



Novel dendritic-poly(urethane-urea) hybrid thin films from hydrogen bond rich dendrons



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ABSTRACT

Hydrogen bond rich segmented poly(urethane-urea) was synthesized from methylene diphenylisocyanate (MDI) and three generations of polyurea-malonamide dendrons as hard segment and polycaprolactone diol as soft segment for thin film applications. The prepared polymers were characterized using spectroscopic, microscopic and thermal analyses. The formation of urethane linkage during the prepolymer reaction and the urea linkage between prepolymer and the dendrons is confirmed by Fourier transform infrared (FTIR) spectroscopy and ^1H nuclear magnetic resonance (NMR) spectroscopy. FTIR shows the presence of hydrogen bonding of $-\text{NH}$ groups with both urethane carbonyl group from hard segment and the ether group from the soft segment. However, the phase mixing of hard and soft segments decreases with the higher generation dendrons, as evidenced from FTIR. This observation was confirmed by phase images of the atomic force microscopy (AFM). The coating when applied to clean steel substrates via dip coating reveals uniform, dense and essentially defect free morphology. The work demonstrates that the mechanical properties of the hybrid thin films are dependent on the generation of the dendrons and provides a platform for surface engineering with tunable elastic modulus.

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1. Introduction

Thin film coatings are widely used to tailor the surface properties of metallic and non-metallic components to impart characteristics such as protection from environment, abrasion and corrosion resistance, anti-friction and anti-flammability, lubrication, biocompatible surfaces, etc. Traditionally, either ceramic or organic thin films had been employed in fields as diverse as optics, microelectronics, tribology, corrosion and biomaterials. However, they have inherent disadvantages such as brittleness and presence of defects (ceramic thin films), mechanically weak films and poor adhesion (organic thin films). This has resulted in a new class of multifunctional hybrid thin films. The major advantages of such multifunctional hybrid thin films are: homogeneity at near molecular level, materials with novel microstructure and high surface to volume ratio of building blocks resulting in higher amount of interaction between the components. The ability to tailor the properties of such hybrid materials, at a molecular level, signifies their enormous potential in a wide variety of technologically

advanced and conventional application fields. Also their properties are strongly influenced by their interfacial characteristics rather than the bulk structures. Hence, it is essential to understand the role of molecular architectures such as linear chain polymers, dendrimers, etc. on interfacial characteristics to exploit their full potential.

Dendrimers have recently emerged as promising candidates for their potential applications in a broad range of areas, from drug delivery agents, protective coatings and hybrids to catalysis. The quantity and tailorability of the dendrimer's terminal functional groups allow the molecular weight of the polymer to build up while still possessing low viscosity, increased solubility and good rheological behaviour. Many developments have occurred since the first dendritic structure was described by Vögtle et al. [1] in 1978, with researchers focussing on developing synthetic methods that avoid tedious deprotection/activation steps in order to produce high yielding, multiple generation dendrimers in an efficient and cost-effective manner [2–8]. While, polyurethane and polyamide dendrimer syntheses using a highly selective addition process had been realized [9,10] already, the requirement of catalysts and the generation of side products have proved this to be a less than ideal synthesis route. Therefore, synthetic procedures that avoid tedious

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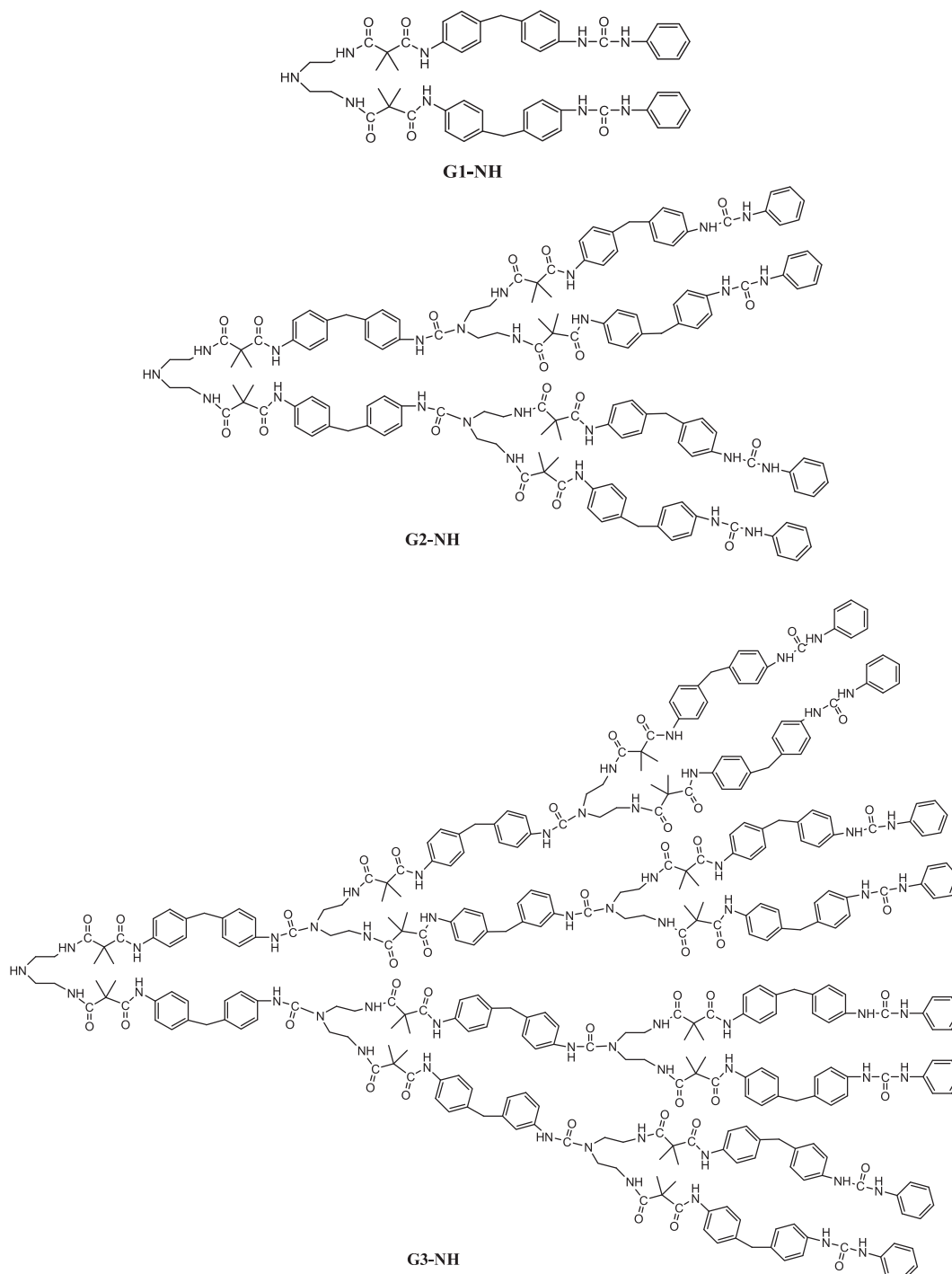
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activation/deprotection steps and the use of catalysts and generation of side products were highly sought after [2–4].

Recently, Chen et al. [3] reported the use of a bifunctional compound ([4-isocyanato-4'(3,3-dimethyl-2,4-dioxo-acetidino)-diphenylmethane], MIA) which, on reaction with bis(2-aminoethyl) amine in an alternating and successive fashion, produces polyurea/malonamide dendrimers. This convergent synthetic route offers high yields with easy purification steps, allowing dendrons up to third generation to be produced. Scheme 1 shows the chemical structure of generations 1, 2 and 3, each with a secondary amino

group to allow the dendron to be covalently attached to other functional polymer chains. These dendrons of generation 1, 2 and 3 are henceforth referred as G1-NH, G2-NH and G3-NH, respectively. The availability of large number of urea and amide linkages in these dendrons provides hydrogen-bonding sites, where inter-urea hydrogen bonding linkages can contribute to three-dimensional characteristics [3,11].

These dendrons, when incorporated into segmented polyurethanes, which are, as such, well known to exhibit micro-phase separation due to their thermodynamic incompatibility between



Scheme 1. Structure of G1-NH, G2-NH and G3-NH dendrons.

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