Novel hyperbranched polymer based on urea linkages

Anil Kumar and E. W. Meijer*†

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600MB Eindhoven, The Netherlands

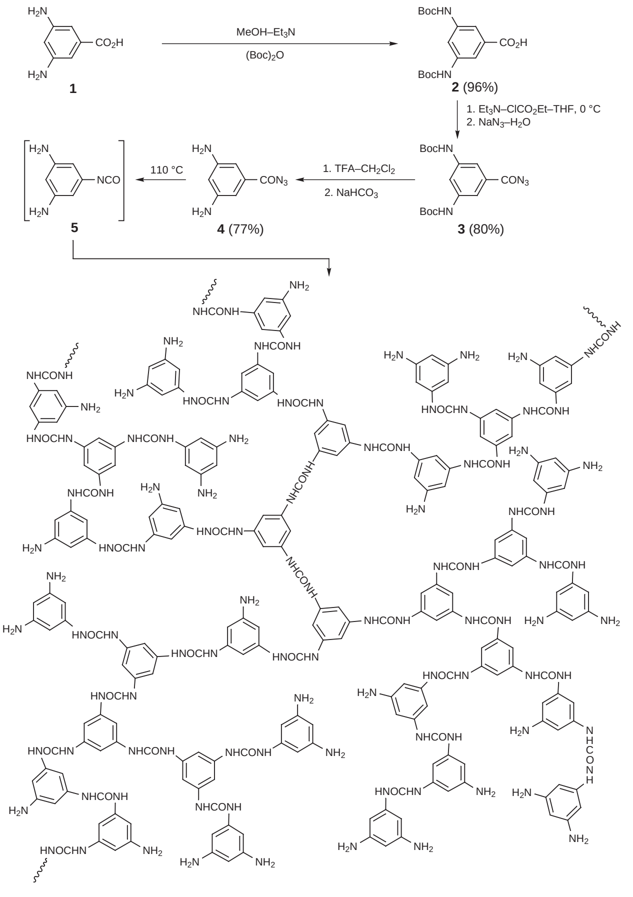
The thermal decomposition of 3,5-diaminobenzoyl azide, to generate *in situ* the corresponding 3,5-diaminophenyl isocyanate, was found to give hyperbranched polyureas, whose structure was established using IR and NMR spectroscopy.

In the last decade synthesis of three-dimensional dendritic polymers by constructing branches upon branches, either in a stepwise fashion to get dendrimers or in a one-step process to get hyperbranched polymers, has received much attention. These highly branched, untangled and globular structures have been explored because of their unusual properties.[1–5] Although dendrimers have been studied extensively for their size, shape and surface functional group related properties, their large scale synthesis has been limited to only a few structures because of the inherent difficulties in the stepwise growth process. However, whilst the one step approach for the synthesis of hyperbranched polymers has potential for large scale preparation, it lacks well defined and monodisperse dendrimers.

Hyperbranched polymers have been synthesized by self-condensation polymerization using an AB_x type monomer in which A and B are functional groups that react with each other and not with themselves. These hyperbranched polymers can be divided into two major categories depending upon the growth process. One is the classical polycondensation involving an AB_x type monomer where the growth of the polymer starts only at the already existing reaction sites A and B; in other words there is no generation of a new growing site during the polymerization. Some examples of this class are polyphenylenes,[6,7] polyesters,[8–12] polyethers,[13,14] polyurethanes,[15–17] polyamines,[18] polyamides[19] and polysiloxanes.[20] The second category is where new growing sites are generated during the polymerization reaction and examples of this class include polystyrene [21–23] and polyacrylates.[24] The consequence of these new reaction sites during polymerization is an increased number of subunits in the polymer. This leads to difficulties in estimating the degree of branching as quantification of each of the subunit structures is not possible.

Dendritic and hyperbranched structures based on amide linkage[25–31] have received considerable attention due to the fact that polyamides are commercially important and these linkages are the backbone of all the naturally occurring proteins and enzymes. Linear polyureas have been studied extensively in order to produce alternative fiber-forming polymers analogous to the polyamides.[32] There is now a much wider range of commercial polymers containing urea groups.[33] Surprisingly there are no reports on the synthesis of hyperbranched or dendritic polymers based on urea linkages. This could be due to the inherent difficulties in the synthesis and purification of monomers containing both amine and isocyanate groups, to obtain the urea linkage, as they are not compatible. Here we report synthesis and characterization of the first example of a hyperbranched polymer based on urea linkages. We developed a novel one-pot route to wholly aromatic hyperbranched polyureas, *via* the *in situ* generation of a diaminophenyl isocyanate monomer **5** by the thermal decomposition of the corresponding carbonyl azide **4** (Scheme 1).

3,5-Diaminobenzoyl azide was prepared starting from 3,5-diaminobenzoic acid as described in Scheme 1. The amine groups were protected with a Boc group[34] and the carboxylic acid was converted to carbonyl azide using the procedure described by Ghatge and Jadhav.[35] Removal of the Boc group with TFA in CH_2Cl_2 followed by treatment with saturated $NaHCO_3$ solution gave pure **4** in an overall yield of 59%. The FTIR spectrum of **4** exhibits a strong absorption at 2136 cm^{-1} indicating the presence of azide groups. Thermal decomposition of the aromatic carbonyl azides has been reported[15,16] to occur at *ca.* 107 °C and, hence, the polymerization was carried out at 110 °C by heating a solution of **4** in NMP. Rapid evolution of N_2 was observed during the initial stages of the reaction, after which the solution was maintained at 110 °C for 7 h. The polymers were precipitated into water, centrifuged, washed with acetone and vacuum dried at 90 °C to give around 90% yields of the wholly aromatic polyureas which are soluble in solvents like DMSO, NMP and DMF. The FTIR spectrum of the polymer indicates the absence of any residual azide (no absorption at 2136 cm^{-1}) or isocyanate (no absorption at 2200 cm^{-1}) and shows strong absorption at 1656 and 3352 cm^{-1} indicating the formation of



Scheme 1

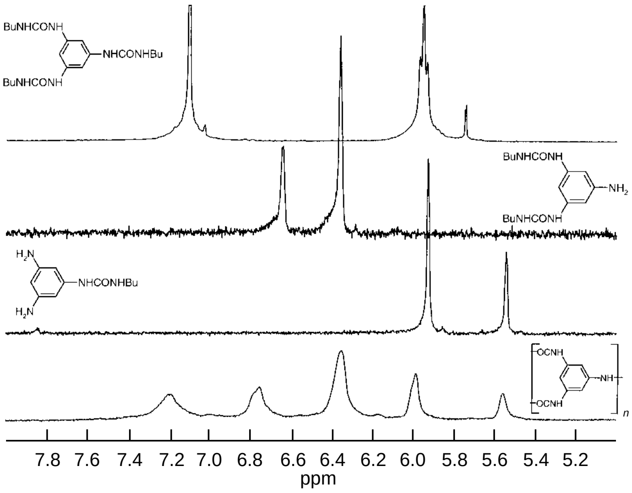
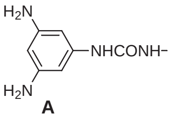
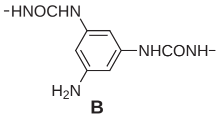


Fig. 1 300 MHz ^{1}H NMR spectra of the polymer and the model compounds in $(CD_3)_2SO–D_2O$

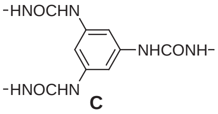
urea linkages. The ^{1}H NMR spectrum of the hyperbranched polyurea (Fig. 1) was analyzed based upon the various possible subunits (**A**–**C**) that may be present. Various peaks in the NMR spectrum of the polymer (Fig. 1) were assigned upon the NMR spectrum of three model compounds that resemble subunits **A**–**C**. The degree of branching calculated based on the ^{1}H NMR spectrum was found to be 0.55. This suggests that the growth process is statistical in nature in agreement with other systems.[36] The molecular mass of the samples was determined by GPC using NMP as solvent and polystyrene as standard. M_w was found to be 19 500 with a polydispersity of 1.56.



A



B



C

The wholly aromatic linear polyureas are generally difficult to process because of their limited solubility and high melt temperatures.[32,37] One approach to increase solubility in organic solvents is the introduction of *N*-alkyl or *N*-aryl substituents along the polymer backbone. Here we have shown that the wholly aromatic hyperbranched polyureas are completely soluble. A closer look at the Boc-protected carbonyl azide **3** reveals that its a novel AB_2 type building block where both A and B groups are protected and can be generated when needed. These types of structures are ideal candidates for the stepwise synthesis of the dendrimers. Currently, work is in progress to generate the corresponding perfect polyurea dendrimers.

This work was supported by the Netherlands Foundation for Chemical Research (SON).

Notes and References

† E-mail: tgtobm@chem.tue.nl

1 J. M. J. Frechet, *Science*, 1994, **263**, 1710.
2 K. L. Wooley, J. M. J. Frëchet and C. J. Hawker, *Polymer*, 1994, **35**, 4489.
3 C. J. Hawker, P. Farrington, M. Mackay, J. M. J. Frëchet and K. L. Wooley, *J. Am. Chem. Soc.*, 1995, **117**, 6123.
4 J. F. G. A. Jansen, E. M. de Brabander van den Berg and E. W. Meijer, *Science*, **266**, 1226.
5 J. F. G. A. Jansen, E. W. Meijer and E. M. de Brabander van den Berg, *J. Am. Chem. Soc.*, 1995, **117**, 4417.
6 Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.*, 1990, **112**, 4592.
7 Y. H. Kim and O. W. Webster, *Macromolecules*, 1992, **25**, 5561.
8 C. J. Hawker, R. Lee and J. M. J. Frëchet, *J. Am. Chem. Soc.*, 1991, **113**, 4583.
9 S. R. Turner, B. I. Voit and T. M. Mourey, *Macromolecules*, 1993, **26**, 4617.
10 W. J. Feast and N. M. J. Stainton, *J. Mater. Chem.*, 1995, **5**, 405.
11 A. Kumar and S. Ramakrishnan, *Macromolecules*, 1996, **29**, 2524.
12 E. Malmstorm, M. Johansson and A. Hult, *Macromolecules*, 1996, **29**, 1222.
13 V. Percec, P. Chu, G. Unger and J. Zhou, *J. Am. Chem. Soc.*, 1995, **117**, 1441.
14 T. M. Miller, T. X. Neenan, E. W. Kwock and S. M. Stein, *J. Am. Chem. Soc.*, 1993, **115**, 356.
15 A. Kumar and S. Ramakrishnan, *J. Chem. Soc., Chem. Commun.*, 1993, 1453.
16 A. Kumar and S. Ramakrishnan, *J. Polym. Sci., Polym. Chem. Ed.*, 1996, **34**, 839.
17 R. Spindler and J. M. J. Frechet, *Macromolecules*, 1993, **26**, 4809.
18 M. Suzuki, A. Li and T. Saegusa, *Macromolecules*, 1992, **25**, 7071.
19 Y. H. Kim, *J. Am. Chem. Soc.*, 1992, **114**, 4947.
20 L. J. Mathias and T. W. Carothers, *J. Am. Chem. Soc.*, 1991, **1134**, 4043.
21 J. M. J. Frechet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc and R. B. Grubbs, *Science*, 1995, **269**, 1080.
22 S. G. Gaynor, S. Edelman and K. Matyjaszewski, *Macromolecules*, 1996, **29**, 1079.
23 C. J. Hawker, J. M. J. Frëchet, R. B. Grubbs and J. Dao, *J. Am. Chem. Soc.*, 1995, **117**, 10763.
24 K. Matyjaszewski, S. G. Gaynor, A. Kulfan and M. Podwika, *Macromolecules*, 1997, **30**, 5192.
25 G. R. Newkome, X. Lin and C. D. Weis, *Tetrahedron: Asymmetry*, 1991, **2**, 957.
26 K. E. Uhrich and J. M. J. Frechet, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1623.
27 R. G. Dekewalter, J. F. Kolc and W. J. Lukasavage, *US Pat.* 4410688/1983.
28 C. Rao and J. P. Tam, *J. Am. Chem. Soc.*, 1994, **116**, 6975.
29 J. Shao and J. P. Tam, *J. Am. Chem. Soc.*, 1995, **117**, 3893.
30 P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati and E. M. Sanford, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1739.
31 P. J. Dandliker, F. Diederich, J.-P. Gisselbrecht, A. Louati and M. Gross, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2725.
32 M. Katz, *US Pat.* 2888438/1959; *Chem. Abstr.*, 1959, **53**, 17582b.
33 A. J. Ryan and J. L. Standord, in *Comprehensive Polymer Science*, ed. G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt, Pergamon, Oxford, 1989, vol. 5, p. 427.
34 E. Ponnusamy, V. Fotadar, A. Spisni and D. Fiat, *Synthesis*, 1986, 48.
35 N. D. Ghatge and J. Y.Jadhav, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 1941.
36 For a critical review see: D. Hölter, A. Burgath and H. Frey, *Acta Polym.*, 1997, **48**, 30.
37 Y. Oishi, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25**, 2185.

Received in Liverpool, UK, 13th May 1998; 8/03676D