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Synthesis, characterization and functionalization of thermally stable hyperbranched polyamide-ethers based on 6-hydroxy-2,4-bis(4′-nitrobenzamide)pyrimidine

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ABSTRACT

Thermally stable hyperbranched polyamide-ethers (HBPAEs) containing pyrimidine moieties were synthesized using new AB_2 type monomer, *6-hydroxy-2,4-bis(4′-nitrobenzamide)pyrimidine* (*NAL*), which was prepared through amidation and its structural characterization was made by FTIR, ^1H, ^{13}C NMR spectrometry and elemental analysis. Polymerization of *NAL* proceeded homogeneously to yield a gel-free polymer (HBPAE 1). End group derivatization of nitro-terminated HBPAE 1 yielded HBPAE 2 and 3. FTIR confirmed the structure and complete modification of ensuing polymers. DB and inherent viscosity (η_{inh}) of HBPAE 1 was found to be 0.41 and 0.23 dL/g, respectively. Modified HBPAE 2 and 3 were soluble in various organic solvents including NMP, DMAc and DMSO but amorphous HBPAE 1 was partially soluble in DMF. Glass transition temperature (T_g) of thermally stable HBPAEs was affected by nature of end groups as well as introduction of pyrimidine rings.

1. Introduction

Polyamide-ether (PAE) copolymers are a fascinating family of thermoplastic elastomers with exceptional physical and processing properties [1]. The distinctive nature of these materials has been endorsed to their structure, which consists of rigid polyamide fragments and flexible polyether segments. Voit and coworkers [2] prepared linear PAE with limited solubility in common polar organic solvents at room temperature. While improved solubility of hyperbranched polymers (HBPs) is a significant feature in conjunction with their multitude end functionality and low solution viscosity. Despite this versatility, there has been little structural characterization of hyperbranched polyamide-ethers (HBPAEs) reported in the literature. Additionally, complete characterization of the branching structure, solution property and thermal persona of pyrimidine containing HBPAE along with their functionalized structure has not been reported yet. The purpose of this article is to present our findings on synthesis of HBPAE incorporating pyrimidine entities and its property profile before and after end group modification. In the context of HBPs, their one-step synthesis permitted them to be more readily accessible and prepared on a large scale for potential applications. This attractive trait has led to the development of novel synthetic routes for the preparation of HBPs [3–30], especially the one-step synthesis based on AB_2 monomers which have A and 2B functional groups situated at 1,3,5-positions of a benzene ring. Highly branched polymeric structures are also attainable through the polymerization of A_2 and B_3 monomers. However, $A_2 + B_3$ polymerization requires careful control of the reaction to produce soluble HBPs [31]. This report concerns the synthesis and exploitation of new AB_2 monomer in one-step preparation of HBPAE 1. The method involves synthesis via nucleophilic aromatic substitution, resulting in the formation of an aryl ether linkage. The nucleophilic reaction had been previously applied to synthesize hyperbranched/dendritic poly(ether ketones) using AB_2 monomers containing a phenolic group and two aryl fluorides [10,29,32]. The synthetic procedure described herein involves nitro group displacement reaction of an AB_2 monomer containing a phenolic group and two aryl nitro groups which are activated toward nucleophilic substitution by amide moieties. Nitro-terminated HBPAE 1 thus prepared could be further derivatized by reacting the terminal NO_2 groups with *p*-substituted phenols i.e., *p*-aminophenol and phenol to produce HBPAE 2 and HBPAE 3, respectively. Properties of HBPAE 1 and the modified HBPAE 2 and 3 were investigated, in conjunction with the effect of introducing pyrimidine rings as well as changes in the nature of the end groups. Heterocyclic pyrimidine units provide not only thermal stability, but also high electron affinity for materials

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useful in electronic applications [33]. Hence, this promising potential led to the synthesis of HBPAEs analogs with the heterocyclic pyrimidine moiety. The structure of the resulting polymers is comparable to hyperbranched polyamides (HBPAs) devoid of pyrimidine units reported by Kakimoto and coworkers [34] which are prepared by the direct amidation instead of nucleophilic substitution. Thus, the structural characteristics of the HBPAEs analog due to the existence of pyrimidine moiety are discussed in contrast with the HBPAs reported earlier [34]. In addition, intermolecular hydrogen bonding between pyrimidine nitrogens and the amide NHs of adjacent molecules provides the basis for material uniqueness. In essence, pyrimidine moieties play an imperative role in producing excellent thermal persona of HBPAEs analogs; therefore, pyrimidine rings influenced the structural and material characteristics of these HBPAEs.

2. Experimental section

2.1. Materials

4-Hydroxy-2,6-diaminopyrimidine (HDAP), 4-nitrobenzoyl chloride, and potassium carbonate (K_2CO_3) from Aldrich were reagent grade and used as received. N-methylpyrrolidone (NMP), toluene, propylene oxide (PO), m-cresol and dimethyl sulfoxide (DMSO) obtained from Merck were used as received. *N*,*N*-dimethylacetamide (DMAc), methanol and *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF) purchased from Aldrich were distilled prior to use. Nitrobenzene, *p*-aminophenol (AP) and phenol (POH) were procured from Fluka.

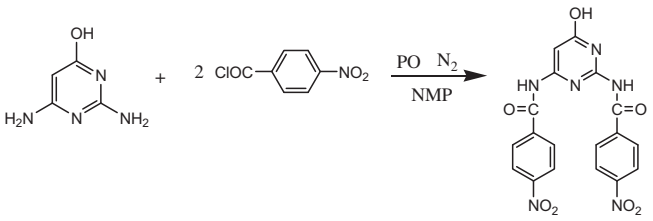
2.2. Measurements

IR spectra of monomer and polymers were recorded at a resolution of 4 cm^{-1}, using Excalibur Series FTIR Spectrometer, Model No. FTSW 300 MX manufactured by BIO-RAD. NMR spectrum was recorded at room temperature using BRUKER Spectrometer operating at 300.13 MHz for ^1H and at 75.47 MHz for ^{13}C NMR using deuterated dimethyl sulfoxide (DMSO-d_6). Elemental analysis was performed using a Perkin-Elmer 2400 CHN elemental analyzer. Inherent viscosity ($\eta_{inh} = \ln\eta_r/c$) was measured in DMSO at 30 °C with an Ubbelohde viscometer on polymer solutions with a concentration of 0.5 g/dL. Qualitative solubility was determined with 15 mg of polymer in 1 mL of various solvents at room temperature. Thermal stability of the polymers was determined by METTLER TOLEDO TGA/SDTA 851^e thermogravimetric analyzer using 1–5 mg of the sample in Al_2O_3 crucible heated from 25 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere with a gas flow rate of 30 ml/min. Glass transition temperature was determined by a METTLER TOLEDO DSC 822^e differential scanning calorimeter, using 5–10 mg of samples encapsulated in aluminum pans and heated at a rate of 10 °C/min under nitrogen atmosphere. X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (3040/60 X'pert PRO) using Ni-filtered Cu Kα radiation (40 kV, 30 mA) with scanning rate of 0.04°/s.

2.3. Monomer synthesis

2.3.1. Synthesis of 6-hydroxy-2,4-bis(4′-nitrobenzamide) pyrimidine (NAL)

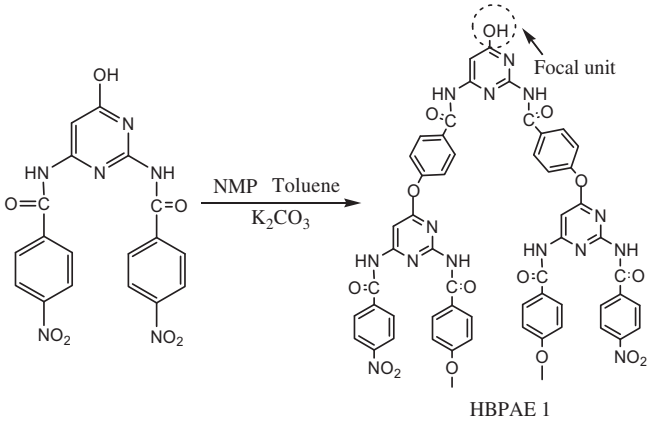
A 100 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 2.5 mmol of HDAP and 15 mL of dry NMP. The mixture was stirred at 0 °C for 30 min, followed by the addition of 3 mL of PO, and after a few minutes 5 mmol of 4-nitrobenzoyl chloride was added with continuous stirring at 0 °C for 30 min (Scheme 1). The temperature was raised to room temperature and the solution was stirred for 6 h. *NAL* was precipitated by pouring the flask content into water. Then it was filtered, redissolved in minimum amounts of NMP and re-precipitated in water. It was filtered, washed several times with hot water and dried overnight under vacuum at 70 °C. Yield: 1.0078 g pale yellow powder, 95%; mp 324 °C; IR (KBr): υ_{max} 3372 (N–H, OH), 3056 (Ar C–H), 1638 (amide C=O), 1602, 1460 (C=C), 1553 (asym N=O), 1351 (sym N=O), 853 (*p*-Ar). ^1H NMR (300 MHz, DMSO-d_6, ppm): δ 10.372 (s, 1H, amide NH), 10.215 (s, 1H, amide NH), 9.381 (s, 1H, OH), 8.488 (d, 4H, $J = 10.1$ Hz, *p*-Ar), 8.234 (d, 4H, $J = 10.2$ Hz, *p*-Ar), 6.433 (s, 1H, pyrimidine). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 166.30, 160.58 (amide C=O), 156.43, 150.12, 136.88, 130.07, 125.46, 124.12, 81.77. Elemental analysis: calculated for $C_{18}H_{12}N_6O_7$, C (50.95%), H (2.85%), N (19.81%); Found, C (50.83%), H (2.78%), N (19.65%).



Scheme 1. Scheme for the synthesis of *NAL* monomer.

2.4. Hyperbranched polyamide-ether synthesis (HBPAE 1)

The procedure used for the synthesis of HBPAE 1 was nucleophilic aromatic substitution in a polar aprotic solvent. *NAL* (3 mmol) and K_2CO_3 (1.55 mmol) were dissolved in 25 mL of NMP in a 250 mL four-neck flask equipped with a stirrer, Dean Stark trap, condenser, nitrogen inlet, and thermometer. Toluene (15 mL) was added as an azeotropic agent (Scheme 2). The reaction mixture was heated to 140 °C for 3 h to dehydrate the solution to 170 °C with further stirring for 6 h. The solution was then cooled to room temperature and diluted with 50 mL of THF. HBPAE 1 was precipitated into methanol/water (80/20 by volume), filtered, washed with water and dried in vacuum. HBPAE 1 obtained as a powder, was insoluble in water at any pH and in most organic solvents. Yield: 1.17 g brown powder, 92%; IR (KBr): υ_{max} 3428 (amide N–H), 3082 (Ar C–H), 1662 (amide C=O), 1551 (asym N=O), 1500, 1475 (C=C), 1380 (sym N=O), 1321, 1242, (C–O), 835 (*p*-Ar). ^1H NMR (300 MHz,



Scheme 2. Scheme for the synthesis of HBPAE 1.