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Facile synthesis of hyperbranched polymers

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A modification of the $A_2 + B_3$ synthetic approach to the preparation of hyperbranched polymers is suggested providing a convenient route to obtaining high-molecular-weight hydrocarbon polymers starting from 1,3,5-triphenylbenzene and 1,4-bis(chloromethyl)benzene.

Hyperbranched polymers are of interest because of their unique chemical and physical properties, as well as their potential applications in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science. Hyperbranched polymers can be prepared by various methods including single-monomer and double-monomer approaches.[1,2] The latter includes the polymerization of A_2 and B_n (where the number of functionalities $n > 2$) monomers.[3] The first intentional preparation of a hyperbranched polymer *via* this approach was reported elsewhere.[4,5]

An electrophilic aromatic substitution reaction in the presence of Friedel–Crafts catalysts was used for hyperbranched polymer preparation as early as 1885.[6] The chloromethyl functional group was involved in the reaction both in the course of preparation of hyperbranched polystyrene[7] and for crosslinking of this polymer to prepare so-called ‘nanosponges’.[8]

The $(A_2 + B_n)$ method of hyperbranched polymer preparation based on Friedel–Crafts catalysts for stimulating an electrophilic aromatic substitution reaction between 1,3,5-triphenylbenzene and 1,4-bis(chloromethyl)benzene was modified. The method consists in a reaction between the co-monomers in dichloroethane at 80 °C during 6 h. The reaction was initiated by the addition of $SnCl_4$ [in a 1:1 ratio with 1,4-bis(chloromethyl)benzene] and stopped by the addition of acetone. The reaction mixture was poured into HCl (1:1) and vigorously stirred. The organic layer was washed with distilled water until a negative reaction for Cl^- ions with $AgNO_3$, and then mixed with an excess of ethanol. The precipitate was filtered off and washed with fresh alcohol. The residual chlorine content was less than 0.5%.

The observed reverse proportionality between the intrinsic viscosity and the molecular weight (Table 1) corresponds to the expected hyperbranched structure of the polymers obtained. The polymers were characterised by FTIR, NIR-FT Raman and fluorescence spectroscopies, DSC, TGA and elemental analysis. The polymer structure is shown in Scheme 1.

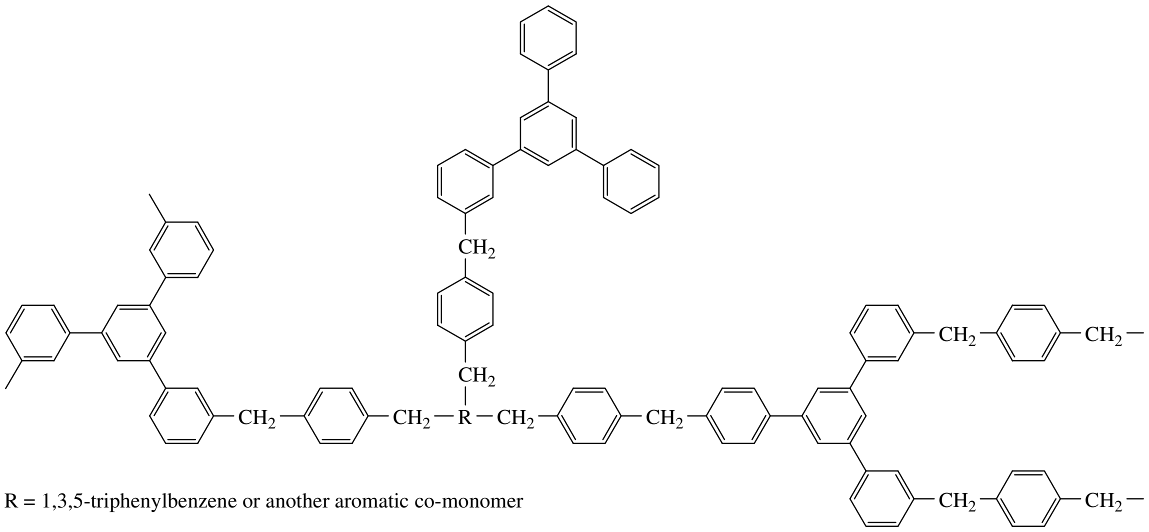
Table 1 Characteristics of hyperbranched polymers.

1,3,5-Triphenylbenzene: 1,4-bis(chloromethyl)benzene molar ratio	Yield (%)	Intrinsic viscosity^a/ dl g^{-1}	V^b/cm^3 g^{-1}	M^c_{SD}/ 10^3 Da
1:1	79.5	0.242	0.911	112
1:1.25	82.1	0.207	0.919	185
1:1.5	85.2	0.136	0.931	445
1:1.75	89.7	0.165	0.945	590

[a]In THF at 25 °C. [b]Partial volume of macromolecules in a THF solution. [c]Sedimentation-diffusion method in THF at 25 °C.

At initial 1,3,5-triphenylbenzene:1,4-bis(chloromethyl)benzene ratios from 1:1 to 1:1.75, white amorphous powdery products have been obtained. Note that no gel formation was observed. The reaction mixtures remained clear and transparent even on heating a 1,3,5-triphenylbenzene–1,4-bis(chloromethyl)benzene (1:1.5) mixture for 36 h or using 1,4-bis(chloromethyl)benzene–$SnCl_4$ (1:2). The resulting hyperbranched polymers were readily soluble in $CHCl_3$, benzene, THF, *etc*.

Although the degree of branching is one of the most important parameters for the comprehensive characterization of hyperbranched polymers, only qualitative assessments of the degree of branching of new hyperbranched polymers are possible. An attempt to evaluate the DB of the resulting polymers using NMR spectra was ineffective because of unusually strong NMR line broadening resulting in the featureless spectra of these



R = 1,3,5-triphenylbenzene or another aromatic co-monomer

Scheme 1

complex molecular structures. An analysis of the FTIR spectra of the products obtained starting from different ratios between the co-monomers demonstrated systematic changes in the pattern of aromatic substitution. Qualitatively, the extent of branching correspond to the partial volume of macromolecules (Table 1).

The suggested synthetic route has the following advantages: (1) a variety of aromatic compounds could be used as the B_3 monomer [*e.g.*, the reaction of 1,3,5-tri(biphenylene)benzene with 1,4-bis(chloromethyl)benzene also yielded hyperbranched polymers]; (2) several co-monomers could be used in the one-pot synthesis (*e.g.*, 1,3,5-triphenylbenzene with small additions of rubrene and diphenylanthracene); (3) other A_2 monomers could be used [*e.g.*, chlorodimethyl ether can be successfully used instead of 1,4-bis(cloromethyl)benzene]; (4) the reaction proceeds under mild conditions ensuring minimal side reactions and provides high-molecular-weight products in good-to-excellent yields; (5) readily soluble products are obtained; (6) further transformation of the reaction products could be made for various purposes (*e.g.*, a hyperbranched macromolecule could be cross-linked by the addition of an A_2 monomer to obtain mono-macromolecule particle). Hypothetically, 1,3,5-triphenylbenzene can be rendered as not a common B_3, but rather as $B_3C_6D_6E_3$ node (where B, C, D and E designate hydrogens accessible in the *para*-, *ortho*- and *metha*-positions of 'external' phenyl nuclei and three hydrogens of the 'internal' phenyl core.

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