Thermal and viscoelastic properties of entangled supramolecular polymer networks as a powerful tool for prediction of their microstructure

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ABSTRACT

Thermal and viscoelastic properties of entangled supramolecular polymer networks, SPNs, depend strongly on binary and collective assembly of associative groups. The collective assemblies can phase separate from polymer matrix chains and form domains with different sizes and shapes, which have different melting point transitions. By increasing content of associative groups along the polymer chains, their high-order association leads to formation of domains, which have higher melting temperatures than other ones. We prepared a SPN system that contains three networks. All networks have similar precursor polymer backbone, but different content of ureidopyrimidinone, UPy, moiety as strong hydrogen bonding associative group. Thermal and viscoelastic properties of these networks were studied by differential scanning calorimetry and dynamic mechanical thermal analysis measurements. Binary-associated UPy groups phase separate into collective assemblies by π–π stacking. These stacks melt at different temperatures upon heating. The presence of transient assemblies is considerably hinder the relaxation of polymer backbone chains. These domains can be observed in the microstructure of networks by optical microscopy. Thermal and viscoelastic properties of sample with highest content of UPy groups are significantly different from the other networks. This is related to the high-order association of UPy motifs, as can be captured by presence of needle-like domains in its microstructure.

1. Introduction

Supramolecular polymer networks, SPNs, are polymeric structures in which a fragment of covalent bonds are replaced with non-covalent associations [1–6]. These transient bonds like ionic attractions [7–11], metal–ligand coordinations [12–16], hydrogen bondings [17–22] or π–π stacking [23,24], are in a dynamic equilibrium between associated and dissociated status. Therefore, SPNs are responsive to appropriate stimuli and have potential to use for designing electronic, [25,26] optic-electronic [27,28], drug-delivery [29–33], and/or self-healing materials [34–39]. In architecture view, the SPNs are divided in two general types. The first type includes telechelic structures in which the polymeric building blocks have associative groups at both extremities. In the second type, the associative moieties are linked to the polymer backbone as side-pendant groups [40].

Hydrogen bonding groups are broadly used for creation of SPNs. The strength of their association is adjustable through controlling of number and configuration of their hydrogen bond interactions [20,41–43]. One of the promising moieties in designing of hydrogen bonding supramolecular polymers is Ureidopyrimidinone group, UPy.

These groups self-assemble together with high strength quadruple hydrogen bond interactions [44–50]. Low molar mass, liquid-like telechelic oligomers convert to the solid polymers after functionalization with UPy moieties [51–56]. When UPy groups attach to the building block chains by urethane or urea linkages, they are promoted to form π–π stacking due to the lateral-secondary hydrogen bond interactions [55,57–59]. These stacks can form crystalline domains. Therefore, their melting transition can be detected by differential scanning calorimetry, DSC, method [60]. The melting temperature of these stacks depends on different parameters like the hydrophilicity, crystallinity, and the stiffness of the building block units [56,60–64]. In telechelic supramolecular polymers based on low molar mass polycaprolactone, the melting temperature of UPy stacks were measured between 40 °C and 90 °C. We showed that this temperature is much higher, 90–120 °C, for SPNs based on the entangled random copolymer of ethylene and vinyl alcohol than that of reported for low molar mass polycaprolctone [60].

Dynamics of *non*-entangled SPNs have been widely studied in literature [65–72]. Lewis et al. investigated a series of *non*-entangled supramolecular copolymers. They used of different hydrogen bonding groups, which had broad range of dissociation energy among them UPy

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had the highest value of enthalpy. They only found a distinct plateau in rheology data of UPy-functionalized samples, even for copolymers containing 1 mol% of UPy groups. The appearance of this plateau suggests that UPy dimers act like chain entanglement [69]. In an earlier, related work, Feldman et al. studied transient networks based on *non*-entangled copolymers containing UPy side groups. They investigated the effect of molar mass of precursor polymers and their UPy content on dynamics and rheological properties of the networks. In the samples consisting of similar *non*-entangled precursor chains the presence of UPy groups extended the plateau of storage moduli to the lower frequencies and postponed the frequency corresponds to the onset of flow region. Moreover, in supramolecular networks containing more than 5 mol% of UPy groups, the slope of storage modulus, G', as a function of frequency, ω, in the flow region is different from the prediction of Maxwell model (2). This deviation from Maxwell model promoted by addition of UPy content and confirms the complex rheological properties. Nonetheless, in the networks with 4 mol% of UPy groups, the trend of G'-ω curve in the flow region was matched to the Maxwell model. In these networks, increasing of the molar mass of precursor chains influenced only on the values and the frequency range of the plateau modulus [66]. In another related work, Li et al. illustrated that the flow's activation energy of 3D UPy-supramolecular network is close to the activation energy of dissociation of UPy dimer [65].

Since dynamics of SPNs with entangled precursor chains is complex, such networks are less studied in comparison to the *non*-entangled ones. Shabbir et al. investigated a model system of random copolymers of butyl acrylate, nBA, and acrylic acid, AA, as a weak, self-complementary hydrogen bonding group P(nBA-*ran*-AA). The results of rheology experiments on this supramolecular system showed that at frequencies greater than the inverse of reptation time of the precursor chains, hydrogen bonds have very weak influence on their linear viscoelastic response. In more detail, they showed that the values of α and β as scaling exponents of storage and loss moduli, G'-ω^{α} and G''-ω^{β}, shift to *0.5*. Furthermore, supramolecular polymer with highest amount of acrylic acid groups (38 mol%) had a second plateau in its storage modulus curve in low frequencies [73]. This second plateau was attributed to the phase separation of polar acrylic acid domains from *non*-polar poly butyl acrylate polymer chains. Based on these findings and other experimental results, Goldansaz et al. suggested a general concept for microstructure of entangled supramolecular networks containing side-chain sticky moieties. They proposed that a part of binary associations phase separate into collective ones. Therefore, these materials are heterogeneous and their thermal, mechanical, and dynamic properties depends strongly on the size, shape, stability, and life time of these phase-separated domains [74,75].

For entangled SPNs with association times shorter than the reptation time of the precursor chains, Leibler et al. have proposed a model for describing their viscoelastic properties. In this model four regions have been considered for the dependency of relaxation modulus on time: (1) small time-scales lower than the longest Rouse time. In this region the transient bonds are associated and the relaxation of supramolecular polymer is similar to the relaxation of linear *non*-sticky chains, (2) The time-scales between the Rouse time and dissociation time of physical cross-links. In this range, the elastic plateau modulus depends on the number of chain entanglement as well as the number of transient bonds, (3) The time scales greater than that of dissociation of stickers, which belongs again to the rubbery plateau. However, this plateau depends only on the number of entanglement (4) Large time scales, include transition to the terminal flow regime. [76] However, for SPNs in which the value of association time of stickers has the same order of magnitude as the reptation time of the precursor chains, the viscoelastic response, especially in low-frequency region, is more complex. This complexity comes from the parallel association/dissociation of stickers and segmental motions of polymer chains [77]. It is clear that the complicate viscoelastic behavior is promoted when the binary associations phase separate into high-order collective ones. Recently, Hawke et al. have proposed a model for describing viscoelastic properties of such networks. They considered four zones in dynamic moduli-frequency curve: (1) the Rouse motion regime at high frequencies, (2) first plateau zone at middle frequencies, (3) the constraint release Rouse relaxation of segments, which are trapped between two collective assembly domains, and (4) the second plateau zone, which is related to the holding stress by these trap segments [78].

In summary, the thermal and viscoelastic properties of an entangled SPNs depend strongly on the binary and collective assemblies of sticky groups. The dissociation of transient bonds in parallel to the reptation motion of entangled precursor chains, makes complexity in dynamic behavior of such networks. Interestingly, this complexity can be investigated by thermal as well as mechanical-thermal analysis methods such as DSC and temperature/frequency sweep mode of dynamic mechanical thermal analysis, DMTA. In addition, while detecting melting transitions of supramolecular collective assemblies can provide valuable information about microstructure of SPNs, utilizing of this method in studying such materials is rare in literature. We have therefore designed an entangled supramolecular system in which the number of associative groups is systematically varied. We studied thermal and viscoelastic properties of these SPNs focusing on understanding of their microstructure. SPNs based on poly (*n*-butyl acrylate-*ran*-hydroxyl ethyl acrylate), P(BA-*ran*-HEA), with different contents of UPy groups, P(BA-*ran*-HEA-UPy) are prepared and the impact of binary, collective, and high-order associations of UPy moieties on their thermal and viscoelastic properties as well as their microstructure are studied.

2. Experimental

2.1. Materials and synthesis

The details of materials and synthesis were discussed in supporting information.

2.2. Characterization

Synthesis of UPy group, conversion of polymerization reactions, grafting of UPy groups on precursor copolymers were studied by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, using of Bruker Avance 500 MHz spectrometer. All chemical shifts were determined downfield from tetramethylsilane in CDCl$_3$ as deuterated solvent at room temperature. In SPNs, the content of side-UPy groups was calculated through the integral of the ^{1}H NMR signal of the amine protons of the UPy group ($\delta > 10$ ppm) in comparison to the CH$_2$ protons close to the acrylate group in polymer backbone (3.8–4.2 ppm).

The molar mass of precursor copolymers and their polydispersity indices were estimated using a Waters gel permeation chromatography (GPC), Waters 410 refractometer as the detector and Waters WISP 712 auto injector with injection volume of 150 μL using three PLgel 5 μ columns: 102 Å, 103 Å and 104 Å. Relative molar masses were calculated using a calibration curve based on polystyrene standards and the apparent molar masses were determined using Mark-Houwink parameters.

Thermal properties were analyzed by DSC on a Mettler-Toledo apparatus under nitrogen atmosphere using heating rate of 5, 10, and 15 °C/min, and cooling rate of −10 °C/min. For all heating and cooling rates, the experiments were repeated twofold, and the results of the second measurement is presented in this manuscript. Viscoelastic properties were evaluated by temperature sweep and frequency sweep mode of DMTA on a Triton-TTDMA instrument. A rectangular film of each SPN with a size of 20 mm × 2 mm × 2 mm was subjected to a sinusoidal deformation in tension mode. In temperature sweep measurement, samples were heated to 100 °C with the rate of 3 °C/min at 1 Hz constant frequency under nitrogen atmosphere. In frequency sweep experiment, samples were studied between 0.01–600 Hz in a