidA state, because it is part of the five-membered ring, and partly exocyclic.
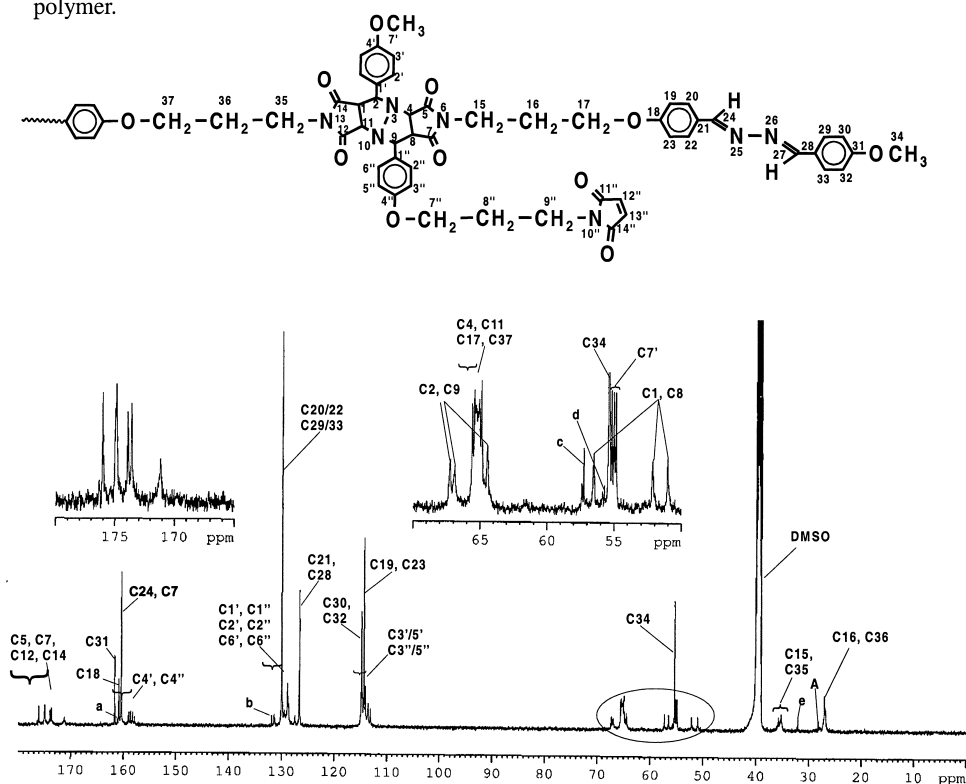
1,3-Dipoles can form a three membered ring in an electrocyclic reaction. This can not be excluded here, but the high reaction temperature of 180-185 °C should prevent the formation of the strained three membered ring.

The cyclodimerization is unlikely due to the considerable steric crowding of the resulting structure.

Finally, the addition of nucleophiles could cause problems. Again, the high reaction temperature should help in part, because the presence of water in the reaction at 180 °C is not very likely. In
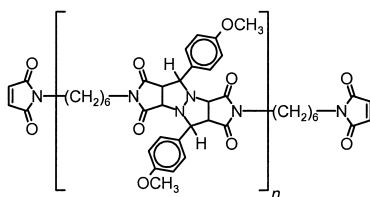
addition, model reactions were performed, in which an azine was reacted with a maleic imide in the presence of phenol as a model nucleophile. The only product found in the resulting product was the cycloaddition product. No reaction with phenol was observed, even at molar concentrations of phenol. Thus, at least at high reaction temperatures the system appears to be quite robust, and undesired side reactions can obviously be avoided.

The carbon 13 NMR spectrum of the hyperbranched polymer **1** is shown in Scheme 7. It looks quite complicated at first sight, but all signals have been assigned by comparison with model compounds. Four isomers of the central tetracyclic ring system (see Scheme 5) have been identified[28]. Scheme 8 compares the spectra of a model compound (all isomers present), a linear model polymer, and the hyperbranched polymer. The similarity of the signal pattern clearly indicates the agreement between the chemical structures of the models and the hyperbranched polymer.
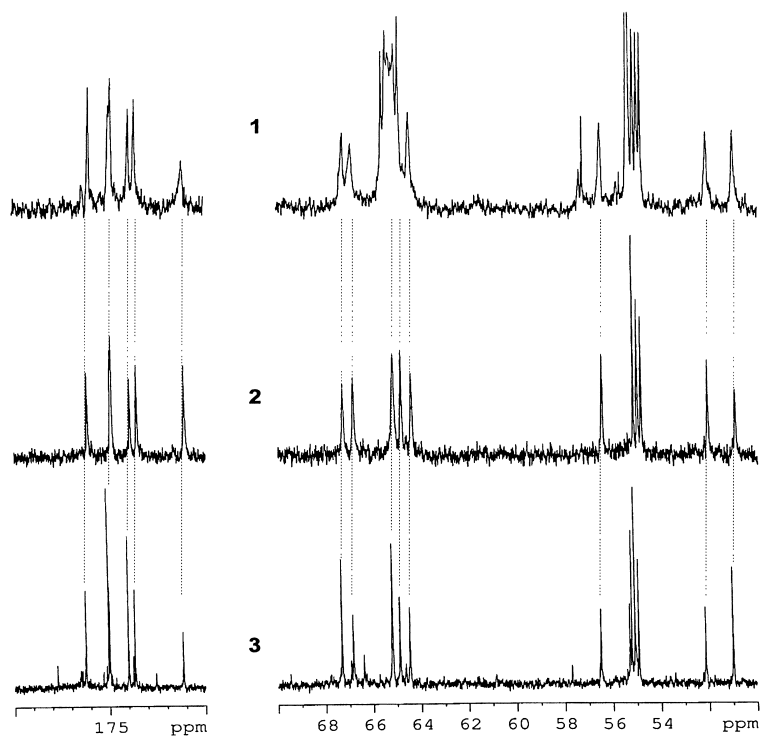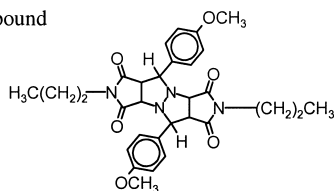

Scheme 7: ^{13}C NMR of the hyperbranched polymer

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2. linear model polymer

3. low molar mass model compound

Scheme 8: Comparison of the ^{13}C NMR spectra of 1) the hyperbranched polymer, 2) a linear model polymer, 3) a low molar mass model compound

Conclusions

An AB$_2$ monomer including an azine group to serve as the two B-functions and a maleic imide group as the A-function was successfully synthesized. Its polymerization at 180-185 °C resulted in the formation of a perfectly hyperbranched polymer. No indication of any defect structures, leading to linear repeating units, were found by NMR spectroscopy or model reactions. Further characterization and improvements of the molar mass of the polymers to determine whether they are closer to perfect dendrimers in their physical properties than conventional hyperbranched polymers is going on.

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