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# Tunable dynamic properties of hydrogen-bonded supramolecular assemblies in solution



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### ABSTRACT

Supramolecular polymers have emerged as a scientifically challenging and technologically important field of polymer science, because of the dynamic nature of the secondary bonds which govern their selforganization and their macroscopic properties. Their response to environmental parameters (temperature, solvent, pH, humidity) offer unprecedented tunability, enabling applications in diverse fields ranging from biomaterials to microelectronics. Thanks to the advances in supramolecular and organic chemistry, the field has gained tremendously in relevance and the fine-tuning of molecular structure has yielded a rich diversity of self-assemblies in solution and in the melt, whose consequences on the respective rheological and mechanical properties are significant but not fully understood. It is clear that the plethora of (mostly) experimental evidence needs to be grouped thematically in order to define the basic knowledge and outstanding issues and eventually advance the field. In this brief review we attempt to contribute in this direction by focusing on solutions of living polymers based on hydrogen-bonding moieties. In this review, we summarize the different possibilities to obtain such supramolecular assemblies, their structural and linear viscoelastic properties along with the basic framework for understanding them, as well as their response to different external fields. We outline the major open challenges, especially regarding nonlinear rheology and briefly discuss the perspectives of this exciting field.

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### 1. Introduction

Secondary associations are ubiquitous in nature. They are commonly used in natural biomaterials to acquire the necessary properties for a particular function [1]. A typical example is the formation of beta-sheets through van der Waals interactions and hydrogen bonding [2]. For instance, spider silk obtains its extraordinary mechanical properties through the connectivity of these

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crystalline beta-sheets in the form of an amorphous macromolecular network [3-5]. These associations are also relevant for synthetic materials and have been utilized to "bequeath" them with some of the extraordinary properties found in natural biomaterials [6-8]. The different types of associations are illustrated in Fig. 1, where the ranges of binding energies for different bonds are presented along with the respective probability of breaking, where associations with lower binding energies are more probable to break. There are two main categories of polymeric materials which are based on reversible associations, associating polymers and living polymers. Whereas there is some overlap, these two classes of polymers exhibit distinct properties which render their grouping necessary. Recently it was suggested that a linear polymer center-functionalized with a bisurea self-associating unit can transition from one group to the other, as revealed by the rheological signatures, depending on the density of stickers (or molecular weight of the linear polymer) [9]; at low sticker densities (or large molecular weights), typical behavior of associating polymers was probed, while at large sticker densities (or small molecular weights) the response of supramolecular living polymers was found due to the self-assembly of the stickers [9]. The following presentation focuses on understanding the main mechanisms and

Abbreviations: 1D, One dimensional; BTA, 1,3,5,-Benzene Tricarboxamide; BPTA, Biphenyl tetracarboxamide; BTAXD, BTA with X of labile hydrogens deuterated; CCR, Convective Constraint Release; CD, circular dichroism; cryo-TEM, Cryogenic Transmission Electron Microscopy; CTAB, Cetyl Trimethyl Ammonium Bromide; CTC, Cyclohexane-Tricarboxamide; C<sub>x</sub>BTA, x number of carbons on the aliphatic side-chain; DE, Doi-Edwards; DNA, deoxyribonucleic acid;; EHAC, erucyl bis(hydroxymethyl)methylammonium chloride; EHUT, 2,4(Ethyl Hexyl Ureido)Toluene; GCB, Germann-Cook-Beris; HEUR, hydrophobically modified ethyleneoxide urethane block copolymers; LVE, Linear Viscoelasticity; N<sub>1</sub>, First normal stress difference; NaSal, Sodium salicylate; PEG, Polyethylene glycol; PEO, PolyEthylene Oxide; SANS, Small Angle Neutron Scattering; TBM, trimethylbenzene; UV-Vis, Ultraviolet visible spectroscopy; UPy, Ureido-pyrimidinone; VCM, Vasquez-Cook-McKinley; Wi, Weissenberg number.

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to break

**Fig. 1.** Different types of secondary interactions and their respective binding energy ranges, in kJ/mol. Inspired from [1]. The color bar represents the probability of a bond breaking spontaneously due to thermal fluctuations. For reference, the thermal energy at room temperature (25 °C) is RT = 2.48 kJ/mol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

differences behind the dynamics and stress relaxation in associating and living polymers. The underlying central feature is the lifetime of associations which controls their dynamics.

### 1.1. Associating polymers

These polymers, which are schematically illustrated in Fig. 2, tend to have sites for reversible bonding not along the backbone which comprises covalently linked monomers, but outside (say, perpendicular to the main backbone) [10]. Usually they aggregate and form supramolecular networks whose properties have been studied extensively, with main representatives being poly-electrolytes and ionomers [11–13] as well as linear or branched polymers linked through metal-ligand coordination [14,15], hydrogen bonding units [16], solvophobic interactions [17,18] or weaker  $\pi$ - $\pi$  stacking [19,20]. Whereas this is not discussed further, the concentration is important as it mediates the intra- versus intermolecular association [21,22]. Of particular interest in applications

(and in this review) are the rheological (e.g., stress-relaxation) and mechanical properties. For example, self-healing has been demonstrated to enable the application of such associating polymers as recyclable elastomers with tunable mechanical strength [23,24]. Note also that vitrimers, a new class of covalent networks based on thermoactivated associative exchange reactions, can also self-assembly to give rise to a rich rheological and mechanical response [25,26].

The dynamic response of associating polymers is complex and, depending of the type of association and structures formed, there are different models that describe their stress relaxation, such as the sticky Rouse [11,27] or sticky reptation [27,28]. Actually, the former is a modified version of the Rouse model that includes the Rouse modes of chain segments between two associating units, with the longest sticky Rouse mode being the one that relaxes once the associations relax. Indeed, after the associations have opened up the system behaves as typical Rouse chains. On the other hand, in the case of sticky reptation the stress relaxation exhibits two plateaulike regions, one due to associations which openup at a characteristic time, beyond which the polymer behaves as a conventional entangled topological network. In both cases (unentangled or entangled associating polymers) the terminal relaxation time is delayed due to the extra modes of stress relaxation introduced by the associations. Recently, the sticky Rouse model was modified [29] in a systematic study of a series of side-chain associative polymers where the number of associations per chain was systematically varied. Specifically, the sticky Rouse model was found to describe the terminal relaxation regime well, but could not capture the rubbery plateau, hence it was slightly modified with respect to the contribution of dangling ends, chain dynamics upon dissociation of a sticker, as well as the placement of the stickers along the backbone. Moreover, the modeling of side-chain UPy-functionalized linear polymers by means of a tube-based approach revealed the crucial role of the interplay between chain length and density of associating groups on the relaxation of such a well-defined system [30]. Several differences between the idealized sticky reptation picture and the associating polymers studied in [30] have been also addressed by simulations [31]. For more complex associating polymers such as hydrophobically modified ethylene-oxide urethane block copolymers (HEUR) [17], which is a telechelic PEO forming loops and bridges, other models have been proposed to describe their longest relaxation such as the Tanaka-



**Fig. 2.** Schematic illustration of associating polymers with different linking groups on the side chains. Chains are depicted with different colors from clarity. Inspired from [10]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Different types of living polymers. (A) Wormlike micelle: red tails represent solvophobic part while blue heads represent the solvophilic part. (B) Telechelic polymer chains functionalized with a reversibly associating motif leading primarily to a large living polymer that has a random-coil like conformation. (C) Small organic molecules self-assembled into a 1D polymer-like array. Inspired from [40]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Edwards [32,33] model or the free-path model of Ianniruberto and Marrucci [34,35].

### 1.2. Living polymers

They are supramolecular assemblies made by building blocks which are connected via non-covalent interactions, primarily along the backbone [36-38]. The bonds can break spontaneously at a given (often room) temperature, making these supramolecular polymers quite dynamic (usually called living polymers, in analogy to surfactant wormlike micelles), in contrast to traditional linear polymers. The most common secondary bonds in supramolecular polymers are  $\pi$ - $\pi$  stacking [39], hydrogen bonds [40,41] and metal-ligand coordination [42]. The key features of these bonds are their directionality and additivity. For example, the combination of hydrogen bonds with a  $\pi$ - $\pi$  stacking moiety yields more stable supramolecular polymers compared to single interactions of one type only [36,43]. By using combinations of these interactions one can tailor the binding energy, hence the properties of the formed networks [44,45]. There are different kinds of living polymers with wormlike micelles being the best known and more widely investigated. The amphiphilic nature of their constituent moieties (typically surfactants or block copolymers) leads to an effective attraction between the solvophobic parts (not always directional), which vields their self-assembly into larger structures (typically one-directional, 1D), while the solvophilic parts interact with the solvent to stabilize the system (protect it against complete phase separation) [40] (Fig. 3A). Telechelic polymer chains constitute another building block, where the ends consist of units that can associate through attractive interactions which may also be directional, leading to long 1D supramolecular polymers (like semiflexible filaments) that can form topological entanglements [36,46–48] (Fig. 3B). However, cyclic molecules may form as well [49,50] and in such a case the viscoelasticity of the system may be strongly affected, as shown experimentally for a system of polystyrene ring-linear blends [51] as well as by simulations of telechelic supramolecular polymers [52,53]. In general, in such a situation the resulting structure involves loops and bridges whose ratio depends primarily on fraction and strength of attractive groups as well as the concentration to telechelic polymers in the case of solutions [17,54-57]. Note also that small organic molecules can self-associate into long 1D assemblies resembling polymer chains [40] (Fig. 3C).

Applications of supramolecular assemblies based on reversible secondary interactions include self-healing and shape memory materials which are easily processable and recyclable [7,58], since at high temperatures they become liquids of molecularly dissolved organic molecules. Furthermore, their dynamic nature and similarities with biopolymers make them strong candidates for understanding and/or synthesizing complex biomaterials [8,59–62].

In general, when the supramolecular interactions yield 1D wormlike self-assembled structures, their dynamics are described by the model of Cates [63-65] for stress relaxation in living polymers. This model, which is discussed in more detail in the next section, predicts a single-exponential decay, even if the wormlike living chains are polydisperse. It has been confirmed, in part, experimentally, while it has formed the basis for further developments in modeling living polymers [37,66,67]. The model is built on the concept that entangled living polymers can reversibly break or exchange monomers while reptating out of their effective tube. However, there are specific predictions of this model which are not supported by experimental evidence. Specifically, there have been reports of different wormlike micellar systems not conforming to the predicted scaling laws for the terminal relaxation time [67-69]. Moreover, in nonlinear deformations the model fails to describe the strain-hardening observed in some living polymers [67,70]. One possible explanation for the discrepancies between experiments and prediction is the semiflexible nature of the real living polymers, which is not addressed in the model of Cates. It is known that semiflexible chains strain harden under large shear deformations [71,72] and the observed strain hardening of wormlike micelles has been previously attributed to that effect [73]. As a background, there have been important advances in understanding the viscoelasticity of rigid and semiflexible polymers (see key contributions by Berry [74,75], Morse [76], MacKintosh [77] and Doi [78]). In a nutshell, these polymers can form mesogenic phases (such as nematically ordered liquid crystals), which is an entropically-driven ordering transition similar to Onsager's theory for hard rods [79] (for a review see [80]). The ordered phases may exhibit negative first normal stress difference (N1) due to the coupling of molecular tumbling under shear flow and the orientation function describing the alignment [81,82], locally, of polymer chains and last but not least, different scaling of viscosity. Semiflexible polymer networks have been also found to exhibit negative N1 even in the isotropic phase, due to the different forcedeformation relation during compression and extension, with the semiflexible network strands being soft to compression but resist to extension [83,84] (for a review see [71]). Regarding the dynamics of entangled semiflexible solutions, the prevailing models are typically based on the concept of reptation [76,85], however a recent Brownian Dynamics simulations study has proposed that the response of semiflexible chains in the concentrated regime is not driven by reptation but by several coupled disentanglement processes that occur due to the correlated dynamics of the network [86], leading to the progressive relaxation of higher order modes due to disentanglement and the eventual terminal relaxation at a time similar to the rotational relaxation time of each chain. Whereas we believe that it is worth investigating further how the semiflexible nature of living polymers affects their dynamics in view of the existing large body of significant work with conventional semiflexible polymers [71,74,76-78], we are not suggesting that flexibility is the only issue associated with the above mentioned discrepancy between experiments and modeling. The role of size distribution (taken to follow Flory's normal distribution) and the constraint release process applies to entangled living polymers are additional formidable challenges to address (see also discussion in Section 2.1 below). Along these lines we note that a new tube-based constitutive model for living polymers has just appeared in the literature and accounts for the effects of constraint release, contour length fluctuations and chain retraction [87].

The architectural complexity of branched polymers with associating ends [14,20] is an interesting and potentially important aspect of this class of materials for which the fundamental understanding of the rheology and dynamics governing relaxation is still in very early stages. Recent work has shown that a highly coarsegrained model for associating star polymers coupled with Brownian Dynamics simulation can successfully reproduce the linear viscoelasticity of the respective (albeit more complex) experimental system, setting the stage for a better understanding of the details of the gel transition [88]. For completeness we mention a recent important development on the analysis of associating polymer chains undergoing head-to-head association by Watanabe and coworkers [89,90]. In brief, a combination of rheological and dielectric experiments with modeling revealed the interplay of motion and kinetic equilibrium through the identification of the important role of respective ratios of unimer (dimer) relaxation times to association (dissociation) times. However, even for the short (Rouse) associating chains are too large compared to the molecular moieties forming the living polymers discussed here.

In this review we focus on the dynamics governing viscoelastic stress relaxation and nonlinear flow of supramolecular living polymers based on hydrogen bonding moieties, with particular attention to solutions. We do not address associating polymers which have been recently reviewed by Colby and coworkers [10]. The process of self-assembly will only be discussed in the context of how it affects the structure and dynamics or how it can be influenced by the environment, while supramolecular chemistry shall not be reviewed [40,44,91–93]. Low molar mass gelators are of interest in several industrial applications such as coatings, lubricants or cosmetics, and here we shall attempt to establish a connection between the structure and dynamics at the scale of the unimers and assess the rheological properties of the resulting materials.

### 2. Theoretical framework for living polymer systems

#### 2.1. Cates model of linear viscoelasticity

In 1987 Cates proposed an extended version of the tube model [85] incorporating micellar reactions that can occur during stress relaxation, leading to a predictive constitutive equation for the viscoelasticity of solutions of wormlike micelles [63]. As will be discussed in Section 3 below, it has been shown experimentally that this model can describe the basic features of the linear viscoelastic response of supramolecular living polymers [68,94]. In linear entangled polymers, the tube has completely relaxed once the chain has passed through. However, in living polymers, due to the breaking and reformation process there are different tubes formed depending on the dynamics of this process. In the fast breaking limit where the breaking time,  $\tau_{\rm b}$ , is much smaller than the reptation time,  $\tau_{rep}$ , the reptation-reaction prediction is recovered. Considering linear micelles, the possible reaction schemes are: (i) the scission/recombination (or reversible scission) scheme, where a micelle can break at some point along its backbone and recombine with itself or with a neighboring micelle; (ii) the end interchange scheme where a micelle "bites" and carries away part of it; and (iii) the bond interchange scheme where two micelles will fuse together, forming a transient structure similar to a 4-arm star polymer and then split again into two differently connected components. These reaction schemes are schematically illustrated in Fig. 4A. These schemes can co-exist, thus one of the assumptions in the model is that the scheme with the fastest rate will dominate.

The stress relaxation function,  $\mu(t) = \frac{8}{\pi^2} \sum_{p,odd}^{\infty} \frac{1}{p^2} e^{-tp^2/\tau}$ , describing the survival probability of a tube segment without a chain broken is the same as for the classic tube model [85]. However, by incorporating the scission/reformation scheme in the fast-

breaking limit ( $\tau_{b} << \tau_{rep}$ ), the original chain ends do not survive long enough for reptation to take place through the same original tube. Instead, the relaxation is controlled by the fact that a tube segment can find itself very close to a chain end due to the random breaking process. The distance a chain end can move by curvilinear diffusion during its lifetime (which is actually  $\tau_b$ ) is  $l \sim (D_C(L)\tau_b)^{1/2}$ , where  $D_C$  is the diffusion coefficient, L is the average length of the living polymer. Note that the living polymers are polydisperse with an exponential length distribution determined from free energy arguments and is directly related to the scission energy per micelle. This leads to the relation  $l/L = (\tau_b/\tau_{rep})^{1/2}$ . The new chain created by the breaking reaction needs time  $\tau = \tau_b L/l$ for a new end to appear within distance *l* to recombine and finally relax (see schematic in Fig. 4B). Thus, the stress relaxation time will be:

$$\tau = \left(\tau_b \tau_{rep}\right)^{1/2} \tag{1}$$

The above process holds also for the end interchange scheme, for which the new chain end is created by the reactive micelle end "biting" into the backbone of another micelle and destroying itself by its own reaction with a central part of another chain (Fig. 4C). In the fast reaction limit, the length of a living polymer "seen" by the tube segment as well as the position of the tube segment along the backbone of the living polymer are randomized by the rapid reaction rate, and this leads to a rapid averaging and consequently nearly identical relaxation rates for all tube segments, yielding the well-known mono-exponential Maxwellian terminal relaxation of living polymers [38,64,66,67,69,95–99]. Last but not least, the scaling laws for the plateau modulus and the relaxation time are:  $G_0 \sim c^{2.25}$ ,  $\tau \sim c^{1.25}$ . A detailed discussion on the experimental findings follows in Section 3.2 below.

When the ratio  $\lambda = \tau_b / \tau_{rep}$  falls below 1/Z with Z being the number of tube segments, the dominant chain-end motion is not the curvilinear diffusion but the so-called breathing modes or contour length fluctuations, well-known for linear polymers. This will change the relaxation time in (1) to:

$$\tau = \tau_b^{\frac{3}{4}} \tau_{rep}^{\frac{1}{4}} Z^{\frac{1}{4}}$$
(2)

The bond interchange reaction is not as effective in relaxing stress since it does not create or destroy chain ends, however it still does promote the relaxation due to the fact that it can bring a distant chain end close to a given tube segment, speeding-up the relaxation compared to an unbroken chain. Furthermore, there is a second effect, the so-called tube evaporation, where two chains can pass through one another. The bond interchange, without the tube evaporation effect, requires the creation of a chain end within a distance *l*. This will lead to a relaxation time which is not the geometric mean of the breaking and reptation times but becomes:

$$\tau = \tau_b^{1/3} \tau_{rep}^{2/3} \tag{3}$$

In the slow reaction limit where the breaking time is comparable to the reptation time ( $\tau_b \approx \tau_{rep}$ ,), the relaxation behavior deviates from Maxwellian and becomes a stretched exponential relaxation. Finally, when  $\tau_b \gg \tau_{rep}$ , a polymeric response with characteristic time  $\tau_{rep}$  is observed.

Zou and Larson have developed a numerical simulation [100] methodology to predict the rheology of wormlike micelles and at the same time calculate structural parameters from the linear viscoelastic spectra determined experimentally, such as the persistence length [99]. The original method includes the ingredients of the Cates model [63–65] and in addition (thermal) constraint release, bending modes associated with the semiflexible nature of living polymers and a cross-over to the tight entanglement regime. The method makes use of the so-called pointer algorithm where pointers along the backbone of the a micelle can track the ends of unrelaxed tube segments, where the pointers can



**Fig. 4.** (A) Schematic illustration of the three different reaction schemes. (B) Snapshots of the relaxation process based on the scission/reformation reaction scheme with 1) being the first snapshot and 4) the last. (C) Snapshots of the relaxation process based on the end interchange reaction scheme with 1) being the first snapshot and 3) the last. [63], Copyright 1987. Adapted with permission from the American Chemical Society.

be created upon breakage events and can be annihilated once the stress has relaxed (through reptation, contour length fluctuations and constraint release). Lately, this simulation method has been extended to account for the relaxation of unentangled micelles and was used in order to obtain structural characteristics from the rheological spectra which were successfully compared against independent SANS data [101].

### 2.2. Extension to nonlinear shear

The reptation-reaction model has been extended to the nonlinear viscoelastic regime [102,103]. Assuming that the system is highly entangled and  $Z^{-1} < \lambda < 1$ , the linear viscoelasticity is described by a Maxwell mode and the reaction rates are unperturbed by the shear flow. Similarly to linear polymers, after a rapid deformation is applied and the tube segments orient under flow, a fast retraction process occurs where the chain ends move towards the center of the tube, essentially evacuating their neighboring tube segments. However, in the fast breaking limit the retraction affects all tube segments equally since each tube has lost memory of its length and position along the chemical backbone of the living polymer due to the rapid scission/reformation process. The stress tensor is

$$\sigma = \frac{15}{4} G_0 \left[ \boldsymbol{W} - \frac{1}{3} \boldsymbol{I} \right]$$
(4)

where  $\mathbf{W}$  is the second moment of the orientation distribution function for tube segments in flow, I the identity matrix and  $G_0$  the plateau modulus (bold symbols represent tensors). W depends on the birth rate  $(B=1/\tau)$  and death rate of tube segments  $(D=v+1/\tau)$ , with v the drift velocity of chain ends towards the center of the tube due to retraction). The birth and death rates assume these simple forms because in the averaging process described above there is no dependence on the position of the tube segments along the chemical backbone of the living polymer. We note upfront that contributions to the stress coming from the kinetics of flow-induced association/dissociation were not considered in this expression. However, they have been accounted for in more recent models (e.g. VCM, GCB models [104,105]) as briefly discussed in Section 3.3 below. The reduced stress  $(\sigma/G_0)$  based on Eq. (4) is plotted in Fig. 5 as function of the reduced shear rate (scaled by the terminal relaxation time). The model predicts a maximum of the stress at  $\sigma^*$  at a shear rate  $\dot{\gamma}_1$ , due to the fact that as a tube segment is subjected to increasing shear deformation, its stress tends to a constant plateau value (the orientation saturates), while the death rate increases indefinitely (due to increased retraction) so the tube segments are renewed faster, causing eventually the stress to fall. This signifies an unstable flow [106], which is characterized by the co-existence of different fluid layers (bands), normal to the velocity gradient direction. This is known as shear banding (and in particular gradient banding, to separate it from voricity banding which is not discussed here [107]). Rheologically,



**Fig. 5.** Reduced shear stress as a function of the Weissenberg number (which is the reduced shear rate,  $Wi = \dot{\gamma} \tau$ ). Long-dashed line: upturn of the stress at high shear rates. Short-dashed line: The (measured) shear stress in the unstable branch region (from 1 to 2). Inspired from [103].

the material exhibits the same stress at different shear rates, one with rate  $\dot{\gamma}_1$  and another with rate  $\dot{\gamma}_2$  which are both on a stable increasing part of the curve. The volume fraction of each of the two bands follows the lever rule to match the macroscopically imposed shear rate [94,103,106-109]. Note that the original Doi-Edwards (DE) model predicts an instability [85] as well. Whereas the possibility of instability in conventional polymers is not excluded in the absence of wall slip [110], the experimental evidence is not yet conclusive and the effect remains a subtle point [111-114]. The DE model has been rectified by incorporating Convective Constraint Release (CCR) [115–118], which is a mechanism for partial loss of entanglements due to flow. CCR corrects for the chain over-orientation predicted in the original DE model, that leads to a drop in the steady state stress. Furthermore, it has been observed that moderate polydispersity can "soften" the instability [119,120]. In fact, this type of flow instability is predicted by constitutive models for both linear and living polymers, but it has been confirmed experimentally only for living polymers in the fast breaking limit. In comparing the two systems one may remark that for living polymers the local nature of the mechanism of stress relaxation, i.e., reversible scission/reformation of living polymers, leads to a stress overshoot even at significantly high shear rates, whereas for synthetic polymers it disappears due to constraint release [121].

## 2.3. Brief discussion on modeling of the nonlinear response and associated instabilities

Microscopic models for the nonlinear flow of living polymers, as the one described in the previous section, have the aim to predict the rheological response of living polymers based on the dynamics of living polymers at a microscopic level. However, these types of models are lacking some of the physical aspects of nonlinear response such as concentration coupling and non-local effects. Thus, the approach that has been followed up to now is the use of phenomenological (macroscopic) constitutive models which due to some adjustable parameters can mimic the living polymer response. In general, these models have the following form

$$\boldsymbol{\sigma_{tot}} = \eta \left[ \boldsymbol{\kappa} + \boldsymbol{\kappa}^{\mathrm{T}} \right] + \boldsymbol{\sigma_{pol}} - p \boldsymbol{I}$$
<sup>(5)</sup>

where,  $\sigma_{tot}$  is the total stress tensor,  $\eta$  the viscosity,  $\kappa$  is the velocity gradient tensor,  $\sigma_{pol}$  is the polymeric stress tensor which is

typically calculated through a molecular orientation tensor such as W in the previous section, I is the identity matrix and p is the isotropic pressure which maintains fluid incompressibility. Typically, the form for the polymeric contribution to the stress

$$\boldsymbol{\sigma_{pol}}^{(1)} = \frac{1}{\tau} + \boldsymbol{f} \left( \boldsymbol{\kappa}, \boldsymbol{\sigma_{pol}} \right) + \mathcal{D} \nabla^2 \boldsymbol{\sigma_{pol}}$$
(6)

where  $\sigma_{pol}^{(1)}$  is some kind of material derivative of the polymeric stress (such as Upper Convected derivative or the Gordon-Schowalter derivative,  $\tau$  is a simple Maxwellian relaxation time, f is an operator that varies depending on the numerical model, D is a diffusion constant which suggests that spatial inhomogeneities of stress eventually relax or diffuse [122–125]. A few examples of experimental validation for these non-local effects and use of such models can be found in [126–128] The stress diffusion term is added in an *ad hoc* manner and essentially introduces a non-local character to the stress which is needed to avoid the infinitely sharp interface between bands of different shear rate but also reproduces robustly the stress value at which shear banding occurs, which was a problem for models lacking the stress diffusion term.

Another modeling development in the field of shear banding involves accounting for the flow-concentration coupling that introduces non-locality [104,129–132]. It has been shown, for the case of linear polymers, that polymers in the low viscosity (concentration) band will move further than those on the high viscosity band and a polymeric chain will move towards the high viscosity (concentration) band [133]. Thus, a relaxing chain will move up the concentration gradient and this effect induces strong concentration fluctuations. Typically, such issues are resolved by introducing the so-called two fluid model [129,131,132], which are based on the different force balance for the micelles and solvent in different fluid elements. In this way any difference in the velocities between the two will give rise to concentration fluctuations (see reviews on the macroscopic modeling of shear banding include [94,107,134,135]).

### 3. Hydrogen-bonded supramolecular living polymers

## 3.1. Effects of different motifs and the environment on the self-assembled structure

A wide range of low molecular weight compounds are used in supramolecular 'polymerizations', both in water and in organic solvents, yielding very long 1D living polymeric structures akin to conventional synthetic polymers. Some characteristic examples are presented here with emphasis on the effect small changes in the molecular structure or environment have on the final selfassembled product. In general, highly directional associations with large association energies are necessary to form long polymer-like supramolecular structures. Fig. 6 illustrates four typical motifs used is such self-assemblies. There is a wide range of applications using these four motifs in the formation of supramolecular living polymers with versatile properties and great sensitivity to slight changes in their environment or structure, which we review below.

Sijbesma and coworkers [36] used UPy to functionalize small alkyl spacers (component 1 in Fig. 7A) at both ends (bifunctional or  $\alpha$ - $\omega$  telechelic), which when dissolved in trichloromethane (CHCl<sub>3</sub>) lead to viscous solutions (effectively good solvency conditions) with the viscosity being highly concentration- and temperature-dependent. In particular, supramolecular solutions based on UPy motifs with the compound 1a (H) exhibit a power-law concentration dependence of the viscosity with an exponent of 3.6 (Fig. 7B), in agreement with the predicted value from the model of Cates for living polymers [63]. On the other hand, motifs with a different compound 1b (CH<sub>3</sub>) yield different assemblies with a more



**Fig. 6.** Motifs for supramolecular self-assembly via different types of bonding interactions: (A) Ureidopyrimidinone (UPy) with quadruple hydrogen bonding [136,137]; (B) Cyclohexane-Tricarboxamide (CTC) with triple hydrogen bonding [138]; (C) Bisurea group with hydrogen bonding and  $\pi$ - $\pi$  stacking [95]; (D) 1,3,5-Benzene Tricarboxamide (BTA) group with triple hydrogen bonding and  $\pi$ - $\pi$  stacking 139,[140].



**Fig. 7.** (A) Structure of the bifunctional and monofunctional compounds for UPy-based supramolecular assemblies. (B) Specific viscosity of solutions of assemblies based on moiety 1 in CHCl<sub>3</sub> as a function of concentration for the two different bifunctional compounds. Squares correspond to compound 1a while circles to compound 1b. The dotted lines have slopes of 3.6 for 1a, and 1 and 6 for 1b. (C) Specific viscosity of mixtures based on diffunctional moiety 1 and monofunctional compound 2 in CHCl<sub>3</sub> as a function of mole fraction of compound 2. Data are taken from [36].

peculiar behavior of the viscosity, characterized by linear dependence at lower concentrations and a much stronger dependence at higher concentrations (with a power-law exponent of about 6). This is attributed to the likely presence of oligomeric rings in solution (formed by the cyclization of a few unimers) based on compound 1b at lower concentrations and the eventual formation of elongated objects at higher concentrations. The unidirectionality of the associations was confirmed by adding the monofunctional compound 2 (Fig. 7A) in solutions of compound 1, showing that depending on the mole fraction of the monofunctional compound one can control the length of the self-assembly, as shown in Fig. 7C, where the specific viscosity ( $\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$ , with  $\eta$  being the



Fig. 8. (A) Chemical structure of UPy motif and schematic illustration of the proposed self-assembled supramolecular polymer. (B) Neutron scattering intensities in deuterated dodecane (squares) and chloroform (circles) [142].

solution viscosity and  $\eta_o$  the solvent viscosity) is plotted as a function of the molar fraction of the monofunctional component. The specific viscosity decreases by an order of magnitude with addition of very small amounts of the end-capper component 2, which results in the termination of the supramolecular polymerization by capping active ends, and thus to much shorter self-assembled structures (provided that there is no uncontrollable gelation or branching taking place).

It is important to note that the self-assembly of moieties into supramolecular polymers depends on the solvent because secondary associations are in general dipolar and can be easily affected by the polarity of the solvent [141] as well as specific solvophobic effects that might occur. For example, Hirschberg and coworkers [142] explored the role of the solvent on the formation of supramolecular polymers based on UPy (Fig. 8A) and reported that the same motif may form small flexible-coil assemblies in CHCl<sub>3</sub> or long helical columnar stacks in dodecane, due to the solvophobic stacking of the aromatic parts of the molecules (Fig. 8A,B). This is unambiguously shown in the  $I(q \rightarrow 0)$  limit of Fig. 8B, where the intercept is proportional to the molecular weight of the self-assembly, but also by the fact that the form factor in the case of dodecane (squares) has already started decaying at the q values explored, while the assembly in CHCl<sub>3</sub> starts to decay at much larger q values. According to the Guinier approximation (valid for  $q \ll R_g$ , with  $R_g$  the radius of gyration) this suggests that the  $R_g$  of the assembly in dodecane is much larger than the one in CHCl<sub>3</sub> [143].

In apolar solvents such as toluene, 2,4(ethyl hexyl ureido)toluene (EHUT, Fig. 9A) is known to self-assemble into thin thread-like (or filament) supramolecular structures at larger temperatures and tube-like structures at lower temperatures, as evidenced by SANS experiments (Fig. 9B) and validated by molecular dynamics simulations [144,145]. The two different structures are characterized by a marked difference in the scattering intensity I(q), where q is the scattering wavevector. Moreover, the fact that I(q) decays as  $q^{-1}$  (see the flat curves in the Holtzer plot of qI versus q) indicates that both structures formed are rigid and seem to have a finite cross-section. Strong solvent effects have been also observed during the self-assembly of bisurea-based moieties and in particular the EHUT. Since one of the structures formed is a hollow tube, in order for it to be stable it needs to be filled with solvent and thus, if one changes the solvent size (even without changing its dielectric constant), the tubular structure would become unstable [146], resulting in the two different pseudo-phase diagrams shown in Fig. 9C and 9D corresponding to the diagrams in phases in toluene and trimethylbenzene (TBM), respectively. The similar transition from the monomer to the thin filament reflects the very similar dielectric properties of TBM and toluene.

Recently, Louhichi *et al.* [67] reported that the viscoelastic properties of EHUT solutions in apolar solvent dodecane, and in par-

ticular the terminal relaxation time, are affected by the level of environmental humidity. This is discussed in more detail in the next section below. Along the same lines, a molecular study by Van Zee et al. [147] demonstrated that the structure and helicity of a novel self-assembling motif based on BTA, biphenyl tetracarboxamide (BPTA), in organic solvent methylcyclohexane change significanlty in the presence of trace amounts of water which interacts with the hydrogen bonding moieties (Fig. 10). In a nutshell, at low temperatures the water molecules in the monomeric state are immersed in an organic oil (e.g., dodecane), interact with BPTA and saturate the supramolecular structure, which has a right-handed helical conformation. There are two types of such wet structures, depending on the ratio (v) of water molecules per BPTA moieties (Fig. 10B). By increasing the temperature, water molecules leave the structure, which eventually dries out and turns into a lefthanded helix (Fig. 10B). The wet-to-dry transition was monitored with circular dichroism (CD) and described by a thermodynamic model which involves three competing, cooperative polymerizations and provides the free energy of deformation for the different states (Fig. 10B) [147].

Similar motifs to those discussed so far can self-assemble in water to yield hydrogels that find many applications as biomaterials [8,59,61]. The self-assembly of a rationally designed BTA derivative has been studied extensively in water by Meijer and coworkers [40,41,44,148,149]. The outer part of this molecule includes a tetraethylene glycol compound to ensure solubility in water, whereas the inner section comprises an alkyl chain that creates a hydrophobic core shielded from water molecules (note different side chains compared to Fig. 6D). Leenders et al. [40] used cryo-TEM to show that the self-assembly of BTA (Fig. 11A) in water yields 1D fibrillar structures (Fig. 11B). They exhibit a periodic change in contrast along their backbone (darker and lighter spots) which is usually found in helical bundles or twisted ribbons. This system has also distinct signatures in the UV-Vis spectra that hint toward a possible supramolecular polymerization mechanism. In particular, Fig. 11C depicts the evolution of the UV-Vis (O.D. is optical density which is proportional to absorbance) spectra of a BTA sample originally molecularly dissolved in methanol (unimer moieties) and subsequently injected in water. The UV-Vis spectrum of BTA in methanol exhibits a maximum at 209 nm which is consistent with the molecularly dissolved state. However, immediately after injection in water the absorption spectrum displays a strong peak at 192 nm (blue curve in Fig. 11C), suggesting that initially the BTAs self-assemble into helical columnar stacks which decay over time and yield two bands at 213 nm and 230 nm (red curve in Fig. 11C), and turns into the structure observed in cryo-TEM. This scenario was later confirmed by molecular dynamics simulations of the self-assembly of the same BTA derivative in water using a coarse-grained model which suggests that BTAs first assemble into disordered aggregates which evolve into ordered stacked



**Fig. 9.** (A) Chemical Structure of bisurea-based motif 2,4(Ethyl Hexyl Ureido) Toluene (EHUT). (B) Holtzer plot of ql versus q for EHUT in toluene at two different temperatures. The plateau indicates the rigid structure formed by EHUT at both temperatures, whereas the difference in aggregation number is evident since at 52 °C the intensity is much lower [144]. Copyright 2005, reproduced with permission from the American Chemical Society. (C) Pseudo-phase diagram of EHUT in toluene. (D) Pseudo-phase diagram of EHUT in TBM [146]. Copyright 2006. Reproduced with permission from the John Wiley and Sons.



**Fig. 10.** (A) Chemical structure of BPTA self-assembling motif. (B) Schematic of the three-component thermodynamic model, inspired from [147]. Discs represent the BPTA which self-assembles into supramolecular living polymer **A**, whereas  $v_B$  and  $v_c$  are the ratio of water molecules to BPTA moieties found in the two wet states **B** and **C**.

BTA oligomers and eventually polymerize to form longer fibers [150]. All supramolecular structures described here are based on reversible interactions; therefore, the dynamics of breaking and reformation are central to their properties and, in general, to the molecular design of living polymers with desired function. For example, the copolymerization of a BTA derivative with branched outer chains is characterized by slower dynamics compared to the same without branches, due to the stabilization of the assembly

by increasing the order in the fibers [148]. In another situation, by slightly changing the length of the aliphatic chain in BTA from 10 carbons to 11,12 and 13 carbons, a progressive slowing-down of the dynamics was observed (Fig. 11C). In the case of the  $C_{10}$ BTA, the exchange takes place rapidly because the 10-carbons alkane is not adequate to shield the hydrogen bonding core from water molecules and thus the self-assembly is halted by the competitive association of water on the hydrogen bonding sites of the BTA core.



**Fig. 11.** (A) Chemical structure of BTA derivative for aqueous systems, note the difference in the side chains compared to Fig. 6D. [40], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry. (B) Cryo-TEM image of the structure created by BTA in water. The periodically varying contrast points to a helical bundle structure. Scale bar is 50 nm. [40], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry. (C) Time evolution of UV-Vis spectra of BTA in water. The system in methanol was molecularly dissolved and injected into water at t = 0. Arrows indicate how curves change over time [40]. The two peaks shown in the red curve are peaks at 213 nm and 230 nm. Grey line is the spectra after 15 min. Note that the y-axis is optical density, a quantity proportional to the absorption. [40], Copyright 2013. Reproduced of DHydrogen-Deuterium exchange mass spectrometry is used to examine the dynamics of motifs comprising BTA with varying alkyl spacer length. The fraction of BTA with only the outer labile hydrogens in the -OH groups is monitored. Over time, the BTA3D changes is indicative of the moiety dynamics. [44], Copyright 2017. Reproduced with permission from Springer Nature.

### 3.2. Bridging monomer dynamics to rheological properties

Given the various intricacies of the self-assembly process discussed above, in particular with respect to the role of the environment or the chemical structure of the motifs, understanding the consequences on the bulk properties of the formed supramolecular living polymers is an extraordinary albeit necessary challenge to address. The model of Cates for wormlike micelles [63] represents the basis (Section 2.1). The stress relaxation is predicted to be Maxwellian, as confirmed by ample experimental evidence [38,64,66,67,69,95–99], due to the reversible nature of the living polymers, which break and reform spontaneously while relaxing stress by reptation. Indicative linear viscoelastic (LVE) data are depicted in Fig. 12. Specifically, Fig. 12A depicts the LVE spectra for an associating BTA derivative in decane at various concentrations. The behavior is clearly Maxwellian as confirmed by the almost perfect semicircular Cole-Cole plot of loss (G") versus storage (G') modulus in Fig. 12C. The same holds for living polymers based on the EHUT motif in dodecane, as shown in the respective Fig. 12B (where the lines represent the fit of the terminal regime with a Maxwell model) and 12D. The deviation from the semicircular shape at higher frequencies (or larger storage moduli) in Fig. 12C and, especially, Fig. 12D, reflects the presence of faster modes, such as

Rouse-modes or breathing modes which are of course not present in a Maxwell element. This is the reason for distinguishing different regions, I, II and III in Fig. 12D. In region I, the data follow the semicircular evolution expected from a mono-exponential relaxation, while in region II they start to deviate from the circle, and eventually they exhibit an unambiguous minimum in region III. The latter is related to the number of entanglements in living polymer solution [65] and has been proposed to provide information about the average length of an entanglement segment [151,152]. A compilation of the plateau moduli  $(G_0)$  and relaxation times as functions of concentration is presented in Fig. 13A and Fig.13B, respectively. The plateau modulus follows the predicted power law (see Section 2.1), whereas this is not the case for the terminal relaxation time, which was recently shown to depend substantially on the environment (humidity) [67]. To rationalize it, accounting for the above mentioned possible limitations of the model, flexibility and constraint release considerations (see Section 2.1) seems appropriate.

Note that in the case of entangled associating polymer networks, obeying the sticky reptation model [28] as described in the introduction, the plateau modulus of the entangled network (i.e., the lower-frequency plateau after the stickers have opened-up) exhibits a similar scaling law to that of Fig. 13A [153]. Actually, in



**Fig. 12.** (A) Linear viscoelastic spectra of a self-assembled BTA derivative in decane at various concentrations (indicated in the legend). [69], Copyright 2004. Adapted with permission from the American Chemical Society. (B) Respective spectra for EHUT in dodecane. Lines represent the fit of the terminal regime with a Maxwell model. [96], Copyright 2007.Adapted with permission from John Wiley and Sons. Data are taken from [96]. (C) Cole-Cole representation of the data in A. The lines are the fits of the data with a semicircle. [69], Copyright 2004. Adapted with permission from the American Chemical Society. (D) Cole-Cole representation of the data from B for various concentrations ranging from 2.9 g/L to 10 g/L. The line is the fit of the data with a semicircle. [96], Copyright 2007. Adapted with permission from John Wiley and Sons.



**Fig. 13.** (A) Compilation of concentration-dependent plateau moduli, as obtained from the minimum of G", for different supramolecular living polymers [37,67,69,96]. Dashed line indicates the power-law prediction of Cates [63–65]. (B) Compilation of terminal relaxation times, as obtained from the inverse cross-over frequency for different systems [37,67,69,96]. Symbols are the same as in (A). Dashed lines indicate scaling laws found in each study.

both cases the same well-known scaling arguments pertinent to conventional synthetic linear polymers apply as well.

### 3.3. Rheological signatures of environmental effects

We now discuss the rheological consequence of the influence of humidity on the self-assembly of supramolecular living polymers, discussed in Section 3.1. Fig. 14A depicts the LVE spectra of an EHUT-based living polymer solution in dodecane [67]. The black circles correspond to the sample measured under dry conditions while the blue stars under ambient humidity conditions. The terminal relaxation time changes by a factor of three while the plateau modulus is virtually unchanged, suggesting that the strength of the entanglement network is not affected by humidity. The terminal response remains Maxwellian. There is also a slight shift of the frequency where G" exhibits a minimum, which



**Fig. 14.** (A) Linear viscoelastic spectra for EHUT-based living polymers in dodecane (5 g/l) under dry conditions (black circles) and ambient humidity conditions (blue stars). Solid symbols represent the storage modulus G'. Arrows indicate the cross-over frequency associated with the terminal relaxation time and the frequency of the minimum in G'' associated with the breaking time of the living polymer. Lines are the fit of the terminal process with the Maxwell model. [67], Copyright 2017, reproduced with permission from AIP Publishing. (B) Transient viscosity versus time at different shear rates (indicated in the plot) for an EHUT polymeric sample (5 g/l in dodecane) measured under both ambient humidity and dry conditions (lines and symbols, respectively). [67], Copyright 2017. Reproduced with permission from AIP Publishing. (C) Stress relaxation after cessation of steady-state shear flow (at different shear rates marked in the plot) for an EHUT polymer in dodecane (12 g/l). At intermediate times the stress exhibits an overshoot. [160], Copyright 2019. Reproduced with permission from the American Physical Society. (D) Experimental flow curve for CTAB/NaSal system with predictions from non-local Giesekus (dashed line) and Germann-Cook-Beris, GCB (solid line), models. [165], Copyright 2016. Reproduced with permission from AIP Publishing. Inset: Flow curve for the EHUT living polymers in dodecane. The stress plateau is characteristic of shear banding. [96], Copyright 2007. Reproduced with permission from John Wiley and Sons.

is attributed to the breaking time of the assembly [67], however the change in the terminal relaxation time is more substantial (Fig. 14A). The change of the terminal relaxation time is attributed to the change in the average length of the EHUT selfassembled structures. Indeed, it has been shown that by adding impurities or monofunctional moieties in a solution of EHUT may result in chain scission, yielding shorter polymers with faster relaxation times [37,154]. It is also possible that water molecules do not just end-cap the supramolecular assemblies but can get incorporated between unimer moieties as suggested by van Zee *et al.* [147] in the case of BPTA, yielding a slightly lower binding energy. Therefore, even tiny amounts of water in apolar solvents (even less than 0.1wt%) can interfere with the hydrogen-bonded self-assembly and influence the macroscopic properties of the solution, as shown for the EHUT-dodecane solution [67]. In this respect, a formidable challenge is to understand why some living polymer systems (say organogels under dry conditions) exhibit a much weaker concentration dependence of their terminal relaxation times than that predicted by Cates (see Fig. 13B) [68]. It has been suggested that this might be related to the consideration of the average contour length predicted by the model since both the breaking and reptation times depend on it. As already mentioned, the model considers the most probable length distribution. Furthermore, again it has been already pointed out that constraint release should play a role in the terminal relaxation and depend on concentration, but it has not been considered in the model [155]. We should also note that the great sensitivity of such measurements to humidity may be an additional reason for the different power laws of Fig. 13B (the data reported are taken without humidity control, with the exception of [67]).

Given the above developments, it is intriguing to examine the influence of humidity on the more challenging nonlinear rheological properties. Louhichi et al. have reported some transient shear stress data of the EHUT-based supramolecular living polymer solutions [67]. An unusual strong transient shear strain hardening was observed, with the steady-state viscosities exhibiting strong shear thinning (Fig. 14B). The former effect has been observed very recently by means of nonequilibrium computer simulations of sheared supramolecular polymer networks formed by telechelic linear chains [156]. It is also reminiscent of the shear strain hardening observed for biological systems such as F-actin and attributed to the semiflexible character of this kind of systems [71]. Interestingly, the effect of humidity is apparent also in the nonlinear viscoelastic regime since the steady-state as well as the peak (overshoot) viscosities measured in ambient conditions are always smaller compared to those measured under dry conditions (Fig. 14B). This might reflect the difference in terminal relaxation times since the two samples are essentially measured at different values of the Weissenberg number. For the same shear rate  $\dot{\gamma}$ , the humid sample is actually measured at smaller Weissenberg number and does not stretch as much, leading to less pronounced overshoots. However, this observation does not exclude a more subtle effect that the humidity might have on the supramolecular assembly, such as the possibility that weakening of associations makes the scission under shear easier and leads to less pronounced peaks. The flow-induced scission [157-159] in these living polymers has been discussed in a different context recently: it was found to be associated with an unexpected nonmonotonic stress relaxation upon cessation of steady-state shear flow (Fig. 14C) [160]. In fact, upon flow cessation (where it is considered that some scission of the supramolecular living polymers takes place) the stress relaxation can become non-monotonic because bonds between broken species can reform and part of the energy released from this process can increase the elastic energy and yield the formation of locally deformed domains with local anisotropy, leading to this unusual intermittent stress increase [160]. Furthermore, and returning to their strong shear thinning, the EHUT living polymer solutions exhibit gradient shear banding [96,161], i.e., the viscosity thinning slope is -1, or more clearly the shear stress-shear rate flow curve exhibits a stress plateau (inset of Fig. 14D). This behavior is typical of living systems as discussed in Sections 2.2 and 2.3; it has been widely observed in wormlike surfactant micelles systems [97,106,151] and in living polymers based on metal-ligand coordination [162]. It is also predicted by constitutive models incorporating the idea of changing shear rate associated with heterogeneities in the system and described by different mechanisms (stress diffusion, stress-concentration coupling) [102,103,94,107-109,134] (see also Section 2.3). Corroborating evidence has been provided by birefringence measurements under flow and particle tracking velocimetry [161,163,164]. As an example of the predictions of different constitutive models, recently the non-local Giesekus model (i.e., the Giesekus model [124] with a non-local stress diffusion term as discussed in Section 2.3) and the Germann-Cook-Beris (GCB) model which is based on the microscopic dynamics of scission/reformation of living polymers (discussed later), were compared against the actual experimental flow curve of a CTAB/NaSal wormlike micellar system [165] and indicative results are shown in Fig. 14D. It is clear that both models capture the low-shear rate regime quite well, however the Giesekus does a better job in capturing the transition to the (steady-state) shear-banding regime. Nevertheless, both models seem to clearly depart from the experimental data in the high-shear rate regime. It was proposed by the authors that for the GCB model this deviation might be rectified by adding a nonlinear relaxation mechanism for the shorter species in the model that accounts for chain stretching [165].

Focusing on the link between macroscopic response and microstructural dynamics of living polymers, we note that a rigorous study of the nonlinear rheological response of the EHUT moiety in toluene combined with flow birefringence, revealed three different banding regimes [161]: (i) one related to the typical steady-state banding observed in wormlike micelles, which is related to mechanical instabilities (similar to those described in the nonlinear Cates model [103]) and takes place at low shear rates (Weissenberg numbers in the range 0.1-1); (ii) and two additional regimes, at intermediate and large Weissenberg numbers (ranges 10-100 and above 1000, respectively) which appear to be related to flowinduced phase separation. Specifically, in the large-Wi regime, an unstable phase was accompanied by highly unstable velocity profiles. The characteristics of shear banding behavior at large values of Wi cannot be captured by the theoretical framework discussed in Sections 2.2 and 2.3. It has been suggested later on, that such complex behavior might be due to the change in length of the supramolecular polymers under flow due to alignment-induced elongation [166]. Despite their importance and overall success, phenomenological constitutive models (such as those discussed in Section 2.3) do not account explicitly for the contribution of the microstructural dynamics of scission/recombination to the stress tensor and typically require very large solvent viscosities to reproduce the stress upturn at large shear rates. On the other hand, the model of Cates [103] (discussed in Section 2.2) is based on the reversible scission/reformation of living polymers, but is limited to small shear rates, where the kinetics of breaking and recombination are assumed to not change under flow. This may be the reason why the model does not predict strong nonlinearities (such as damped oscillation or "ringing") observed in wormlike micelles. In this formulation of the model, shear banding due to the alignment of tube segments is similar to the response of the Doi-Edwards model without the scission/recombination kinetics [167].

In this context, the Vasquez-Cook-McKinley (VCM) model [104], based on a discrete version of the Cates model [63], includes the microscopic dynamics of living polymers and qualitatively reproduces the experimental rheological findings. Simply put, it is a two-species model (initial species of length L that can break to form species of length L/2 which can in turn recombine to form species with length L), not based on reptation but with the dynamics of scission/reformation being incorporated into an elastic network theory which tracks entanglement strand in the entanglement network formed by the wormlike micelles [104,168]. The key element of the VCM model is that the large chains are subjected to convection under shear flow and can break due to stretching. However, as pointed out in a series of publications by Germann et al. [105,169], it is not thermodynamically consistent because the breakage rate of the large species depends explicitly on the velocity gradient tensor. In those works, a thermodynamically consistent analogue of the VCM model was developed [105,169] (GCB model) and tested against the non-local Giesekus [170] model which has been largely used to model the shear banding of wormlike micelles where the breakage rate depends on the conformation tensor. It should be pointed that the rate dependence of the breaking coefficients (or breaking rates) has been also evidenced by Briels and co-workers who performed coarse-grained simulations on erucyl bis(hydroxymethyl)methylammonium chloride (EHAC) wormlike micelles [171]. As already mentioned, there are quantitative differences between the GCB model and experimental data at large shear rates that require the introduction of intermediate micellar species as well as the nonlinear relaxation term accounting for micellar stretch, while there is a need for more experimental work about flow-induced breakage of living polymers [170]. In this context, the developments over the control in the dynamics of hydrogen-bonded polymers as described in the previous sections, but also the ones in the following sections, can be



Fig. 15. (A) Chemical structure of the BTA motif. (B) Chemical structure of the telechelic motif BTA-PEG-BTA. [177], Copyright 2020. Reproduced with permission from the American Chemical Society.

useful since one can tailor the dynamics of such systems, providing an important testing ground for models such as the VCM and GCB that incorporate the breaking/reformation kinetics of living polymers. Recently, a discrepancy between the VCM model (short and long Hookean dumbells) and Brownian dynamics simulations was reported [172]. They were attributed that to the fact that the original VCM does not keep track of the conformations of individual dumbells when they fuse into a longer two-dumbell chain, and rectified by introducing a multi-bead-spring model on top of the reaction kinetics of the original VCM model [172]. It might be possible for such a model to accommodate subtle effects such as alignment-induced elongation of living polymers under shear flow that has been suggested to lead to extreme shear thinning [166]. A very important development in this are is the recent consitutive model of Peterson and Cates [87].

### 3.4. Competing interactions in living polymer mixtures

Supramolecular living polymers such as those described here exist both in organic solvents and in water. Up to now, low molecular weight hydrogelators have been studied only in terms of how effective they are in forming hydrogels [41,173] for materials with potential use in biomedical engineering. The common central theme of these works is the combination of a hydrogelator (low molecular weight compound similar to those in Fig. 6, although with hydrophilic ligands to allow self-assembly in water) with a telechelic polymer chain functionalized at its ends. The hydrogelator forms hydrogels due to entanglements of the long fibrillar structures and the telechelic chain forms hydrogels due to the bridging of small micellar aggregates that are created by its closed-loop structure, similar to what has been observed in the past for amphiphilic block copolymers [54,174,175]. These complex hydrogelators have been considered as potential candidates for tissue engineering [60,176]. Importantly, their mixtures exhibit an intriguing non-monotonic dependence of the mechanical properties with mixing ratio of the two components [60,176,177]. This is quite similar to works on wormlike micelle mixtures with hydrophobically modified polymers [178,179], where the mechanical properties also depend non-monotonically with mixing ratio. However, in the case of wormlike micelles there are different association mechanisms at play between the two binding moieties, rendering the interpretation and control of properties complicated. On the other hand, with supramolecular living polymers it is possible to study mixtures having the same basic associating motif in order to simplify the problem. This is the case of a recent study with BTA-based assemblies [177], where the self-assembly of two derivative compounds based on BTA was exploited with respect to the resulting properties of the living polymeric systems and their mixtures. BTA (Fig. 15A) self-assembled in water, forming long fibrils [40,41,180,181], while a telechelic BTA (Fig. 15B) comprising a small polyethylene glycol chain (20 kg/mol) functionalized with a BTA unit at each end (BTA-PEG-BTA) yielded smaller fibrillary micelles, occasionally bridged, depending on concentration [177].

The two supramolecular systems based on the same associating BTA compound exhibit very different linear viscoelastic behavior, as shown in Fig. 16A, with the BTA-PEG-BTA behaving as a transient network with a very fast cross-over of the two moduli which is related to the relaxation or "unsticking" of the bridges but with a second mode at lower frequencies that leads to terminal relaxation. On the other hand, the BTA exhibits an extended plateau modulus over 7 decades in frequency before eventually reaching terminal Maxwellian relaxation, akin to that predicted by the model of Cates [63]. The value of the plateau modulus is much smaller (by about 2 decades) compared to the telechelic BTA-PEG-BTA component. When mixing the two systems, a nonmonotonic dependence of the plateau moduli with mixing ratio is observed, as clearly shown in Fig. 16B. The same holds for the terminal relaxation time (here taken as the inverse of the cross-over frequency), suggesting that the interaction of the two species is complex, leading to possible changes in the dynamics and spatial arrangement of the components [177]. From hydrogen-deuterium exchange mass spectrometry and cryo-TEM experiments it was inferred that the association strength of the two species BTA and BTA-PEG-BTA is very different, with the latter being less associative due to the hydrophilicity of the PEG segment. Additional insight was gained from coarse-grained molecular dynamics simulations. The BTA/BTA-PEG-BTA mixture was modeled as a mixture of two different components, associating through a Lennard-Jones-type pair potential (with different strength of attraction) and an angular potential emulating angular rigidity. The BTA unit was modeled as a strongly associating unit while BTA-PEG-BTA was the weakly associating unit. The information about association strength is enough for the simulations to produce qualitatively similar results to the experimental ones (see the dependence of the plateau modulus on mixing ratio from the simulations in Fig. 16C) suggesting that a key ingredient of the non-monotonic rheological properties is the different association strengths between the two components and their coupling, and the way that this affects their spatial rearrangement. The latter is evidenced in the simulation results of Fig. 16D where the fraction of particles having coordination number z=3 (or in other words forming cross-links, i.e., branches) is plotted as a function of the mixing ratio. It is clear that, at first by increasing the mixing ratio the system is driven to form more cross-links. Once the network of the strong component is sparse, then the number of cross-links starts to reduce leading to the nonmonotonicity in the mechanical properties.

### 3.5. Use of controlled interactions to tailor material properties

In this brief section we attempt to summarize recent works regarding the opportunities available for tuning the properties (mainly rheological) of materials based on supramolecular polymers. One recurring theme is the use of competitive associations in the self-assembly to induce a pathway to complexity that will ultimately lead to the tunable material properties. We believe that this accumulated knowledge opens-up new perspectives in the field of



**Fig. 16.** (A) Linear viscoelastic spectra of the pure BTA-based supramolecular assemblies components of Fig. 15 and two mixtures. The spectra for BTA are represented by the blue circles, for BTA-PEG-BTA by the red squares, for the 50/50 mixture by purple upward triangles and for the 75/25 mixture by green downward triangles. The lines represent the spectra as obtained from the conversion of the creep compliance to dynamic moduli [177]. Open symbols and dashed lines represent the loss modulus G' while solid lines and filled symbols the storage modulus G'. (B) The experimental plateau modulus of the pure components and mixtures as extracted from the minimum of tan ( $\delta$ )=G''/G', as a function of mixing ratio. The lines are drawn to guide the eye. (C) The plateau modulus extracted from molecular dynamics simulations as a function of the mixing ratio of the two components. (D) Fraction of particles forming cross-links, as defined by their coordination number (z=3). The fraction of component-I particles is shown by red squares. The fraction of total particles with coordination number z=3 is shown by the blue circles while the fraction of component-II particles is shown by red squares. Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tunable supramolecular materials that will be discussed in the following section.

From the above discussion it is clear that the dynamic nature of the associations allows for the supramolecular building blocks to self-assemble into structures which can be varied by changing some parameters, such as concentration [182], temperature [144], solvent [183] or by tuning the monomer structure on the molecular level [184]. This affects the structure and dynamics of the assemblies [44,148,185] (discussed in sections 3.1 and 3.2) and eventually dictates material properties. Typically, concentration and temperature are the two easiest parameters one can experiment with and according to the model of Cates [64,94], there should be an expected concentration dependence of the contour length of the micelles, but this should not affect the rheological in an unexpected manner since the scaling is the same over all concentration regimes (i.e.  $L \sim c^{1/2}$  [63]). Temperature tends to weaken associations in an Arrhenius manner which yields a strong viscosity reduction at larger temperatures where the supramolecular polymer solution becomes a solution of non-interacting moieties. Furthermore, in analogy to the well-known case of wormlike micelles [68,98,186], supramolecular living polymers can also undergo phase transitions by varying the concentration and/or tem-

perature as discussed for example in Section 3.1 for EHUT [146]. However, temperature can have unexpected effects on the selfassembly of supramolecular moieties. For example, the recent work from Van Zee et al. [147] shows a change in the structure of the supramolecular polymer when the temperature is varied due to the incorporation of trace amounts of water in the solvent used (see Section 3.1). Similarly, a recent work from Bouteiller's group shows that by introducing competing interactions in the design of supramolecular polymers can result in complex thermal response [187]. In particular, it was shown that the competition between different hydrogen bonding moieties within the supramolecular polymer yields a temperature-dependent conformation of the supramolecular polymer formed which results in a thermo-thickening material in apolar solvents. This is based on the conformational change probed by SANS, where the weak long range order at low temperatures is lost as the temperature is increased. The hypothesis is that in the isotropic phase there is a larger number of entanglements than in the phase exhibiting long-range order and this promotes a thermo-thickening behavior. The intensity of the phenomenon was shown to vary by carefully tuning the chemical structure of the binding moiety (see also Section 3.1). Along these lines, the early observation of the role of

free ions on the thermal breakage and associated linear viscoelastic properties of wormlike surfactant micelles (the case of added sodium salicylate to CTAB [188]) is certainly inspiring for possible applications in supramolecular living polymers.

Introduction of competitive pathways in the self-assembly results in similarly complex phenomena associated with the induced self-assembly by dilution of porphyrin based supramolecular polymers [182]. Pyridine was employed as an axial ligand affecting the self-assembly of porphyrins. It was shown that at a critical pyridine concentration there was a sharp transition to a depolymerized state that was followed by re-assembly at lower concentrations, essentially exhibiting a re-entrant phase transition. It is also interesting to think about the potential consequences of the sensitivity of hydrogen-bonding motifs (such as BPTA [147] and EHUT [67]) to humidity on the conformation and ultimately the viscoelasticity of the formed supramolecular assemblies and resulting materials. In the case of EHUT [67], water molecules seem to act as chain stoppers leading to variations in the viscoelasticity of the material (Section 3.3), however more work with different motifs is necessary in this direction in order to unravel the complex role of humidity on structural and rheological properties. It is not yet clear whether humidity affects other properties as well, such as the thermo-thickening behavior [187]. Finally, the preliminary investigation of mixtures with competing interactions (Section 3.4) opens the route for many further studies, experimental and simulations, aiming at tailoring properties of composites comprising supramolecular assemblies.

### 4. Concluding remarks and perspectives

Despite the recent advances in the emerging field of supramolecular assemblies and gelators, as briefly outlined in this article, there is still much that is not understood, in particular regarding the interplay of interactions and its implications in the bulk properties of the resulting materials. Increasing evidence suggests that the rational design of materials with tunable structural and rheological properties relies heavily on competitive interactions which depend on a broad range of parameters, including solution variables such as concentration [182] or solvent [144,146], environmental cues such as temperature [147,187] or humidity (for organogels) [67,147], as well copolymerization, i.e., the self-assembly of units with similar associating motifs but with different association energies and dynamics [44,60,148,176,177]. In Section 3.4 we discussed recent work [177] where the nonmonotonicity of mechanical properties of a mixture comprising supramolecular assemblies based on two different associating moieties was shown to reflect the complex interplay of the two different interactions. Qualitatively similar results were obtained in a number of related systems in the past [60,176,178,179], but overall the results remain inconclusive [176,188]. It is important to better understand the details of these competing interactions down to molecular level by exploring systematically the parameter space and focusing on atomistic simulations, something that will promote the applicability of tailored material design. For example, it is interesting to study the effect of the rigidity and the length of the linker, different ratios of associating energies, as well as different geometries other than just linear telechelic chain (e.g., branched polymers). The rigidity and/or the length of the linker seem to be important since they will dictate the loop/bridge ratio, as shown in the work by Noteborn et al. [176] where the non-monotonicity was exhibited with rigid linker (double-stranded DNA) but not with flexible (PEO) linker. In this context, it is certainly worth mentioning that mixtures of wormlike micelles with hydrophobically modified polymers were reported to exhibit a monotonic [188] or non-monotonic [178] increase of their mechanical properties with mixing ratio, pointing to the crucial role of subtle differences in molecular parameters, charge interactions and amphiphilicity.

The nonlinear rheology of supramolecular living polymers is far from being understood (see also Section 2.3), but available evidence suggests an interesting interplay of the competitive interactions (driven by the different association strengths), environmental conditions and the imposed (rate of) deformation. An example discussed in Section 3.3, concerns the effect of humidity on the degree of shear-strain-hardening of EHUT solutions in dodecane [67]. Such a phenomenon can be exploited to rationally design tunable strain-hardening materials which are known to find important applications in tissue engineering since a large number of biological tissues exhibit strain-hardening behavior [72,189]; the latter was recently shown to be associated with cellular signaling pathways [190]. Another rheological feature unique to associating systems is the stress upswing during relaxation of the stress following cessation of steady-state shear flow (see Section 3.2) [160]; exploring its potential universality or range of validity (in terms of molecular, environmental and flow parameters) will help not only to better understand the supramolecular assembly process of these materials but also their biological implications, since there are strong similarities to polymerization processes of microtubules [191,192].

An interesting development in the field is the potential control over the sequence of monomers along the supramolecular polymers. This is essentially the formation of multiblock copolymers from supramolecular moieties held together by non-covalent associations. Most supramolecular block copolymers have been known to involve a kinetically arrested state [193,194]. However, recently the formation of thermodynamically stable supramolecular block copolymers was reported [195,196]. These types of materials have been already proposed for use in functional organic heterostructures that can prove useful in optoelectronic or catalytic applications [197]. We believe that the rheology of such materials is a particularly interesting area of research. Judging from the atomic force or fluorescence microscopy images [194-196], it seems that they comprise one quite flexible and another rather rigid component. This seems to be "bequeathed" into the block copolymer of the rod-coil type, i.e., having flexible and rigid blocks, or to adopt a completely different conformation with variation in both the crosssectional diameter and the rigidity. This could lead to interesting properties, for example the formation of local mesogenic organization for the rigid blocks under quiescent or flow conditions, with important consequences on rheology [198-200].

In view of all these, supramolecular copolymerization could also be an effective approach to tune other mechanical properties of such materials besides the viscoelastic modulus, with direct link to applications. For example, one may think of the brittleness of an emulsion of oil droplets in water stabilized by an ionic surfactant, which can be bridged by PEO polymers dissolved in water, which was explained by the reversible nature of the bridges formed, which are based on hydrophobic interactions [201]. Once a bridge is open or the polymer forms a loop, this can be considered as a microfracture that will expand to create a bulk fracture. One could then use techniques described in this review to alter the dynamics of the system, which represents one of the determining factors for the observed brittleness [201], but also alter the bridge/loop ratio in systems such as those described earlier (telechelic chains/low molecular weight moieties, Fig. 15). In the context of mechanical properties we note that recently associative hydrogels (polyampholyte hydrogels) have been used to demonstrate the principle of the development of dynamic memory storage similarly to the function by which the human brain dynamically loses memories that are not useful, and in stark contrast to the storage media used in everyday life (e.g., hard drives, flash drives) where the memory storage is static. This principle is based on three steps: (i) moving the hydrogel from a cold bath to a hot one, where the water uptake is fast and where there is strong reorganization of the dynamic bonds [202]; (ii) the formed structure is quenched in a cold bath, thus resulting in frustration and the slow evolution towards equilibrium properties by shrinking (releasing water) and reorganization of the reversible bonds; (iii) actually, the memory writing process is the water uptake and reorganization in the hot bath and the 'forgetting process' is the return to equilibrium. It is a worthy challenge to study supramolecular materials such as the dynamic hydrogels that can be formed by the mixture of two supramolecular polymers or gelators (Section 3.4) under the same principle. The non-monotonic dependence of both modulus and dynamics of such a system can prove to be an important parameter to tailor the lost memory ('forgetting') time in such dynamic memory systems. Moreover, it could be possible for such materials to have 'enhanced memory' effects triggered by the action of a nonlinear mechanical stimulus that can have a similar phenomenology to [202], where the frustrated structure is formed by a spatial reorganization of the bonds, which can be the fast encoding process, while the 'forgetting' process is essentially the return to the equilibrium structure. The specifics of the system's dynamics will play a role for the 'forgetting' time, but the amplitude of the mechanical deformation can be used as well, since it basically dictates how far out of equilibrium the system is. Finally, a topic not addressed here is that of thermodynamic versus kinetic control of the supramolecular assemblies, which relates to the chosen preparation protocol and has significant consequences on their properties. The interested reader is referred to [203-206].

In conclusion, supramolecular polymers based on hydrogenbonding motifs are established as an important class of soft materials with unique and tunable properties and wide-ranging applications, but also with outstanding challenges centered on the effects of slight changes in molecular structure or the environment and their consequences on the macroscopic rheological properties, in particular the nonlinear response.

### 5. Credit author statement

Both authors participated in all aspects of the work from conceptualization to final edits of the text.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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