Soluble hyperbranched polymers with high inner surface areas

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Fully soluble rigid hydrocarbon hyperbranched polymers exhibit high inner surface areas.

Hyperbranched polymers (HP) are macromolecular species with a three-dimensional dendritic-type architecture, which can be prepared through a one-pot synthesis. Due to their unique physical and chemical properties and potential applications in various fields, such materials attract rapidly growing interest.[1]

Nanoporous materials are of great technological importance owing to their large and accessible surface areas (typically, 300–1500 $m^2\ g^{-1}$).[2] They include zeolites (alumosilicates), some bulky metal chelates, activated carbons and hypercrosslinked organic polymers.[3,4]

High inner surface area in organic linear polymers was firstly reported for substituted polyacetylenes containing bulky substituents, best represented by poly(1-trimethylsilyl-1-propyne).[5] A family of non-network polymers that form microporous solids simply because their highly rigid and contorted molecules cannot fill space efficiently was described recently.[6] Note that, in both cases, linear polymers were concerned. Inherent nanoporosity and high inner surface area are characteristic of individual macromolecules, so-called nanosponges, which were prepared by the intense intramolecular crosslinking of individual polystyrene coils.[7] Spherically shaped nanosponges are soluble in appropriate solvents (THF, $CHCl_3$ and toluene), but they do not form films or membranes.

Here we report the high inner surface area of HP prepared by means of an electrophilic aromatic substitution reaction (in the presence of a Friedel-Crafts catalyst) between 1,3,5-triphenylbenzene (TPB) and 1,4-bis(chloromethyl)benzene (BCB).[8] Monomer ratios and some properties of HP are given in Table 1. Samples with TPB:BCB ratios from 1:1 to 1:1.75 were obtained as white amorphous powders fully soluble in solvents like $CHCl_3$, benzene and THF. Transparent films can be cast from the polymer solutions. However, the surface areas of the films are lower than that in powders and depend on both the solvent evaporated and the solvent evaporation rate.

Elemental analysis and spectroscopic data of the polymers are consistent with their proposed structures.

It was found that polymers obtained by precipitation from solutions have high and steady surface areas (Table 1). Notable inner surface appeared in the sample with TPB:BCB = 1:1.5 and became very large with a 1:1.75 ratio. This tendency correlates with corresponding growth of partial volume of macromolecules in THF solutions (Figure 1).

We believe that the occurrence of a free inner surface and growth of the partial volume in solutions are connected with the influence of two factors. Firstly, the macromolecules incorporate rigid TPB fragments, which promote the formation of stiff enough spatial structures. Secondly, at ratios more than 1:1.5, there is an excess of BCB, which could occupy any free position of both TPB and BCB fragments within the hyperbranched macromolecule.[7,8] This could lead to the formation of additional branches and hence to the formation of more crowded structures, which cannot pack into dense globules and then into a nonporous solid phase. The growing free volume within hyperbranched species obviously becomes accessible to argon atoms and remains less accessible to larger THF molecules (Figure 1).

Table 1 Monomer ratio, yield and some characteristics of HPs.

TPB:BCB molar ratio	Yield of reaction (%)	MW[a]/ 10^{-3} g mol^{-1}	S^b_{BET}/$m^2\ g^{-1}$	V^c/$cm^3\ g^{-1}$
1:1	79.5	112	34.4	0.911
1:1.25	82.1	185	35.5	0.919
1:1.5	85.2	445	80	0.931
1:1.75	89.7	590	485	0.945

[a]Ultra-centrifuge sedimentation method in THF. [b]The apparent specific inner surface area was measured by the thermal desorption of argon and calculated according to the BET equation. [c]Partial volume of macromolecules in THF solution.

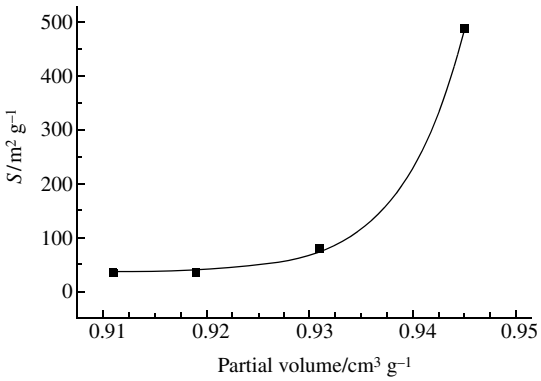

Figure 1 Corrrelation between inner surface area and partial volume (see Table 1 for data). Curve represents exponential growth.

Nanoporous materials, when in a dry state, must experience strong inner stress that can be relaxed on wetting with following expansion. Indeed, similar to the strong swelling of all hypercrosslinked polymers in any liquid, including non-solvent,[3] hyperbranched materials obtained increase their volume in methanol and hexane (by a factor of 2.1 or 2.2, respectively, for the HP with TPB:BCB = 1:1.75).

Resuming, we present here a possibly general approach to nanoporous hyperbranched polymeric species. It consists in the synthesis of macromolecules with an extremely high degree of branching from rigid building blocks.

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