Stabilization of supramolecular polymer phase at high pressures

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Abstract

We utilize dynamic light scattering (DLS) and passive microrheology to examine the phase behavior of a supramolecular polymer at very high pressures. The monomer, 2,4-bis(2-ethylhexylureido)toluene (EHUT), self-assembles into supramolecular polymeric structures in the non-polar solvent cyclohexane, by means of hydrogen bonding. By varying concentration and temperature at atmospheric pressure, the formation of viscoelastic network (at lower temperatures) and predominantly viscous phases, based on self-assembled tube and filament structures respectively, has been established. The associated changes in the rheological properties have been attributed to a structural thickness transition. Here, we investigate the effects of pressure variation from atmospheric up to 1 kbar, at a given concentration. We construct a temperature-pressure diagram that reveals the predominance of the viscoelastic network phase at high pressures. The transition from viscoelastic network organization of the tubes to a weaker viscous-dominated structure of the filaments is rationalized by using the Clapeyron equation which yields an associated volume change of about 8 Å^3 per EHUT molecule. This change is further explained by means of Molecular Dynamics simulations of the two phases, which show a decrease in the molecular volume at the filament-tube transition, originating from increased intermolecular contacts in the tube with respect to the filament. These findings offer insights into the role of pressure in stabilizing self-assemblies.

Pressure is often considered to be a forgotten thermodynamic variable, in part because pressure-dependent experimentation is far more challenging than its temperature-dependent counterpart. Yet, over the years several investigations of static and dynamic properties of soft materials at high pressures have been reported in the literature. For example, moderate pressures of the order of 100 bar were found to influence the second virial coefficient and radius of gyration of flexible polymers in different solvents.[1] Increasing pressure (up to about 4 kbar) was reported to increase the intrinsic viscosity of polymer solutions, with the Huggins coefficient exhibiting a non-monotonic dependence with a broad minimum.[2] Clearly, pressure affects the miscibility in polymer mixtures, promoting miscibility in LCST polymer solutions[3] and in UCST polymer blends[4] due to volume changes on mixing. More complicated is the effect of pressure on triblock copolymer micelles, where it is found to promote crystal to liquid transition, but often the micellar liquid is topologically interacting.[5] Furthermore, pressure is found to affect the glass transition and associated alpha relaxation (typically increasing the glass temperature) in supercooled liquids[6] and a wide range of shape-persistent polymeric materials with intrinsic orientational order, for which the lack of thermal energy rather than free volume is proposed to be responsible for vitrification [7]. In general, soft materials experience high pressures in a variety of applications or during their transformation, which renders relevant studies necessary. The application of pressure was found to increase the yield stress and strain of polymeric solids undergoing tensile deformation.[8] Additional examples involve processing and capillary flow of polymer melts,[9-14] drilling operations with fracturing fluids,[15] the use of high pressure to obtain protein crystals from spider silk[16] and the high-pressure preparation of dairy products (emulsions).[17]

Despite the above advances, it appears that the role of pressure on the properties of self-assemblies, and in particular their phase behavior, has not received much attention. Recently, pressure was reported to stabilize dynamic supramolecular assemblies of the host-guest type (enhancing their binding equilibria) and maintaining a constant viscosity (in contrast to crosslinked fluids, which may suffer pressure-induced viscosity thinning).[18] That work shows that pressure is an important variable that may affect supramolecular associations and exploiting its consequences is an outstanding challenge. In this letter, we present a methodology to address this challenge by using as archetype a reversible supramolecular polymer built from 2,4-bis(2-ethylhexylureido)toluene (EHUT), based on a bis-urea moiety. Its synthesis, thermodynamic and rheological properties have been discussed quite extensively in the literature.[19-29] In non-polar solvents such as toluene, cyclohexane or dodecane, at high enough concentrations EHUT self-assembles into long supramolecular polymers, which have tube structure at lower temperatures and filament structure at higher temperatures. Their viscoelastic behavior is similar to wormlike surfactant micelles whose rheology depends on the bonding lifetime and overall length .[20,23-30] A similar bis-urea was recently found to exhibit thickening of high-pressure (345 bar) supercritical propane with implications in fracturing fluid processing for enhanced oil recovery operations.[31] Here we investigate the effects of pressure on the thermoreversible supramolecular assemblies of EHUT in cyclohexane..

The synthesis of EHUT was achieved by reacting racemic 2-ethylhexylamine with 2,4-toluene diisocyanate.[20] An apolar solvent, cyclohexane (99.7 % pure) was used as received, obtained from Sigma Aldrich. Its dielectric constant is 2.02.[32] The solutions were prepared under conditions of atmospheric humidity and room temperature, by adding the EHUT powder to the solvent and stirring for at least 48 hours.[27]

A homemade high-pressure cell was coupled to a single scattering DLS setup (from ALV, Germany) for the high-pressure DLS (HP-DLS) experiments (Fig.S1 of the Supporting Information, SI). The pressurized chamber comprises 6 optical windows corresponding to scattering angles of 45, 90 and 130^{o}, and the light beam was focused with a 50x objective lens before reaching the sample, in the middle of the cylindrical cell. Nitrogen was compressed by means of a membrane compressor and entered the cell from the top. Details concerning the cell, windows and sealing are described elsewhere.[33,34] The experiments were performed at pressures ranging from 1 to 1200 bar and temperatures from 20 to 70^{0}C (the latter were controlled by means of a recirculating water/alcohol bath and measured with a thermocouple attached at the surface of the sample cell). Since the pressure-transmitting medium is compressed nitrogen, special care was taken for the measurement time and the selected sample volume in order to avoid diffusion of nitrogen molecules into the measurement pointwhere the laser beam enters the sample. [35] Further details about this as well as the analysis of the autocorrelation function (or intermediate scattering function, ISF) $C(t)$ are provided in the SI.

To better appreciate the difference in dynamics between tube (viscoelastic network) and filament (predominantly viscous) phases, high-pressure microrheology experiments[36,37] were conducted as well, using polymethylmethacrylate (PMMA) particles as tracers[38,39] (see also SI).

Molecular Dynamics (MD) simulations were performed with the Materials Studio (MS) software on a tube and a helical filament of EHUT molecules.[23,40,41] Details are given in the SI. The volumes of conformations generated during the simulations were determined by rolling on the molecules a dummy atom that acts as a spherical probe (Fig. S8). The contact is defined between the Van der Waals radius of the probe and the Van der Waals radii of the atoms (as implemented in the Dreiding force field[42] used to do the MD simulations). The radius of the probe was given different values: 0 Å, 0.8 Å, 1.6 Å (typical of a hydrogen atom), and 2.4 Å. In addition to the tube and helical single filament, a molecule was extracted from the simulated assemblies, and its conformation was used to evaluate its van der Waals and Connolly volumes in the absence of packing with neighbors, i.e., as an isolated molecule. For the three systems, the volumes were calculated on six different conformations and averaged.

The phase diagram of EHUT solutions in cyclohexane is schematically depicted in Fig.1. Depending on concentration and temperature, EHUT solutions may be monomeric or form self-assembled filaments or tubes, under atmospheric pressure, qualitatively similar to the respective behavior in toluene.[22,23,43] Both filament and tube structures are long chains of molecules held together by hydrogen bonds, but the cross-section of the former contains a single EHUT monomer, whereas that of the latter contains three monomers, which leads to a slowing-down of the chain scission process and eventually to viscoelastic behavior. Of interest in this work is the specific concentration c=4 g/L, where a tube-to-filament transition is observed at 49°C. SANS and IR spectroscopy experiments indicate a structural thickness transition at $T \approx 52^0$C, P=1 bar and c=10.4 g/L.[44] Characterization of the tube-filament transition at low pressures is given in Table S1. The effects of pressure will be discussed below. Note that there is no macroscopic signature of phase separation in this solvent, as the samples remain visually transparent. We have also measured the pressure-dependent solvent viscosity (see Fig.S5) and accounted for it, as well as for the respective temperature dependence in the presentation of the experimental data in order to emphasize the net effect of pressure on the supramolecular polymer organization. Indeed, in Fig.2 below the DLS data or dynamic viscoelastic data have been appropriately normalized by the solvent viscosity at the respective pressure and temperature (see in Fig.S6 the effect of pressure on the relative viscosity of a 4g/L EHUT/cyclohexane solution). Moreover, since the thrust of the present investigation is the effects of pressure on the EHUT-based supramolecular polymers, we work in conditions of ambient humidity without considering its effects on the viscoelastic properties of the solutions.[27]

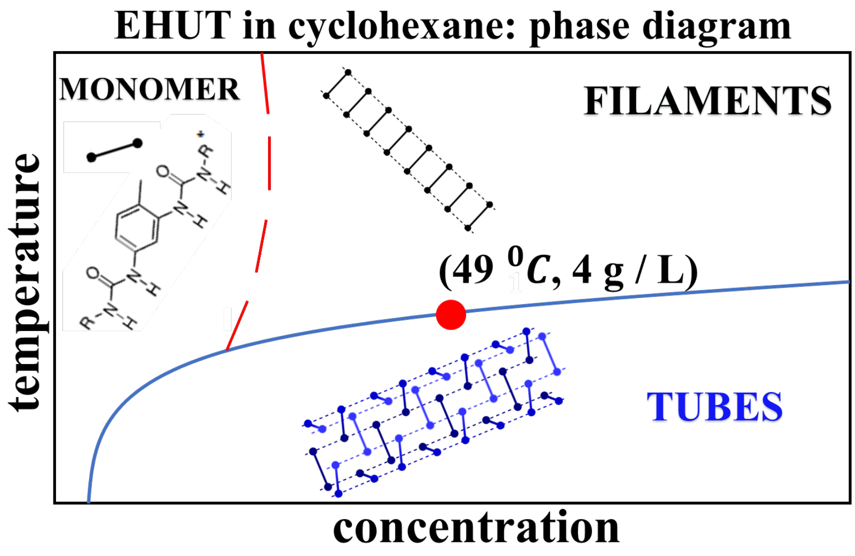

Figure 1: Schematic illustration of the phase diagram for EHUT solutions in cyclohexane at atmospheric pressure. Three regimes are identified: monomeric, self-assembled thin filaments and self-assembled tubes. The cartoons illustrate the molecular structure of the EHUT monomer, and the self-assembled filaments and tubes (the dotted lines illustrate the links (hydrogen bonds) between units which are shown by circles). The red filled circle indicates the observed structural transition from filament to tube for c=4 g/L and T=49 ^{0}C, which is in excellent agreement with the literature[44] (see also Table S1).

First, we investigated the dynamics at atmospheric pressure. As can be seen in Fig.2a, there is a transition from a predominantly unimodal ISF at high temperatures (T ≥ 49^{0}C) to bimodal ISF at low temperatures (T<49^{0}C) with a significant slow mode. A quantitative analysis of the relaxation modes (amplitudes and times) is presented the SI (Figs. S3,S7, Table S2). We attribute the presence of a second, slow relaxation process (readily observed by eye) to the appearance of self-assembled EHUT tubes, which are known to exhibit strong viscoelasticity accompanied by a plateau modulus[26-28] ; entangled polymers have been reported to reveal a clear second slow mode in their ISF, assigned to the relaxation of the entanglement network.[45-48] This distinction is also corroborated by the total scattering intensity as a function of temperature, which is depicted in the inset of Fig.2a upon heating and cooling at 1 bar; the tube-to-filament transition is marked by a change in intensity. Note that in some cases (higher pressure or lower temperature) a weaker third slower mode is detected (Table S2), which reinforces the assignment to tube phase. Consequently, we use the existence of significant slow mode(s) in the ISF as a signature of the formation of tubes, in order to construct a phase diagram, which is depicted in Fig.3. To this end we examine the shape of the ISF of a given EHUT/cyclohexane solution (c=4 g/L) at different temperatures and pressures (see also Fig.S7 and Table S2). For example, the typical ISFs at three temperatures and P=325 bar (Fig.2b) indicate that at 49^0C we have a tube phase while at 58^0C (where the slow mode progressively disappears) we have a filament phase, hence there is a shift of the tube-filament transition from about 49^0C (at atmospheric pressure, Fig.2a) to about 58^0C (at 325 bar). At 600 bar, the supramolecular solution forms only tubes throughout the examined temperature range (Fig.2c). Furthermore, an examination of the microrheological linear viscoelastic spectrum indicates sharp differences between low (1 bar) and high (600 bar) pressures, i.e., filaments and tubes (Fig.2d and Fig.S6). At this particular semidilute concentration of 4 g/L, a loose arrangement of filaments is formed at 49^0C and 1 bar (see also Fig.1 and Ref.27), which exhibits the rheological signature of a viscous liquid (with low viscosity of ~ 3 mPas, see Fig.S6) . However, on increasing the pressure to 600 bar at the same temperature, the viscoelastic spectrum changes drastically, signifying the response of an entangled network of supramolecular tubes[27] (and a slow mode in the ISF). The eventual terminal regime of this network gives rise to a viscosity which exceeds that of the filaments by a factor of about 330 (Fig.S6). We note that both tube and filament solutions were completely transparent without visual hint of phase separation. The interesting finding of Fig.3 is that high pressures appear to stabilize the tubes, which are the only self-assembled structure at this concentration. It is also important to emphasize that the observed tube-filament transitions are reversible and all measurements were performed in equilibrium conditions (very fast kinetics due to the dynamic character of this supramolecular system). Finally, the high-frequency viscoelastic response of tubes and filaments in Fig.2d compares favorably with that of wormlike surfactant micelles and other semiflexible polymeric materials. The latter were reported to exhibit an intermediate and high-frequency power-law dependence of G'' with exponents of 5/9 (Rouse-Zimm) and 3/4 (internal bending modes), respectively, with the transition occurring at the scale of the persistence length.[49,50] The analysis of the high-frequency response is presented in the SI.

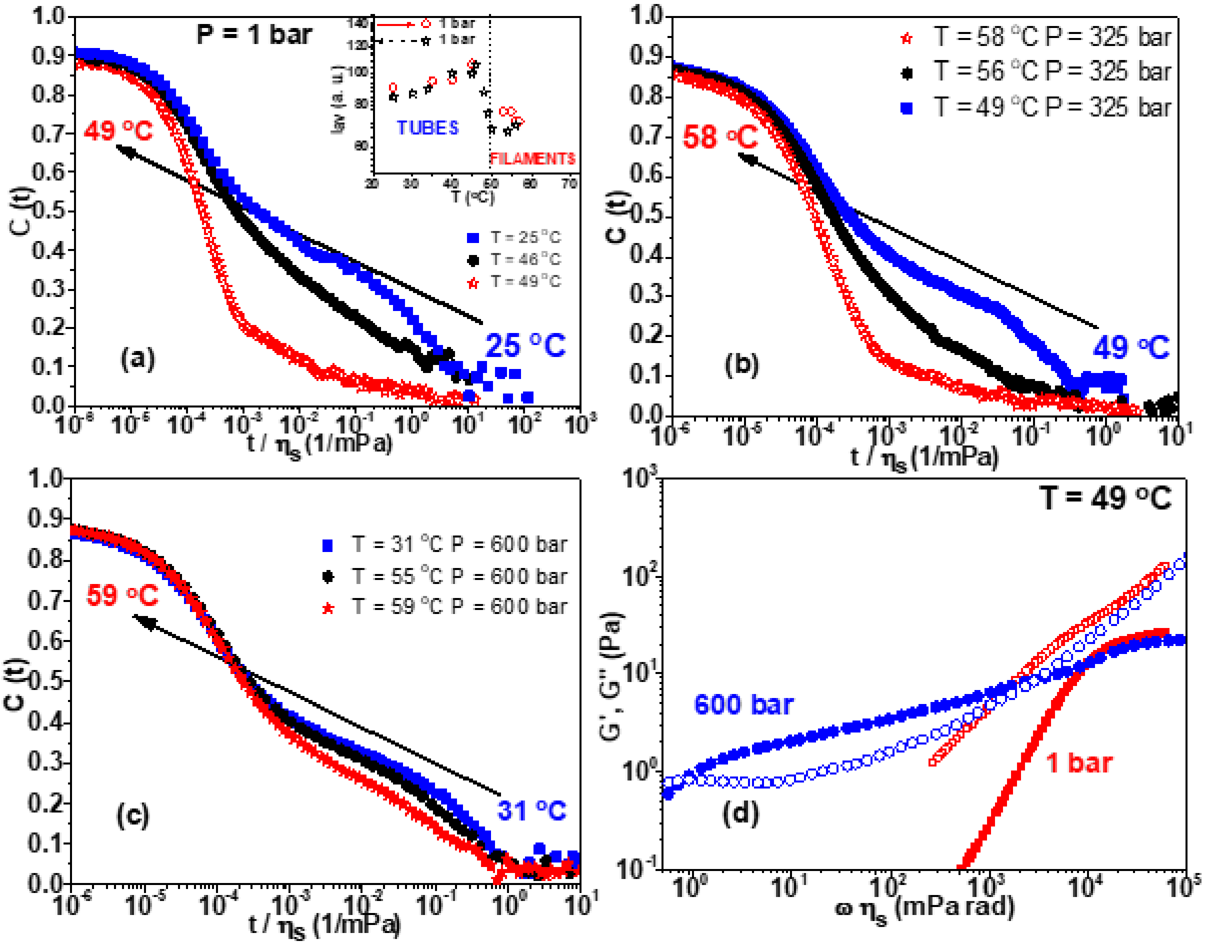

Figure 2: Experimental data of EHUT/cyclohexane solution at 4 g/L, with the time divided by the temperature- or pressure-dependent solvent viscosity (see also SI). (a) Intermediate scattering functions (ISF); the open (filled) symbols correspond to filament (tube) structures. Heating from 25^{0}C (two modes) to 49 ^{0}C (one dominant mode) at 1 bar in the direction of the arrow. Inset: Average total scattering intensity at different temperatures and 1 bar; red data and arrow indicate the direction of heating, whereas black data and dashed arrow the cooling direction. (b) ISF upon heating from 49^{0}C to 58^{o}C at 325 bar (direction of arrow). The former corresponds to tubes and the latter to filaments. The temperature of 56 ^{o}C likely corresponds to a mixture of tubes and filaments with predominance of the former because of the presence of the slow mode (see Table S2). (c) Respective ISF data on heating from 31^{0}C to 59^{0}C at 600 bar (direction of arrow). (d) microrheological viscoelastic spectra at 49^{O}C and two different pressures, 1 bar and 600 bar, corresponding to the limit of filaments (red squares) and tubes (blue circles). Open (filled) symbols refer to loss modulus G'' (storage modules G'). The closeness of the high-frequency data suggests that local processes do not have substantial, if any, dependence on pressure (see Fig.S8). The tube data exhibit typical response of a viscoelastic network and the filament data reflect the behavior of a viscous liquid. The respective data without the scaling of the time are shown in Fig.S7.

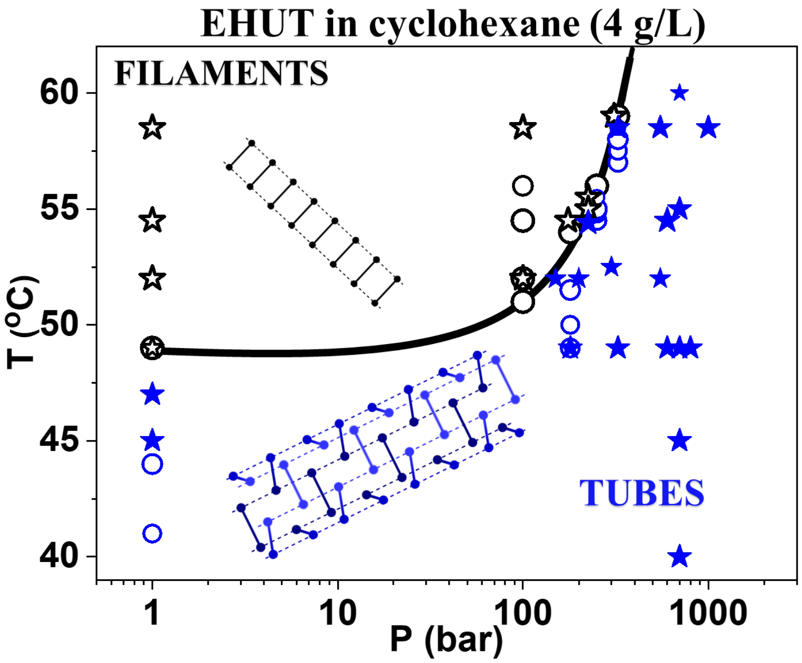

Figure 3. Phase diagram of a 4 g/L EHUT / cyclohexane solution in the (T, P) space. Star symbols correspond to passive microrheological data (see Fig.S3). Circles correspond to DLS (without added particles). The black line is drawn to guide the eye. Blue (black) color indicates tubes (filaments).

In general, the effect of pressure can be accounted for by approximating it as a first order transition and invoking the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T^{*}\Delta V}$$

where T^{*} is the tube-filament transition temperature at reference (atmospheric pressure), ΔH is the latent heat per molecule associated with the tube-to-filament transition and ΔV the associated difference in molecular volumes. The results of Fig.3 suggest that upon increasing the pressure to 300 bars, i.e., $\Delta P \approx 300$ bar, the transition temperature approaches 60°C, i.e., $\Delta T \approx 10K$. This yields $\frac{\Delta H}{\Delta V} \approx 9.7\text{x}10^{8}$ Pa. Note that ΔH is about $1.7k_{B}T$ at low pressures (see Table S1 and Ref.7), and we assume to a first approximation that it has the same dependence on pressure with ΔV. This leads to $\Delta V \approx 8$ Å^{3}/molecule.

In order to rationalize that volume change, MD simulations were carried out on model systems for the filament and the tube (see details in SI), along with calculations on an isolated EHUT molecule as reference. The simulations indicate that the van der Waals volume decreases from the isolated molecule to the filament, as the interactions between the molecules, especially the formation of H bonds, leads to an overlap of the van der Waals volumes (see also Fig.S8). The volume is further reduced when the filament evolves to a tube, on the order of 10 Å^3/molecule, which conforms to the experimental results (Table S3). The volume decrease from filament to tube reflects the increase of contacts between neighbors. In both structures, the hydrogen bonds between urea moieties drive the assembly, but in the filament, the cores interact by π-π stacking and segregate from the alkyl chains that protrude in the environment, while in the tube, the cores and alkyl chains intercalate to form a continuous, dense medium minimizing its exposure to the environment (Fig. 4). .

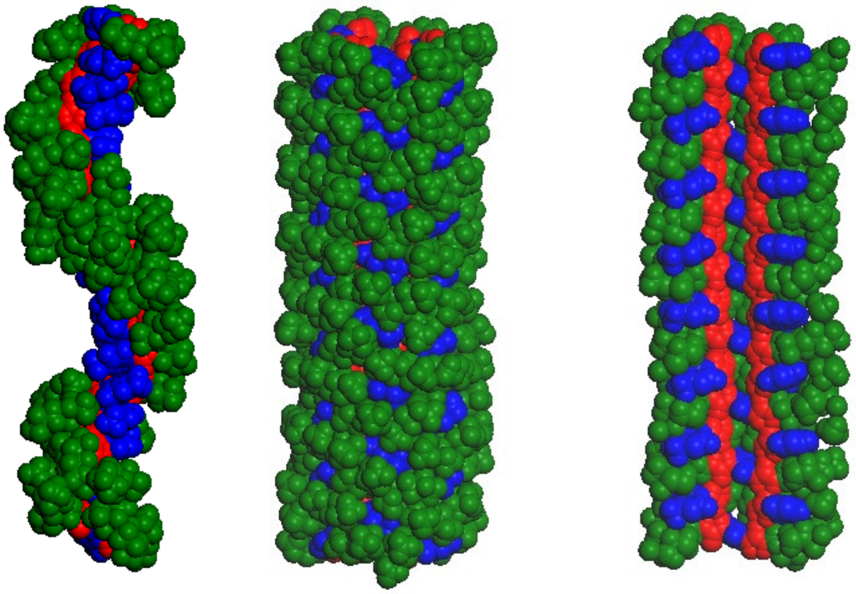

Figure 4. Pieces of filament (left), tube (center), and tube longitudinally cut in two to expose its inner part (right). The assemblies are of the same length (72 Å); the atoms are rendered as spheres having the Van der Waals radius of the elements (CPK representation). The urea moieties are in red, the toluene cores in blue, and the alkyl chains in green.

In this approach, the possible reorganization of the solvent has not been considered explicitly. Nevertheless, we investigated the accessibility of cavities in the EHUT assemblies to solvent molecules, we used probes with different radii and found that an isolated molecule has the smallest Connolly volume, while it has the largest van der Waals volume, when compared to the two assemblies. The larger Connolly volume in the assemblies is explained by the formation of new cavities inaccessible to solvent upon molecular packing. When comparing the Connolly volumes of the filament and tube, the volume changes vary with the probe size, as expected. More importantly, the tubes always appear more compact (i.e., have a higher density) than the filaments (see Table S3 and Fig. S10), again pointing to the higher density of intermolecular contacts in the tubes.

An important question is whether the stabilization of the tube structure at high pressures reflects a kind of host-guest effect, due to more favorable interactions between the tube and the included solvent, or if it is a more general phenomenon. Concerning the former situation, we note that solvent interactions inside and outside the tubes have been found to be different.[51] In the latter case, it should also occur in other hydrogen-bonded assemblies by enhancing bonding at high pressures. Finally, the consequences of pressure-dependent structural changes on the viscoelastic properties of supramolecular assemblies will be addressed in the future.

In summary, high-pressure DLS in the single scattering limit and passive microrheology were employed to construct the PT phase diagram of a supramolecular polymer, EHUT. We found that pressure substantially affects the phase behavior by promoting the tube phase. The tube-to-filament transition is rationalized as a quasi-first order transition and the associated volume change of about Å^3/molecule, can be ascribed to a higher density of intermolecular contacts in the tube, as determined from molecular modeling simulations.

ASSOCIATED CONTENT

Supporting information: I. Experiments : Experimental apparatus and methodology, DLS data and microrheology, Viscosities of solvent and EHUT at two pressure limits corresponding to different phases, Analysis of DLS signals, Analysis of high-frequency loss modulus. II. Simulations

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