Preface: Special Issue on Double Dynamics Networks

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Polymeric gels and networks are ubiquitous in daily life (foodstuff and cosmetics) and high-added-value applications (tissue engineering, adhesives, coating, drug release, portable batteries, and additive manufacturing). They can be either permanent (covalently cross-linked) and resistant to flow or physical (reversible) and easy to process while creeping at long times. The grand challenge is to efficiently combine and control within the same material, distinct features of these two classes of networks, such as large mechanical strength, deformability, swelling, and self-healing, in order to create multiply responsive materials for new applications. These last two decades, as discussed in the review by Cui and Gong [1] on the dynamics and fracture mechanisms in double dynamics networks (DDNs), there has been a spectacular development in designing polymer networks and gels with excellent mechanical properties, showing both improved strength and stretchability.

In this Special Issue, the properties of a series of polymer networks and gels containing at least two dynamics (one fast and one slow) are investigated, in order to understand their synergistic effects and enable us to selectively tailor their macroscopic properties at the molecular level. In addition to the different articles, the issue presents the discussions that we had about these works at the final conference of the European Marie Skłodowska-Curie network "DoDyNet" on DDNs [H2020-MSCA-ITN-2017].

DDNs can have many different compositions. They can either be formed by two interpenetrated networks (one fast and one slow), or be a dual network, i.e., a single network containing both fast and slow associations along the chain backbone. The weak physical associations can be of different nature (H bonds, metal-ligand association, phase separation, and ionic interactions), different density, and localized at the extremities or along the chain backbone. The building blocks can be entangled or not. As it is shown through the contributions of this issue, these different characteristics have a large impact on the dynamics, mechanical properties, and final properties of the materials:

First, a very high density of associating groups or stickers along the chain backbone can have a significant impact on the glass transition temperature (T_g). This is discussed in Yang *et al.* [2], who studied the linear viscoelastic properties of double-associative ionomers based on poly(hexyl methacrylate). Increasing the amount of stickers leads to a large increase of T_g, especially if the number of stickers exceeds the number of Kuhn segments. Interestingly, the authors show that the reversible junctions do not have the same delay effect on the glass transition as on the terminal relaxation.

The influence of the stickers on T_g is also discussed in [3] by Yavitt *et al.* The authors have synthesized different structures of entangled amine functionalized polyolefins, characterized by a very high density of functionalized amine branches able to weakly associate via H-bonding. The way the T_g and both the association and the entanglement dynamics are affected by the length and the nature of the backbone is discussed. In particular, the authors show that the collection of many fast-associating groups leads to rapid and very good self-healing properties.

A high density of stickers along a chain also favors intrachain associations, which are further favored if the chains are diluted in a solvent and, therefore, have less interactions. In [4], Parisi *et al.* study this effect by analyzing the intrinsic viscosity and flow curves of aqueous poly(vinyl alcohol) solutions with various degree of hydrolysis. They propose a "sticky-blob" model to explain the delay observed in the terminal relaxation due to the interchains associations. This model should apply to all solutions of associating polymers as long as there are many stickers per correlation blob.

In [5], Nicolella and Seiffert also play with the ratio between interchain and intrachains associations in order to change the network properties of DDNs formed by a tetra-poly(ethylene) glycol functionalized on each arm with two dynamic motifs: a terpyridine capable of undergoing metal-complexation and a thermo-responsive unit consisting of poly(*N*-isopropylacrylamide) (pNIPAAm) capable of undergoing temperature-dependent nanophase-separation. The authors show that by increasing the length of the pNIPAAm chains, interchain associations are promoted, therefore enforcing more networks. On the contrary, shorter pNIPAAm chains favor the collapse of the star chains on themselves.

In the entangled semidilute regime, the size of the correlation blob is also an important parameter as it defined the applicability of the Rouse or Zimm models, as highlighted in [6] by Indei *et al.* In this work, the authors use diffusing-wave spectroscopy to investigate the single chain dynamics of entangled poly(ethylene oxide) in semidilute aqueous solutions by high-frequency microrheology. This technique has the advantage that it can be applied on a larger time window compared to classical shear macrorheology. Based on their results, they propose a simple method to estimate the limit of the Rouse regime.

On the other hand, in the melt state, the relaxation of unentangled sticky chains is well described by the sticky Rouse process. In [7], this process is re-analyzed by Liu *et al.* based on experimental results. The authors show that the effective lifetime of a sticky junctions depends on its surrounding, being trapped or not within the network. They also discuss the importance of considering a random distribution of stickers along the chains. This allows them to develop a

Note: This paper is part of the special issue on Double Dynamics Polymeric Networks

more accurate single-chain model where sticky junctions are allowed to quickly move in space without dissociating.

As a future step, this approach could be extended to unentangled chains containing two types of cross-linkers. Such DDNs are investigated by Xu *et al*. in [8], who examine the linear viscoelastic properties of model supramolecular networks formed by mixtures of two different bis-Pd(II) cross-linkers with poly(4-vinylpyridine) in dimethyl sulfoxide. In this work, the authors highlight the fact that when two types of cross-linkers are blended, their respective relaxation times are still observed; however the faster cross-linkers relax more slowly than when the slow cross-linkers are absent. They attribute this effect to reduced mobility of the polymer strands localized between a fast and a slow cross-linker.

It is interesting to note that not all the DDN containing two types of stickers show a two-step relaxation. This is discussed in [9] by Li *et al*., who study the viscoelastic properties of the entangled telechelic star able to create a network through metal-ligand association. By using simultaneously zinc and copper ions to form, respectively, weak and strong coordination complexes, they obtain a polymer network characterized by a single relaxation time, localized between the relaxation times of the two single networks. The authors attribute this effect to the long relaxation time of the star building blocks, which has to associate and dissociate several times to be fully disentangled, thus leading to an averaging effect of the stickers.

On the contrary, when the same system is deformed under nonlinear shear, the signature of the two types of ions is observed, with the appearance of a double overshoot in the stress growth coefficient. This is discussed in [10] by Pyromali *et al*., who also show that these DDN exhibit stronger mechanical coherence (rate-dependent fractional viscosity overshoot) and accumulate larger strain at steady-state flow compared to single-ion counterparts.

While containing both long and short lifetime stickers, the DDN presented in [7–9] are all flowing at high temperature or long time, which limits their resistance to creep. In order to suppress the creep, the long lifetime stickers should be replaced by either permanent or very stable bonds. Such systems are investigated in [11] by Carillo *et al*., who study the dynamics of industrial pressure sensitive adhesives comprising double networks with an entangled acrylate-based polymer and two types of intermolecular cross-linkers, permanent (epoxide) and reversible (metal-chelate). By comparing the dynamics of the double networks with the respective individual responses of the single networks, the authors quantify the contributions to each relaxation mechanism, with a particular focus on the interplay between disentanglement and bond association/dissociation processes.

A similar system is investigated in [12] by Zhao *et al*., who study the fracture properties of dual cross-link hydrogels, which is made of a small fraction of covalent bonds and a majority of dynamic bonds based on metal coordination bonds and propose a molecular picture to explain their mechanical behavior. In particular, the authors show that despite the fast dynamics of the coordination bonds, the latter largely toughen the gels even if they are deformed at very low stretch rates at which the reversible bonds should behave as if they were "invisible." They explain this observation by the fact that fast exchanging dynamic bonds remain slow compared to the characteristic time of bond scission, thus able to share the load upon covalent bond scission.

Double dynamics also allows delaying the shear-induced debonding of soft solid such as adhesive tapes. As shown by Ju *et al*. in [13], before debonding, local failure takes place within the sample. To observe it, the authors use multiple speckle diffusing wave spectroscopy, a powerful technique to measure spatially and temporally heterogeneous mechanical behavior in soft solids. Based on a mathematical approach, they quantify the highly heterogeneous deformation rate distribution related to shearing and peeling under loading, which reveals an increase in deformation localization hundreds of seconds before full debonding.

Time-resolved microstructural changes are also investigated in [14] by Donley *et al*., based on coarse-grained molecular dynamic simulations. The networks studied are soft particulate gels composed of one or two components. The authors connect the changes in dynamic moduli during large oscillatory shear deformation to the microstructural changes including the nonaffine displacement of particles, and the breakage, formation, and orientation of bonds.

Since DDN containing covalent bonds cannot be reshaped and reprocessed, one can wonder if it is possible to produce pressure sensitive adhesives that can resist flow at high temperatures but without introducing permanent bonds. This question is raised in [15] by Coutouly *et al*., who designed specific polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene triblock copolymers (PS-b-PnBA-b-PS) in order to observe a lower disorder-to-order temperature and thus, induce a microphase separated and ordered state at high temperature. The authors show that these samples do not reach their flow regime even at temperatures well above the glass transition of the PS.

On the contrary, many thermoplastic elastomers lose toughness with increasing temperature. However, as shown by Sbrescia *et al*. in [16], their temperature resistance can be improved by increasing the network connectivity, which depends on the dynamics of hard block association, on chain entanglements and on the number of associating groups per chain. To further understand the interconnected role of molar mass, temperature, and deformation rate on the mechanical properties, the authors perform temperature scanning stress relaxation tests and investigate the high-temperature stress-bearing properties of these samples.

Besides network connectivity, fast relaxation dynamics is also required as it provides good self-repairing ability. In [17], Song *et al*. present a double dynamics hydrogel, which combines connectivity and self-healing properties, thanks to the combination of cross-linking junctions of same nature but with high and low functionality. Based on nitrocatechol coordination to Fe_3O_4 nanoparticles, the high-functionality junctions represent a particularly attractive motif for replacing covalent moieties, as the resulting networks display a measurable relaxation time, while keeping their elastic solidlike properties.

Slow dynamic covalent networks (DCNs) are also an interesting alternative to permanent junctions, as they behave as permanent networks below a specific temperature, while keeping the ability to be reprocessed at higher temperature. In [18], Lyons *et al*. investigate the viscoelastic properties of

DDN formed by a slow dynamic covalent network diluted in a metallosupramolecular network composed of unentangled sticky chains. The authors show that the equilibration dynamics of the DCN are fully governed by the dissociation/reassociation dynamics of the surrounding metallosupramolecular chains. This offers large possibilities to control the creep-recovery and shape memory properties of the DDN.

The possible shape memory properties of DDNs are largely investigated by Tavsanli *et al*. in [19]. The authors study the influence of interconnecting interpenetrated polymer networks (IPN) obtained by *in situ* polymerization of poly(*n*-octadecyl acrylate) in the melt of butyl rubber (IIR) bearing pendant vinyl groups. Significant improvement in the mechanical properties is observed, with complete self-recovery behavior induced by heating. This improvement is due to vinyl groups pendant to IIR backbone increasing the extent of cross-linking between the IPN components.

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