A Novel One-pot Synthesis of Hyperbranched Polyurethanes

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The thermal decomposition of 3,5-dihydroxybenzoyl azide, to generate *in situ* the corresponding AB_2-type dihydroxy isocyanate monomer, was found to give hyperbranched polyurethanes, whose structures were established using IR and NMR spectroscopy.

Hyperbranched polymeric structures, also referred to as dendrimers, starburst polymers and arborols, have attracted the attention of both synthetic chemists[1] and theoreticians[2] recently. The interest in such macromolecules stems from the possibility that, owing to their novel, highly branched, globular and unentangled structure, they may be expected to show new and interesting behaviour both in solution and in bulk. Two distinct synthetic approaches to such hyperbranched macromolecules have been developed. One is the single-step process, where an AB_x-type monomer (where A or B is a functional group that reacts only with the other and not with itself) undergoes self-condensation polymerization, and the other approach is a stepwise growth process,[1,3] involving a protection–deprotection or a functional group interconversion strategy at evey step of the growth process. Although the latter approach yields monodisperse polymers with well defined structure, it often requires chromatographic purification of the products at every step of the growth process and therefore may be unsuitable for large-scale preparation. The former approach however, while being more suitable for scale-up, gives polymers with varying degrees of branching and also less precise molecular structure. The advantage of this one-pot AB_x approach, of course, lies in its potential for greater general applicability, should this class of polymers exhibit some potentially useful properties.

The theoretical description of AB_x polycondensation was given by Flory in 1952[4] and the first synthetic attempt gave poorly characterizable material *via* the Friedel–Crafts alkylation polymerization of benzyl chloride.[5] The difficulty in developing strategies for AB_x-type polycondensation lies in the selection of appropriate functional groups A and B that are sufficiently activated (yet stable) or activatable by some external agent, for effective polycondensation. Recently, development of effective methods for activating dormant functional groups has necessitated a relook at AB_x-type polycondensation strategies. Approaches towards the synthesis of hyperbranched wholly aromatic polyesters,[6] polyethers,[7] poly(aryl ethers)[8] and polyphenylenes[9] have appeared recently. We report here the development of a novel route to hyperbranched polyurethanes, *via* the *in situ* generation of a dihydroxyphenyl isocyanate monomer **2**, by the thermal decomposition of the corresponding carbonyl azide **1** (Scheme 1). 3,5-Dihydroxybenzoyl azide was prepared from the corresponding methyl benzoate, *via* the carbonyl hydrazide, using a modification of the procedure previously described.[10] The purity of the carbonyl azide, being one of the critical factors for attaining high molecular weight polymer, was established to be greater than 99% by HPLC. The thermal decompositon temperature of the carbonyl azide **1** was found to be 107 °C from DSC measurements. The polymerization was therefore carried out at 110 °C by heating a solution of **1** in dry dimethyl sulfoxide (DMSO) (in the presence of a catalytic
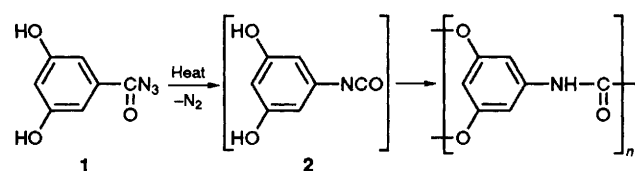
amount of dibutyltin dilaurate). Rapid evolution of nitrogen was observed during the initial stages of the reaction, after which the mixture was maintained at 80 °C for 8 h. The polymer was isolated by precipitation into water, purified by redissolution in tetrahydrofuran (THF) and reprecipitation in $CHCl_3$, and dried to give a 95% yield of the polyurethane (PU-1). In another experiment, the polymerization was carried out in refluxing toluene, in which both the monomer and polymer are insoluble and hence may be considered a dispersion polymerization, where the polymerization occurs in the solid state to give the polyurethane (PU-2) in 96% yield.

The molecular mass of the samples was determined by GPC against polystyrene standard. PU-1 had an M_w of 2500, while that of PU-2 was found to be 9100. It is interesting that the dispersion polymerization in toluene yielded a significantly higher molecular mass than the solution polymerization in DMSO. This may be due to the inherently higher purity of toluene (specifically, the lower water content). In the solid state, the monomer is also more likely to react with itself than with impurities in the solvent. The polydispersity of PU-2 is 3.23 while that of PU-1 is 2.02, which reflects the poorer mobility of the monomers in the solid state as compared to the freely diffusing monomers in solution.

The hyperbranched polyurethanes were insoluble in water, but dissolved in aqueous base, suggesting the presence of several ionizable phenolic end groups. The polymers were also soluble in several organic solvents like THF, acetone and DMSO. The IR spectrum of the polymer indicates the absence of any residual azide (no peak at 2152 cm^{-1}) and exhibits strong absorptions at 3280 and 1725 cm^{-1} indicating the presence of the urethane linkages. The ^1H NMR spectrum of the polymer (Fig. 1) was analysed based upon the various possible subunits (**A–D**) that may be present. The concentration of **D** may be neglected as each molecule is expected to contain only one such unit (after the hydrolysis of the isocyanate functionality). Based upon the NMR spectrum of some model compounds† that resemble subunits **A** and **C**, the
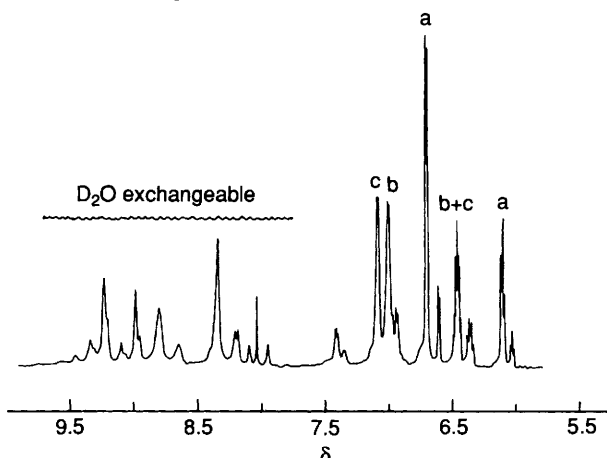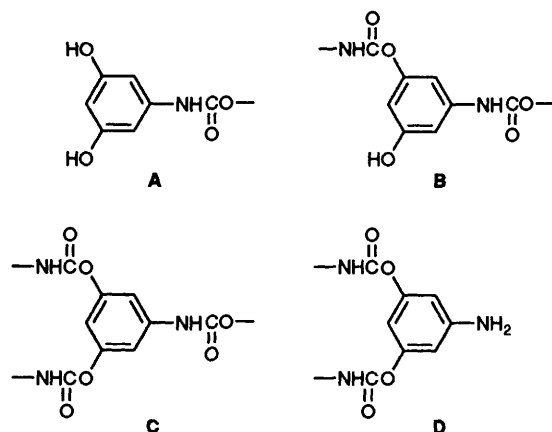

Fig. 1 200 MHz ^1H NMR spectrum of PU-1 in $(CD_3)_2SO$. Peaks marked a, b and c are due to the aromatic protons belonging to subunits **A**, **B** and **C**, respectively.

† The model compound for unit **A** was prepared by heating the 3,5-dihydroxybenzoyl azide with excess of phenol and that for **C** by treating model **A** with phenyl isocyanate.

Scheme 1

NMR spectrum was analysed to calculate the degree of branching (see ref. 6). The ^{1}H NMR spectra of PU-1 and PU-2 were similar and the degree of branching in both was found to be about 0.59. This suggests that a significant proportion of unreacted subunits **B** is trapped in these polymer structures. This may be due to the inaccessibility of these phenolic groups trapped in a sterically hindered environment as the polymer groups.

The wholly aromatic linear polyurethane prepared from 4-hydroxybenzoyl azide is completely insoluble[10] and only upon incorporation of ethylene spacers in the polymer backbone did the resulting polymer become soluble.[11] We have shown that wholly aromatic hyperbranched polyurethanes, on the other hand, are completely soluble. It appears reasonable that, in general, incorporation of an optimum amount of AB_x monomers into otherwise insoluble AB-type linear polymers may serve as an excellent approach for their solubilization. We are currently investigating the copolymerization of AB and AB_2 type monomers to achieve this optimum composition in both polyurethanes and polyesters.

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