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Rheology of hydrogen-bonded dendritic supramolecular polymer networks in the melt state

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ABSTRACT

We investigate the rheological properties of a series of complex supramolecular dendritic polymer networks in the melt state, which are generated by the association between tri-barbiturate (Ba) functionalized poly(*n*-butyl acrylate) (P*n*BuA), (Ba-(P*n*BuA-Ba)$_2$), and several bis-Hamilton wedge (HW) functionalized polymers, including a semifluorinated copolymer HW-P(*n*BuA-*co*-PFPA)-HW, (PFPA, 2,2,3,3,3-pentafluoropropyl acrylate); a semifluorinated homopolymer HW-PPFPA-HW and two non-fluorinated homopolymers HW-P*n*BuA-HW and HW-PI-HW (PI, polyisoprene). The association of the different polymers leads to dendritic phase segregated structures, held together solely by specific H-bonding moieties in the sense of a key/lock system. It is known that frequency-dependent rheology is suited to exploit the time- and temperature-dependent association of supramolecular polymers in the melt state. Moreover, any change of the polymer backbone related to a change of its polarity and glass transition temperature (T_g) will lead to a strong effect on the thermo-rheological properties. For the stoichiometric mixture of Ba-(P*n*BuA-Ba)$_2$ with its linear complementary partners, such as HW-P*n*BuA-HW, HW-P(*n*BuA-*co*-PFPA)-HW, and HW-PPFPA-HW rubbery materials have been observed in all cases, each of them revealing a pronounced rubbery plateau in frequency-dependent rheology measurements from 0 to 50 °C driven by hydrogen-bonding (H-bonding) association. Distinct network effective strands (ν_e) and supramolecular bond lifetimes (τ) have been determined by rheology measurements. Moreover, as the small angle X-ray scattering (SAXS) profiles do not indicate the formation of supramolecular clusters or disordered micelles in the melt state, the formation of homogeneous, dendritic supramolecular networks has been proposed.

1. Introduction

When noncovalent bonds are placed within polymer chains, a new dynamic feature is placed inside the polymer chain, resulting in supramolecular polymers as a new class of soft materials. As the dynamics of the additionally placed bond(s) can strongly influence the overall material properties, the rapidly growing field of supramolecular chemistry in polymer and materials science has been actively explored during the last several decades [1–9]. One of the most attractive and practical advantages in comparison to covalently linked polymers is the design of easy processable and novel smart adaptive materials, such as stimuli-responsive- [10], self-healing- [2,11,12] and erasable materials [13]. Not surprisingly, H-bonding interactions [13–15], metal coordination [16] and ionic interactions [17,18] have been actively explored aiming at the design and formation of a magnitude of supramolecular materials for a variety of applications [19,20].

H-bonds in particular have been intensively used for creating a wide range of supramolecular polymers with fascinating structures in solution as well as in the melt state [1,4,6,8,21,22], as here the strength, the dynamics, as well as the resulting assembled structure can be adjusted and adapted quite nicely, when using H-bonds of a different chemical nature [1,12,23–27]. Especially when moving from purely linear architectures to branched structures, e.g. polymer gels [28], dendritic architectures [29], or supramolecular polymer networks [30–33] linked *via* H-bonds have been generated. We have recently reported the intermolecular complexation between a trivalent V-shaped supramolecular polymer, Ba-(P*n*BuA-Ba)$_2$ with the complementary bis-HW-functionalized linear polymers HW-P(*n*BuA-*co*-PFPA)-HW, HW-PPFPA-HW and HW-PI-HW,

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capable of generating unusual, hierarchical micelles driven by strong multiple H-bonding interactions in solution evidenced and demonstrated by ^{1}H NMR and diffusion-ordered NMR spectroscopy and transmission electron microscopy [34]. These systems are characterized by two different aggregation processes: one arising from specific H-bonding interactions, the other attributed to the segregation of the immiscible polymer chains (fluorinated/non-fluorinated polymers), related to their strongly differing Flory-Huggins parameters, similar to known covalently linked di- and triblock copolymers [35,36]. The formation of dendritic aggregates in the melt state is proposed, mainly attributed to the architecture of the used polymer systems, additionally driven by the formation of weakly phase segregated structures by polymer immiscibility. However, the dynamics and transient association of these supramolecular polymers in the melt state are unclear so far. We therefore in the present work investigate the rheological properties of a series of H-bonded supramolecular polymer networks (Fig. 1) in the melt state in order to contribute to the understanding of the dynamic behavior and the relaxation lifetime of these polymer networks. Since P*n*BuA, P(*n*BuA-*co*-PFPA), PPFPA and PI are characterized by a low glass-transition temperature ($T_g < 0\,°C$), they all are ideal candidates to investigate the association/aggregation of H-bonding moieties in the melt state at ambient temperature. Therefore, frequency (time) and temperature dependent oscillatory rheology measurements, enabling to gain insight into the aggregation behavior and structure of the supramolecular groups, together with their dynamic behavior have been chosen to investigate the time- and temperature-dependent association/aggregation of such systems. In related, simpler systems using self-aggregative cooperative H-bonding systems, the formation of internalized clustered [37,38] or even nano-fibrous [39–41] structures could be proven in urea-based polymers *via* melt-rheology, where clear regions of chain dynamics *vs.* specific H-bonding-aggregation dynamics could be discriminated, depending on the

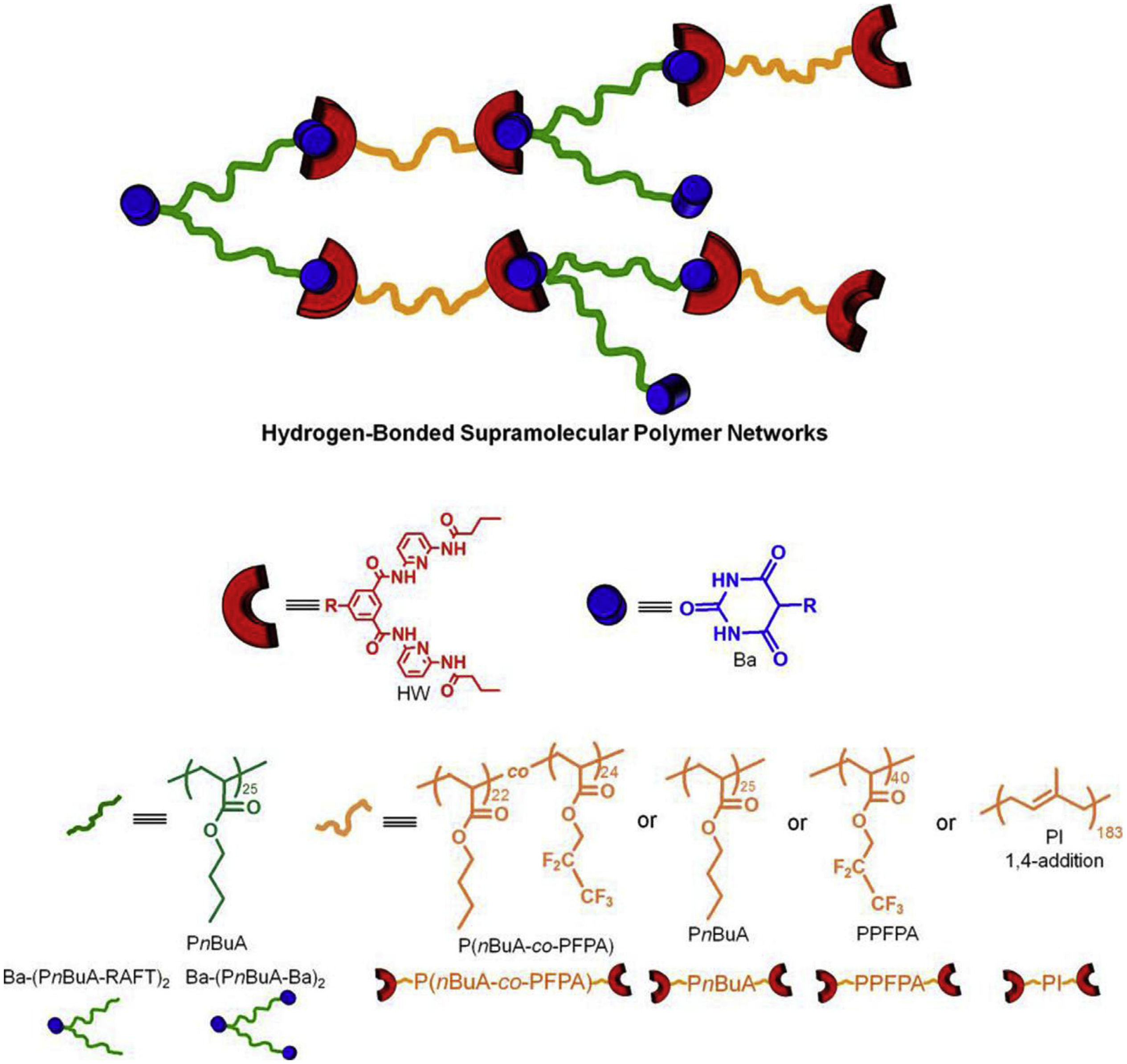

Fig. 1. Schematic representation of H-bonded supramolecular polymer networks built up by polymer blends composed of barbiturate-functionalized P*n*BuAs and several bis-Hamilton-wedge functionalized homo- or copolymers.