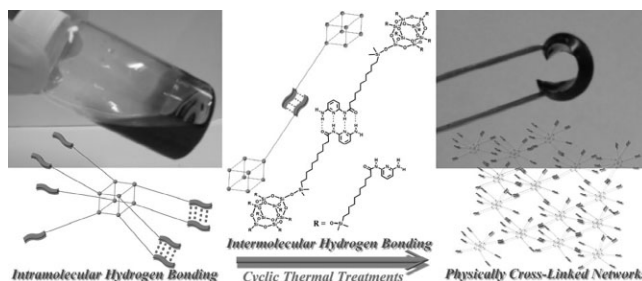


# Self-supporting Polymer from a POSS Derivative<sup>a</sup>

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A new polyhedral oligomeric silsesquioxane macromer, octakis[*N*-(6-aminopyridin-2-yl)-undecanamide-10-dimethyl-siloxy]silsesquioxane (POSS-C11-Py), containing eight diaminopyridine arms, is able to self-assemble to form a physically crosslinked polymer-like structure with good mechanical properties (tensile strength = 46.1 MPa, tensile modulus = 0.58 GPa, elongation = 49.3%) through quadruple hydrogen bonding interactions between these arms. POSS-C11-Py is the first organic/inorganic supermolecule possessing polymer-like mechanical properties as a result of self-complementary interactions, providing a potential route toward the design and fabrication of polymer-like supramolecular materials.



## Introduction

Supramolecular self-assembly has attracted great attention recently through highly complementary molecular recognition events.<sup>[1,2]</sup> For the well-known 2-ureido-4[1*H*]-pyrimidinone (UPy) derivatives,<sup>[3–5]</sup> self-assembly mediated by quadruple hydrogen bonding allows the rapid formation of self-supporting thin films exhibiting unique physical properties, such as high specificity, controlled affinity and reversibility. Nevertheless, only a limited number of reports have appeared so far regarding self-supporting and flexible films.<sup>[6–9]</sup> Several non-covalent polymers formed through complementary molecular groups exhibit characteristic of conventional polymers while feature reversibility in the bonding between macromer units.<sup>[10]</sup> However, controlling the secondary (and higher) structures of non-covalent polymers still remains a challenging task.<sup>[11,12]</sup>

Organic/inorganic hybrid nanocomposites based on polyhedral oligomeric silsesquioxane (POSS) derivatives have attracted considerable interest<sup>[13–15]</sup> because they possess several advantageous features over inorganic or organic compounds as a result of the unique physical property of their cage structure.<sup>[16–20]</sup>

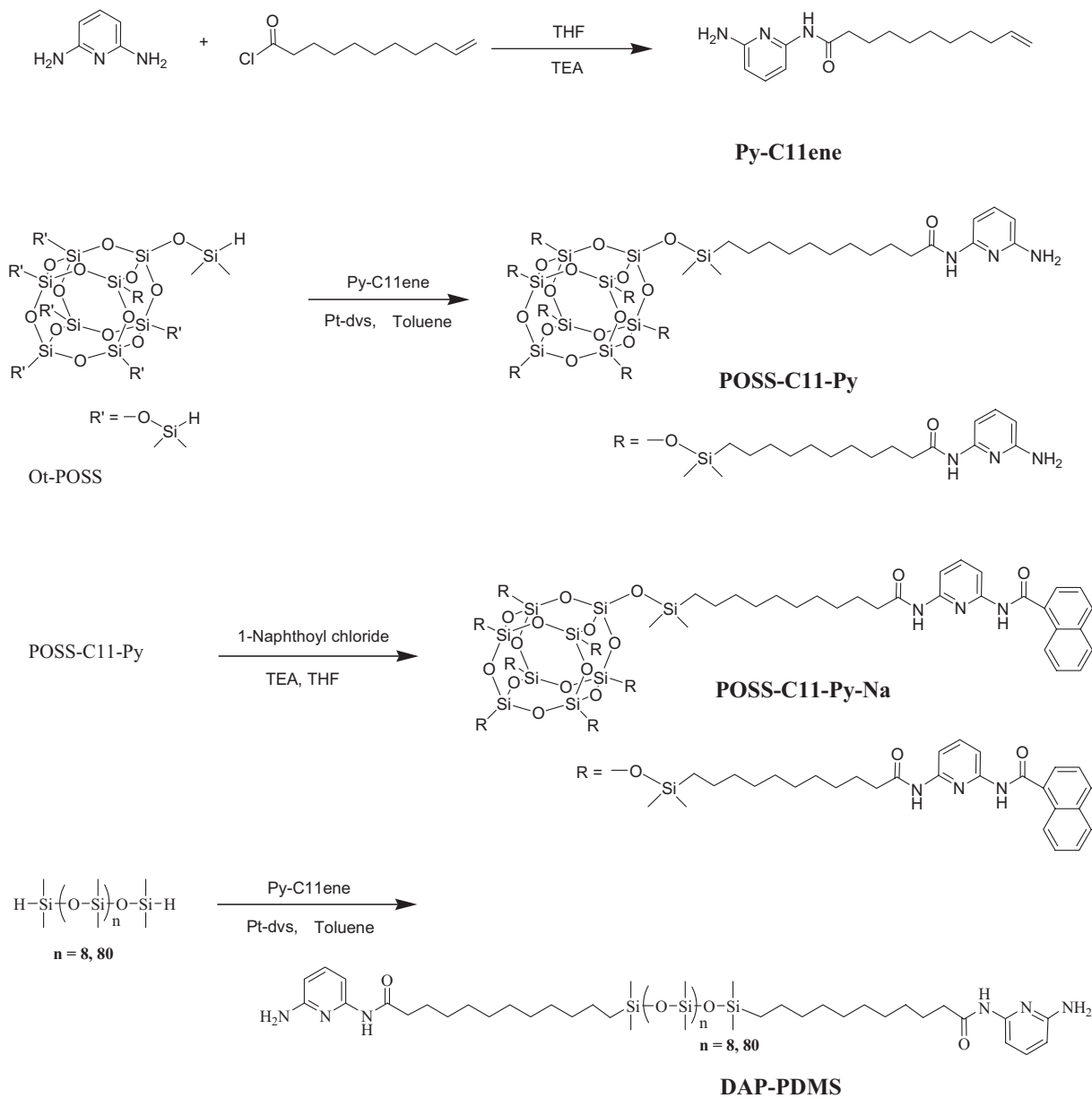
Through appropriate design of the architectures, these POSS derivatives can be tailored for specific applications.<sup>[21–23]</sup> Recently, Rotello et al.<sup>[14]</sup> reported the preparation of a POSS derivative with one diaminopyridine arm which was able to self-assemble through thymine-functionalized monolayers on gold surfaces. Based on previous studies, POSS derivatives having eight multiple hydrogen bonding groups may facilitate the formation of relatively more ordered structures and result in superior properties. In this paper, a POSS-based new star-like supermolecule has been synthesized that possesses enhanced film-forming ability and mechanical properties due to multiple hydrogen bonding interactions.

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## Results and Discussion

Through hydrosilylation (Scheme 1) between octakis-(dimethylsiloxy)silsesquioxane (Ot-POSS) and a diamino-

<sup>a</sup> Supporting Information for this article is available at Wiley Online Library or from the author.



■ Scheme 1. Synthetic procedures used to obtain POSS macromers and related derivatives.

pyridine-functionalized terminal alkene (Py-C11ene),<sup>[10]</sup> the new star-like diaminopyridine-based POSS derivative, POSS-C11-Py, was synthesized. The main challenge in the synthesis of POSS-C11-Py is the purification process. Ultimately, we recovered POSS-C11-Py through chromatography with a high yield (82%) and precisely controlled molecular weight ( $[M + Na]^+ = 3239$ ), consistent with its expected structure.

Figure 1(a) presents DSC thermograms of Py-C11ene and the freshly prepared POSS-C11-Py. The Py-C11ene exhibits a glass transition ( $T_g$ ) at  $-40^\circ\text{C}$  while  $T_g$  from the first heating

curve of POSS-C11-Py is at  $-25^\circ\text{C}$ , an indication that the Py-C11ene units are indeed attached to the POSS cage and result in enhancement in the molecular motion temperature. Of particular note, the second heating scan of POSS-C11-Py gives two  $T_g$ s at  $-4$  and  $+26^\circ\text{C}$ . The third and fourth heating scans result in an identical single  $T_g$  at  $38^\circ\text{C}$ , indicating that a stable and highly complementary hydrogen bonded structure is finally formed. Based on DSC analysis, this POSS-C11-Py possesses an amorphous nature in the bulk state. FT-IR measurements at room temperature after cyclic thermal treatments at  $150^\circ\text{C}$

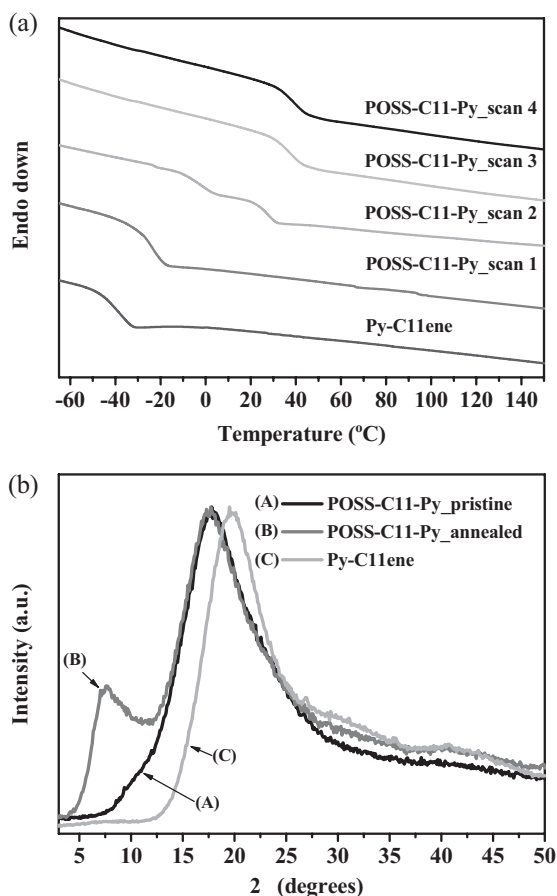


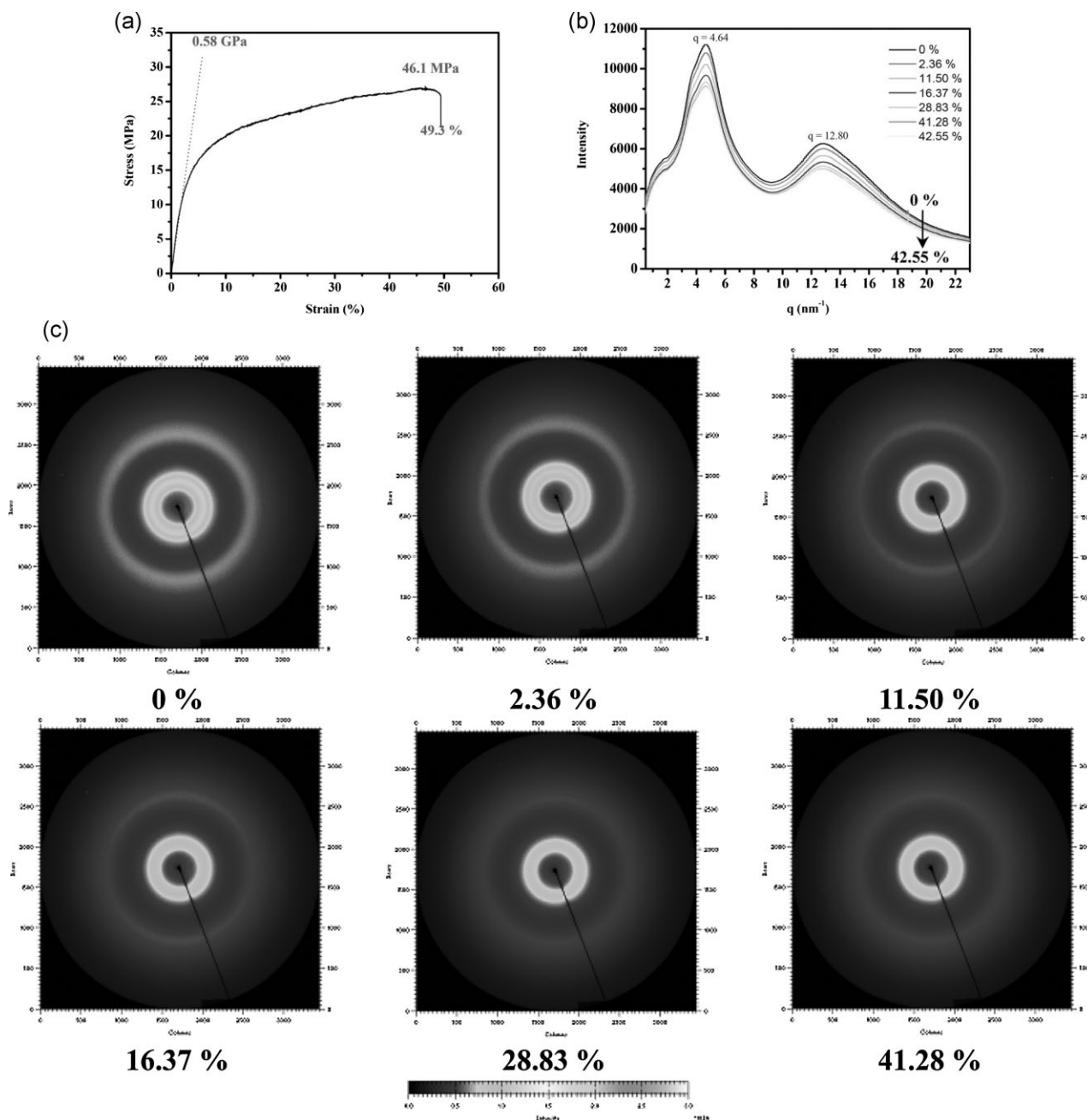
Figure 1. (a) DSC curves and (b) WXR data for POSS-C11-Py and Py-C11ene.

showed that the stretching of the hydrogen bonded N – H ( $3214\text{ cm}^{-1}$ ) and carbonyl groups ( $1678\text{ cm}^{-1}$ ) remained nearly unchanged (see Supporting Information, Figure S4), implying that the overall hydrogen bonding extent did not change through thermal treatments. In other words, thermal treatment induced the transition from the kinetically favorable intra-molecular to thermodynamically favorable intermolecular hydrogen bonding interaction and resulted in an increase in physical crosslinking and higher  $T_g$ .<sup>[24]</sup> Thus, we examined the influence of the chain end group in an attempt to avoid the formation of both intra- and intermolecular hydrogen bonding interactions, and a naphthalene group was introduced to the POSS-C11-Py to form POSS-C11-Py-Naphthalene, as shown in Scheme 1 and the Supporting Information. The DSC analysis showed that  $T_g$ s of the POSS-C11-Py-Naphthalene using similar cyclic heating scans remained constant at  $67^\circ\text{C}$ . This is reasonable because a bulky naphthalene group inhibits the free rotation of the POSS-C11-Py-Naphthalene and leads to an enhanced  $T_g$  value, indicating that the bulky naphthalene groups on the chain ends possess a steric

effect to hinder the formation of the intermolecular hydrogen bonds (Figure S6(b) in the Supporting Information). Therefore, we speculate that the  $T_g$  increase of POSS-C11-Py comes from the increase in the fraction of the intermolecular hydrogen bonding interaction to form greater physical crosslinkage. The change in the hydrogen bonding interaction from the intra-molecular into intermolecular hydrogen bonding upon thermal treatment is the unique property of the POSS-C11-Py.

The flexible POSS-C11-Py film was prepared by casting a DMF solution of POSS-C11-Py onto a smooth glass substrate, air drying and thermal annealing at  $150^\circ\text{C}$ . The resultant film was retained for at least one week at room temperature to make certain the completion of the transition of the hydrogen bonding interaction.  $^{13}\text{C}$  solid-state NMR spectra (Figure S5 in the Supporting Information) suggest that the thermal annealing procedure does not change the chemical structure of the POSS-C11-Py because of its high decomposition temperature ( $T_{d,5\%} = 318^\circ\text{C}$ ). Unlike films prepared as Langmuir-Blodgett films made from low molecular weight compounds,<sup>[25–27]</sup> this POSS-C11-Py film retained its shape without the need for any support, prompting us to further characterize the microstructure and hydrogen bonding interaction of the POSS-C11-Py through wide-angle X-ray diffraction (WXR) analysis. The WXR patterns of both Py-C11ene and POSS-C11-Py (fresh) exhibit broad amorphous halos centered at  $19.7^\circ$  and  $17.8^\circ$ , respectively (Figure 1(b)). Surprisingly, the annealed POSS-C11-Py gives a new peak at a lower angle ( $7.3^\circ$ ), reflecting the formation of the complementary complex on the  $d$ -spacing of the POSS-C11-Py film. In order to compare with POSS-C11-Py, we also synthesized poly(dimethylsiloxane) macromer containing DAP end groups (Scheme 1 and Supporting Information). This difunctional macromer can only form a long chain structure through end-to-end hydrogen bonding without physical crosslinking, therefore, it gives poor mechanical properties and poor film-forming ability (Figure S8 in the Supporting Information). Moreover, the tensile strength of the thermally treated POSS-C11-Py film is determined as  $46.1\text{ MPa}$ , with an elongation at break of  $49.3\%$  (Figure 2(a)). Its tensile strength is higher than some common polymer films, such as polyurethane and polyethylene.<sup>[28]</sup> In addition, the film is stable, flexible, and readily undergoes bending (Scheme 2).

To further understand the tensile strength results, simultaneous wide-angle X-ray scattering (WAXS) and stress-strain measurements were carried out to demonstrate the deformation behavior of the POSS-C11-Py film.<sup>[29,30]</sup> As shown in Figure 2(b), no crystallization was observed during deformation with the incident beam vertical to the film, indicating that the quadruple hydrogen bonding interaction simultaneously suppresses crystallization of the POSS cages and the long alkyl chains of the film under different strains. In addition, the intensity and

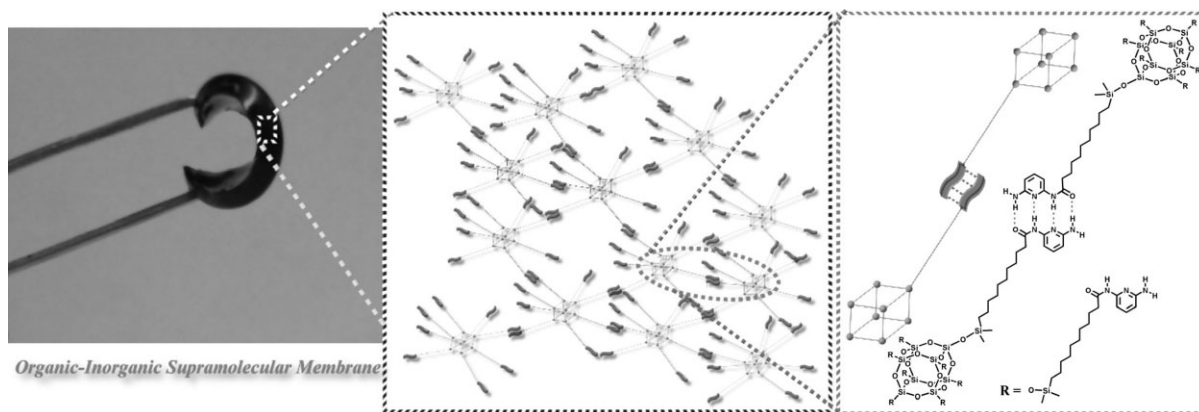


**Figure 2.** Simultaneous WAXS and stress–strain measurements during deformation for POSS-C11-Py film: (a) Stress–strain curve, (b) One-dimensional WAXD profiles and (c) Two-dimensional WAXD patterns along the equatorial direction at different strains.

position of POSS-C11-Py film are slightly decreased, probably due to the dissociation of certain units affecting the deformation behavior. This intriguing behavior led us to investigate the microstructures of this phenomenon in more details through 2D WAXS measurements.

In situ 2D WAXS patterns of POSS-C11-Py film under different strains are shown in Figure 2(c). At initiate state (strain = 0%), the segmental separation between the inter-chain (inner halo) and intra-chain domains (outer halo) is

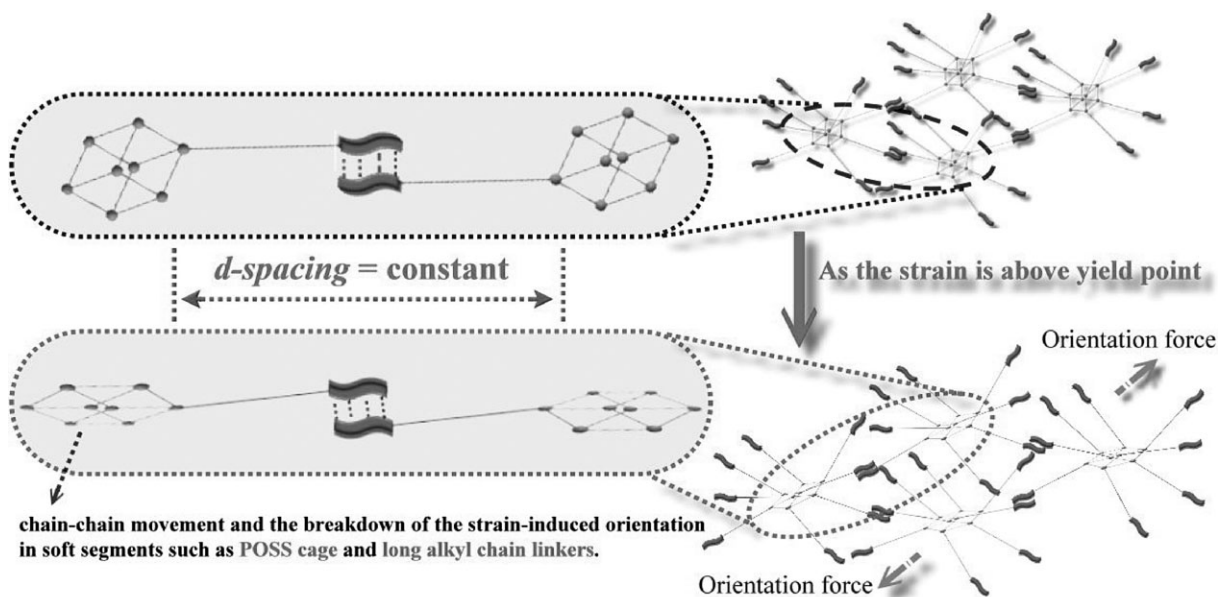
clear, as shown in Figure 2(c). When the strain is below 2.3%, the presence of the quadruple hydrogen bonded interaction aligned network prevents orientation, therefore, the outer halo is preserved and fixed as a result of the protection from these self-interacted multi-diaminopyridine units. In contrast, when the strain is above 2.3%, the outer halo begins to orientate along the stretching direction, which results in an elliptical ring in the pattern, but, however, the shape and intensity of the inner halo remain nearly unchanged, which



■ Scheme 2. Photographic image and graphical representations of the self-supporting film formed from POSS-C11-Py.

is different from conventional cases. The orientation created in the outer halo during the deformation process deforms almost entirely, which is attributed to the rapid orientation of the corner group to the silicon-oxygen skeleton within the POSS moiety,<sup>[31,32]</sup> suggesting that intra-chain deformation is dominated by chain-chain movement and the breakdown of the strain-induced orientation in flexible segments, such as the POSS cage and long alkyl chains. However, when the strain is very large, permanent deformation of the physically crosslinked network would occur. In addition, there may be disassociation of physical crosslinking points and reformation of new crosslinking points during the deformation process. Attenuated total reflection (ATR) FT-IR spectroscopy was also employed to investigate the motion

of these functionalities at different strains (Figure S9 in the Supporting Information). ATR-FT-IR measurements agreed well with the 2D WAXS results. When the POSS-C11-Py film is strained from origin to 42%, the hydrogen bonding interactions formed through the amide and amine groups are not appreciably changed, indicating that they are not dissociated during the deformation process. (the ATR-FT-IR results are described in more detail in the Supporting Information). Consequently, the highly crosslinked structure is restrained due to the intermolecular fixing effect (Scheme 3) from quadruple hydrogen bonding interactions. According to all the above, these POSS-C11-Py films exhibit higher mechanical properties and more stable molecular motion compared to other non-covalent self-supporting supramolecular films.



■ Scheme 3. Graphical representations of the molecular motion of the POSS-C11-Py film during deformation process.

## Conclusion

In summary, we have demonstrated a new POSS-C<sub>11</sub>-Py macromer that exhibits good film-forming and mechanical properties, which have rarely been observed in a non-covalent macromer system. Both  $T_g$  and the mechanical properties of the synthesized macromer increase and eventually level off through thermal annealing or a cyclic heating process. The hydrogen bonding interactions between those diaminopyridine groups from the freshly prepared POSS-C<sub>11</sub>-Py consist mainly of the intramolecular hydrogen bonding interaction with relatively lower physical crosslinkage. During thermal treatment, a portion of those intramolecular interactions transform into thermodynamically more stable intermolecular interactions and form a highly crosslinked structure possessing enhanced  $T_g$  and mechanical properties (tensile strength = 46.1 MPa, tensile modulus = 0.58 GPa, elongation = 49.3%). POSS-C<sub>11</sub>-Py is the first organic/inorganic supermolecule possessing polymer-like mechanical properties as a result of self-complementary interactions, providing a potential route towards the design and fabrication of polymer-like supramolecular materials.

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