Synthesis and Properties of Aromatic Hyperbranched Polyureas and Hyperbranched Copolyureas Using Blocked Isocyanate Monomers

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Abstract — 3, 5-diamino phenyl phenylcarbamate- an AB$_2$-type blocked isocyanate monomer was synthesized. Step-growth polymerization of this monomer was found to give a hyperbranched poly (aryl-urea). The polymers were characterized by FT-IR, ^{1}H-NMR, TGA and DSC measurements. Molecular weights (Mw) of the polymers were determined using GPC. The polydispersity indexes were relatively narrow due to the controlled regeneration of isocyanate functional groups for the polymerization reaction. The polymers were found to be soluble in DMF, DMSO, NMP, DMAc, and THF. All the polymers underwent two-stage decomposition and were stable up to 220 ℃. Functionalized end-capping of poly(aryl-urea) using phenylchloroformate changed the thermal properties and solubility of the polymers. Copolymerization of AB$_2$-type blocked isocyante monomer with functionally similar AB monomer was also carried out. The molecular weights of copolymers were found to be higher than homopolymers with narrow dispersity. It was found that the Tg's of poly(aryl-urea)s were significantly less compared to copoly(aryl-urea).

Key words: AB$_2$ type monomer, hyper branched poly ureas, isocyanate, copolyureas.

I. INTRODUCTION

Star-branched polymers, graft (co)polymers, and dendrimer-like star-branched polymers are representative branched polymers and characterized by the number and position of the branch point. These polymers have been widely studied for a long time because of their interesting properties and behavior in the solution, melt, and solid states, different from corresponding linear polymers as well as their synthetic challenge.[1–6].

Since the synthesis of HBPs is easier than dendrimers, and many of their properties are apparently similar to that of dendrimers, the HBPs are potentially promising alternative materials to the dendrimers. [7] Because HBPs lack chain entanglements, they could not be used in place of linear polymers to make tough utility articles.

However, they can be used as optical materials, electronic and magnetic materials, polymer electrolytes, nano and biomaterials, coatings and lithographic materials, supramolecular materials, modifiers, chemical sensors, and additives for different processes and materials. [8].

Spindler and Frechet [9] reported hyperbranched polyurethane using blocked isocyanate monomer. Later, hyperbranched poly (ether-urethane)s were reported; [10] the methodology involved azide-type monomers. Hyperbranched polyurea [11] and poly(urethane-urea) [12] are also reported via relatively simpler methods compared to the method to be discussed here, but they are fully hard segmented. Recently, Long and coworkers [13] reported segmented poly (urethane-urea) elastomers via A$_2$ + B$_3$ approach using conventionally prepared polyurethane prepolymers and commercially available triamines as A$_2$ and B$_3$ monomers, respectively. Nasar and coworkers synthesized hyperbranched poly(ether-urea), hyperbranched (ether-alkyl-urea) [14], poly(ether-urea) dendrimers[15].
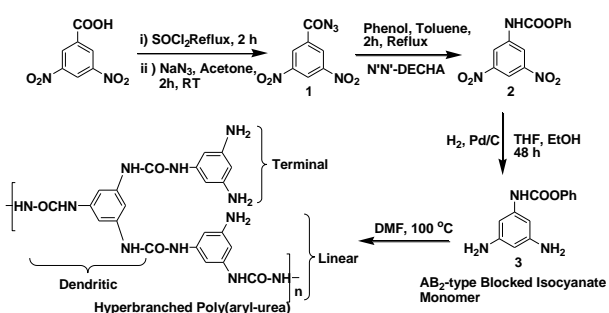
II. RESULTS AND DISCUSSION

Synthesis of AB$_2$- and AB-Type Blocked Isocyanate Monomers

3,5-diaminophenyl phenylcarbamate (3)—an AB$_2$-type blocked isocyanate monomer was prepared starting from 3,5-dinitro benzoic acid as described in Scheme 1. The acid group of starting material was converted into carbonyl azide by the reaction with thionyl chloride followed by sodium azide. Heating of 3,5- nitrophenyl carbonyl azide (1) with phenol in toluene in the presence of catalytic amount of N,N-diethylcyclohexylamine (DECHA) at reflux temperature gave corresponding blocked isocyanate (2) in high yield, which, on reduction in 1:1 mixture of ethanol and tetrahydrofuran using palladium catalyst under hydrogen at room temperature gave the monomer (3) in an overall yield of 90%. It is noteworthy to mention here, that the monomer (3) could not be prepared directly from (1), since the direct reduction product showed that carbonyl azide had

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also been affected and was no longer detectable in the product; thus the conversion of carbonyl azide to isocyanate followed by blocking the functionality is inevitable.

The FTIR, ^{1}H-NMR, ^{13}C-NMR, mass spectral data and nitrogen content estimation unambiguously confirm the structure of the monomer (3) and its precursors (1) and (2). The electron impact mass spectrum of the monomer is found to be a typical example of a blocked isocyanate. [16] The base peak appearing at m/z 94 is due to phenol expelled from the blocked isocyanate moiety of the monomer and, the m/z for the monomer after deblocking appeared at 149; the molecular weight of the blocked isocyanate monomer is 243.

Scheme 1 Synthesis of AB2-type blocked isocyanate monomer and corresponding hyperbranched poly(aryl-urea).

3-aminophenyl phenylcarbamate (6) (an AB-type blocked isocyanate monomer) was prepared starting from 3-nitro benzoic acid as described in Scheme 2. Since the functional group transformations involved in this synthesis are the same as in the case of synthesis of AB$_2$ monomer (3), the experimental procedures adopted for monomer (3) were replicated for (6). The spectral data and nitrogen content estimation confirm the structure of the monomer (6) and the intermediates (5) and (6). The electron impact mass spectrum of the monomer (6) is again found to be a typical example of a blocked isocyanate.
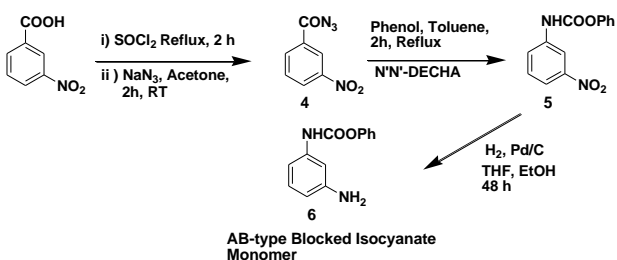
Scheme 2 Synthesis of AB-type blocked isocyanate monomer

Synthesis of Hyperbranched Poly(aryl-urea)s from Blocked Isocyanate Monomer and Properties of the Polymer

A blocked isocyanate is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed in such a way as to regenerate the isocyanate and the blocking agent. The regenerated isocyanate can react with a substrate containing amine or hydroxyl functional group to form comparatively thermally more stable bonds. Considerable amount of work has been done in this field from our laboratory and is available in the literature. The blocked-isocyanate moiety of monomer (3) is a mimic of phenol-blocked phenyl isocyanate. Solid-state deblocking of phenol-blocked phenyl isocyanate is reported to occur at 120 °C [17]. The FTIR spectra of the monomer (3) taken at different temperatures indicates that it deblocks at 125 °C. Solvent like DMF will favor the deblocking reaction to occur in a more controlled manner, and as a consequence polymer will be formed with narrow molecular weight distribution. Thus, the solution polymerization was carried out at 120 and 75 °C in DMF and like solvents. The structure of the polymer was confirmed using FTIR and ^{1}HNMR spectroscopy. In the FTIR spectrum of the polymer, absorption due to urea N-H appeared strongly and broadly at 3368 cm^{-1}. Absorption due to the urethane C-O of the monomer disappeared at 1729 cm^{-1} while the urea C-O appeared at 1645 cm^{-1}. Similarly, in the ^{1}H-NMR spectrum of the HBP, peak due to the urethane N-H proton of monomer (3) disappeared at 10.1 ppm while two different urea N-H protons of polymer appeared at 8.5–8.8 ppm. Also, it is found that the peak corresponding to free amine protons broadens significantly due to polymerization occurred. Representative ^{1}H-NMR spectrum of hyperbranched poly(aryl-urea) is given in Figure 1.
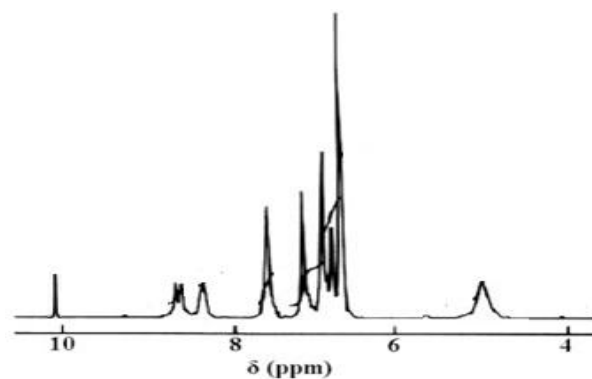

Figure 1. 400 MHz ^{1}H-NMR spectrum of hyperbranched poly(aryl-urea) in DMSO-d$_6$.

The molecular weights of the polymers were determined by GPC using polystyrene standards. Among the variables in solution polymerization, reaction time and temperature showed promising effect on molecular weight. The polydispersity values were found to be relatively narrow. This is mainly due to controlled regeneration of isocyanate functional group the GPC results showed relatively narrow distribution. (Table 1)

The inherent viscosities (η_{inh}) of the polymers were plotted against molecular weight; the plot was a typical example of HBP.[7]

Table 1 Synthesis and Properties of Hyperbranched Poly(aryl-ether-urea)

Polymer Code	Temp (°C)	M_w (g/mol)[b]	M_n (g/mol)[b]	P.D	η_{inh} (g/dL)[c]	Td^d (°C)	Tg^e (°C)
HBP1[a]	75	18400	15300	1.2	0.57	286	168
HBP2[a]	85	19500	14000	1.4	0.58	276	--
HBP3[a]	100	19000	14600	1.3	0.51	280	166
HBP4[a]	110	16000	10000	1.6	0.48	268	175
HBP5[a]	120	22000	15700	1.4	0.51	278	--

[a] Calculated amount of monomer was dissolved in 10 mL of DMF

[b] Determined by GPC method.

[c] Measured at a concentration of 0.5 g/dL at 30 8C in DMF using

Ubbelhode viscometer.

[d] Decomposition temperature measured by TGA.

[e] Not observed up to 250 °C.

The thermo gravimetric analyses (TGA) of polymers showed that they invariably undergo decomposition with two distinct stages; the first stage starts at 260 °C and the second stage starts at 370 °C. The weight loss of first stage decomposition is only 18–25% and is cumulatively due to loss of phenol present at focal group of polymer chain for which the thermo grams do not show any indication below 200 °C and loss of gaseous product formed during the cleavage of urea groups. The results indicate that the polymers are reasonably thermally stable. The glass transition temperatures (T_g) of the polymers were determined using DSC. The samples were quenched from 250 to 100 °C and then reheated to get clear T_g.

Reactive End Functionalization of Hyperbranched Poly(aryl-urea)s

Since all the polymers reported here possess reactive amine terminal groups, they could be used as cross linkers for many cross linking processes. The scope of the materials will be more if the terminal functional group is converted into a different kind. It is well known that such modifications affect the physical, thermal and solubility of the polymer. In the present work, the terminal amine functional groups of Polymer-5 were converted into Boc-protected amines and blocked isocyanate groups by the reaction with di-t-butyl dicarbonate and phenylchloroformate, respectively, (Scheme 3). The therm ograms are distinctly different from one another, indicating that the thermal stability of polymers is changed significantly. Thermo grams of

both of the modified polymers showed only one major weight loss.
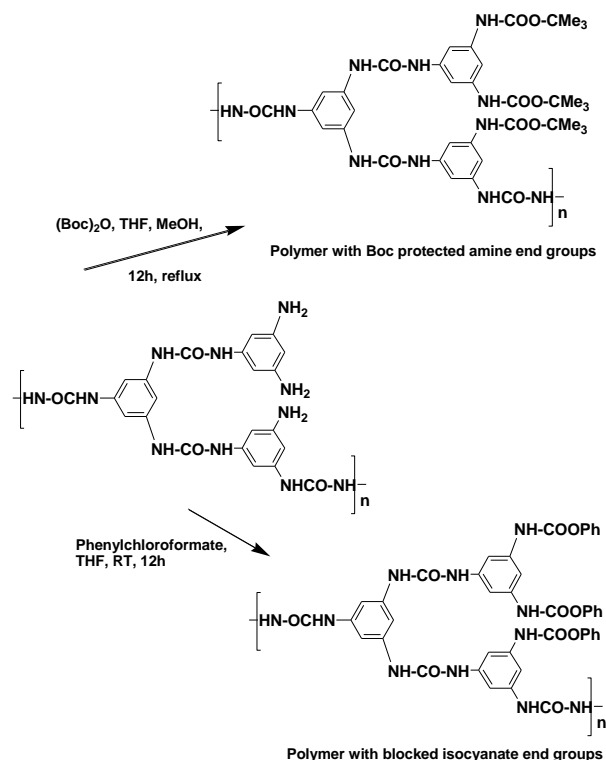
Scheme 3. Reactive end fictionalization of hyperbranched poly(aryl-urea).

The hyperbranched poly(aryl-urea)s varying in molecular weight were found to be soluble in highly polar solvents and were fully or partially soluble in tetrahydrofuran and acetone. Methanol and ethylacetate were found to be non-solvent for these polymers.

Copolymers of AB2- and AB-Type Blocked Isocyanate Monomers and Their Properties

Copolymers with different AB2:AB monomer feed ratio were prepared in good yield FTIR spectra of copolymers are identical with those of hyperbranched homopolymers due to similar functional groups present in both homo and copolymers. Thus, it can be concluded, that the ^{1}H-NMR and FTIR data confirm unambiguously the formation of copolymers. Copolymers are found to be insoluble in THF and acetone whereas hyperbranched homopolymer is soluble in these solvents. The polydispersity indexes are again found to be very narrow. The thermal stability of copolymers is similar to that of hyperbranched homopolymers due to identical chemical structure and composition of basic unit of polymers. (Figure 2)
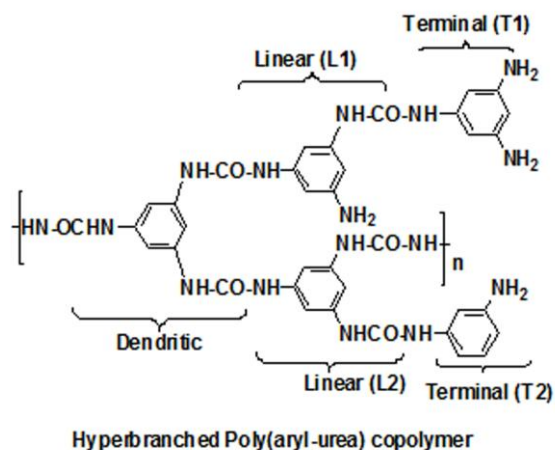
Figure 2. Possible structure of hyperbranched poly (aryl-urea) copolymer obtained from monomer (3) and (6)

CONCLUSIONS

To summarize, we present here a facile general synthetic route for the synthesis of hyperbranched poly(aryl-urea) and copolymer. Since the AB_2-type monomer (3) reported here is designed with blocked isocyanate group, the isocyanate functionality is regenerated in a controlled manner during polymerization in the solvents like DMF and hence gives poly(aryl-urea)s with narrow molecular weight distribution. It was found that the monomer (3) yielded low molecular weight polymers at relatively lower temperatures; the low molecular weight and narrow dispersity are important criteria for HBPs to be used as cross linkers. [18] Importantly, the terminal amine functional groups of poly(aryl-urea) were modified into blocked isocyanate groups and into Boc-protected amine groups. The Boc-protected amine-terminated hyperbranched polyurea can be used as a potential building block for novel synthesis.

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