# Supramolecular Interfacial Polymerization: A Controllable Method of Fabricating Supramolecular Polymeric Materials

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*Abstract: A new method of supramolecular polymerization at the water–oil interface is developed. As a demonstration, an oil-soluble supramonomer containing two thiol end groups linked by two ureidopyrimidinone units and a water-soluble monomer bearing two maleimide end groups are employed. Supramolecular interfacial polymerization can be implemented by a thiol–maleimide click reaction at the water–chloroform interface to obtain supramolecular polymeric films. The glass transition temperature of such supramolecular polymers can be well-tuned by simply changing the polymerization time and temperature. It is highly anticipated that this work will provide a facile and general approach to realize control over supramolecular polymerization by transferring the preparation of supramolecular polymers from solutions to water–oil interfaces and construct supramolecular materials with well-defined properties.*

Supramolecular polymers refer to polymers in which monomers are held together through highly directional noncovalent interactions, such as hydrogen bonding, host–guest interactions, π–π interactions, and metal coordination.[1–15] Owing to the dynamic nature of the noncovalent interactions, supramolecular polymers exhibit unique properties such as reversibility, stimuli-responsiveness, self-healing, and good processability.[16–30] Over the past decades, significant advances have been made in developing methods of supramolecular polymerization, from spontaneous to controllable and living supramolecular polymerization.[31–38] Furthermore, supramolecular polymers have displayed potential applications in many interdisciplinary fields, such as molecular muscles,[39–41] self-healing materials,[42–44] self-healing organic electronics,[45,46] heterogeneous catalysis,[47] degradable drug nanocarriers,[48] and stimuli-responsive supramolecular gels.[49–51]

Supramolecular polymers are normally prepared in homogenous media, which requires the monomers to be dissolved in the same solvent. It is highly desirable to develop new methods of supramolecular polymerization for immiscible monomers. For instance, when one monomer is water-soluble and the other is oil-soluble, traditional homogenous supramolecular polymerization cannot work. Thus, there exists urgent and wide demand to develop supramolecular interfacial polymerizations (for example, at the water–oil interface) to face this challenge. Considering that the molar ratio of the monomers needs to be strictly controlled in order to fabricate supramolecular polymers with high molecular weight in homogenous media, we can envision that interfacial polymerization could be insensitive to the molar ratio of monomers.[52–54] Therefore, supramolecular interfacial polymerization may provide a new and facile method of fabricating supramolecular polymers with controlled compositions and structures.

Herein we aim to introduce a new and controllable strategy to fabricate supramolecular polymeric materials through supramolecular interfacial polymerization. Inspired by traditional interfacial polymerization, two monomers with opposite solubility are designed to be dissolved in two immiscible solvents. To endow the polymers with supramolecular characteristics, one monomer can be a supramonomer, which is constructed by noncovalent interactions but able to polymerize by conventional methods of polymerization.[55–58] Using the mild and highly efficient click reaction as the polymerization approach,[59] two monomers can be linked together at the water–oil interface, leading to the formation of supramolecular polymers. Compared with conventional method of fabricating supramolecular polymers in solution, supramolecular interfacial polymerization has many advantages, such as easy operation, insensitivity to the molar ratio and concentration of monomers, and feasibility for immiscible monomers, to name a few. Therefore, we anticipate that supramolecular interfacial polymerization may become a powerful method to construct supramolecular materials with well-defined properties.

To this end, as a proof-of-concept, we designed and prepared two types of monomers containing maleimide groups and thiol groups (Scheme 1). The water-soluble monomer (noted as MA-C12) was synthesized and characterized by ^{1}H NMR and ESI-MS. The oil-soluble supramonomer (UPy-SH)$_2$ containing two thiol end groups was formed by the dimerization of ureidopyrimidinone (UPy) units on the basis of quadruple hydrogen bonds. By dissolving MA-C12 in the water phase and (UPy-SH)$_2$ in the chloroform phase, supramolecular polymers could be obtained at the water–oil interface by the thiol–maleimide click reaction. Moreover, it was hoped that the chain structure of supramolecular polymers could be tuned by changing the interfacial reaction conditions.

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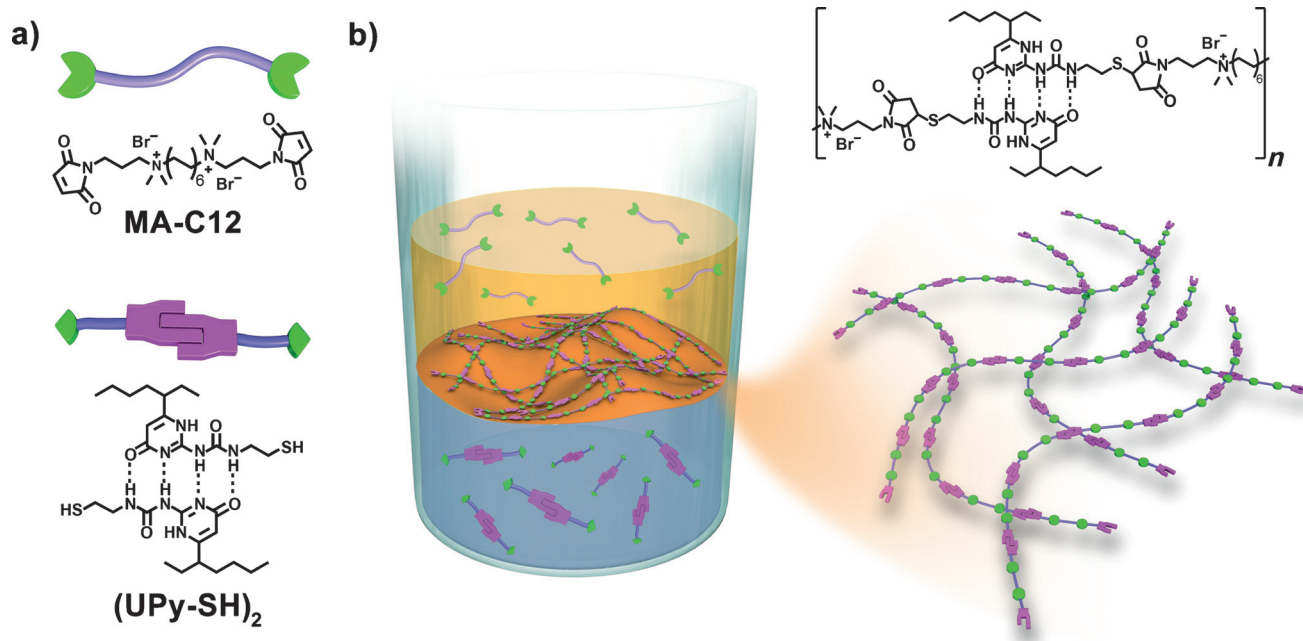
***Scheme 1.*** a) Chemical structures of the designed water-soluble monomer MA-C12 and oil-soluble supramonomer (UPy-SH)₂; b) a diagram of supramolecular interfacial polymerization at the water–oil interface.

To confirm the formation of supramonomers, ^{1}H NMR and ESI-MS were performed. As indicated by ^{1}H NMR, the NH signals of UPy showed a downfield shift (between 10.0 and 13.5 ppm), suggesting the formation of quadruple hydrogen-bonded supramonomers (Supporting Information, Figure S3). The ESI-MS showed molecular ion peaks with mass-to-charge ratios of 625.34 [(UPy-SH)₂ + H]⁺ and 647.32 [(UPy-SH)₂ + Na]⁺, which are in good accordance with the calculated molecular weights of supramonomers with one positive charge. All of the above results prove that owing to the strong quadruple hydrogen-bonding interaction between UPy units, the supramonomers with well-defined composition and structure can be successfully constructed in the chloroform phase. Moreover, the supramonomers are stable at the temperature of 60.0 °C (Supporting Information, Figure S6), exhibiting good thermal stability for further supramolecular interfacial polymerization.

We explored whether the thiol–maleimide reaction could occur at the water–oil interface. In a typical experiment of the supramolecular interfacial polymerization, an aqueous solution of MA-C12 (0.20 mol L⁻¹, 0.60 mL) was carefully added onto the surface of a solution of the supramonomer (UPy-SH)₂ in CHCl₃ (0.20 mol L⁻¹, 0.60 mL). A brown-colored film formed at the water–oil interface within one minute (Supporting Information, Figure S5). The brown film was free standing, which was removed for characterization by ^{1}H NMR and ESI-MS. As shown in Figure 1, the disappearance of the maleimide proton peak ($\delta = 7.1$ ppm) and the almost disappearance of the thiol proton peak ($\delta = 2.4$ ppm), and the appearance of a new peak ($\delta = 4.1$ ppm) belonging to the addition product of thiol and maleimide indicated that the two monomers underwent the click reaction at the interface of the two phases. Moreover, from the ESI-MS, a molecular ion peak with a mass-to-charge ratio of 579.37 was detected,

which agrees well with the calculated molecular weight of the product of thiol–maleimide reaction with two positive charges. Therefore, linear supramolecular polymers are formed by the thiol–maleimide click reaction at the interface.

We have relied on FTIR spectra and solid-state ^{1}H NMR to confirm that the quadruple hydrogen bonds exist in the solid films. The existence of N–H stretching vibration around 3222 and 3125 cm⁻¹ (Supporting Information, Figure S8) in the FTIR spectra suggested the formation of self-complementary hydrogen bonds. Moreover, direct evidence for the presence of quadruple hydrogen bonds in the solid films was provided by solid-state ^{1}H NMR. As shown in Figure 2, a high-resolution solid-state ^{1}H NMR spectrum was obtained with the aid of magic-angle spinning (MAS) and the high
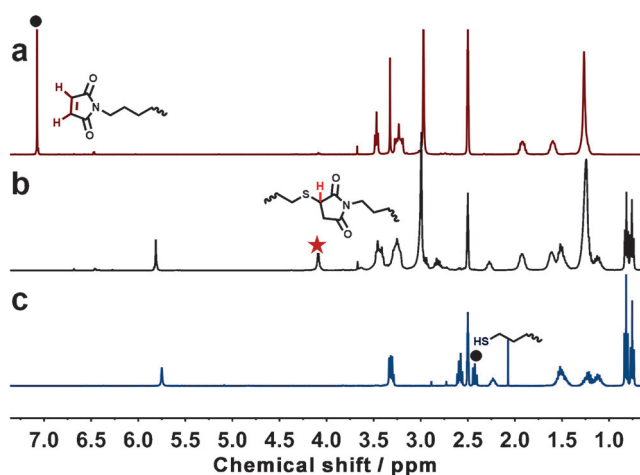


***Figure 1.*** ^{1}H NMR spectra (400 MHz, [D₆]DMSO) of a) the water-soluble monomer MA-C12, b) the product at the water–oil interface, and c) the oil-soluble monomer UPy-SH.
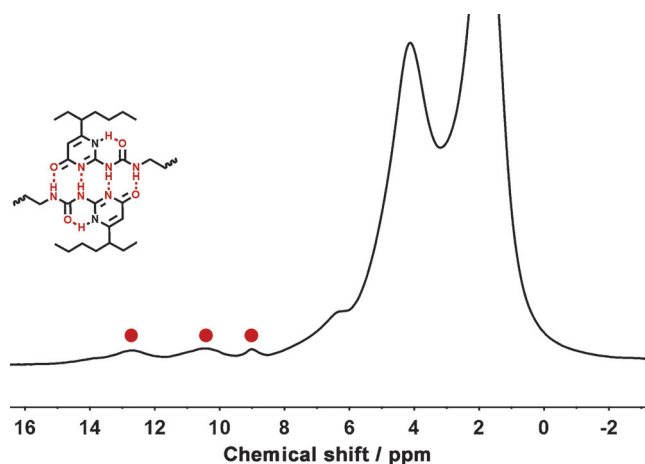
**Figure 2.** Solid-state $^1H$ NMR spectrum of the solid films (600 MHz, spinning frequency of 60 kHz).



**Figure 3.** DSC curves and $T_g$ of the supramolecular polymers prepared with different reaction times while keeping the reaction temperature of 8°C.

spinning frequency of 60 kHz on a 600 MHz spectrometer. The three characteristic amide proton peaks in the downfield region (between 9.0 and 13.0 ppm) were clearly differentiated from the aromatic and aliphatic protons due to the high spinning frequency. The downfield shifts of the amide protons indicated the existence of quadruple hydrogen bonds in the solid state. These results confirm that the solid films formed at the water–oil interface are supramolecular polymers whose building blocks are connected by the quadruple hydrogen bonds of UPy units.

The degree of polymerization of the obtained supramolecular polymer was estimated by end-group analysis measured by $^1H$ NMR. The degree of polymerization of the solid supramolecular polymer was estimated to be 52, corresponding to the molecular weight of 68 kDa. This result confirms that supramolecular polymers with high molecular weight can be successfully fabricated by supramolecular interfacial polymerization.

To study the properties of the supramolecular polymers, X-ray diffraction (XRD) and thermogravimetic analysis (TGA) were conducted. As shown in the Supporting Information, Figure S11, the diffraction pattern of a solid supramolecular polymer sample displayed diffuse diffraction without any sharp Bragg peaks, indicating that the as-prepared films were amorphous polymers. From the TGA curves (Supporting Information, Figure S12), the thermal decomposition temperature at 5% weight loss of the supramolecular polymer was 238°C; above this temperature the decomposition rapidly accelerated. In contrast, the thermal decomposition temperatures at 5% weight loss of the two monomers were 206°C and 293°C, respectively. Therefore, the supramolecular polymers are amorphous polymers with good thermal stability.

To understand whether the chain structure of the supramolecular polymers could be modulated through supramolecular interfacial polymerization, the glass transition temperature ($T_g$) of the supramolecular polymers prepared under different conditions was determined by differential scanning calorimetry (DSC). As shown in Figure 3, at the reaction temperature of 8°C, increasing the reaction time from 10 min
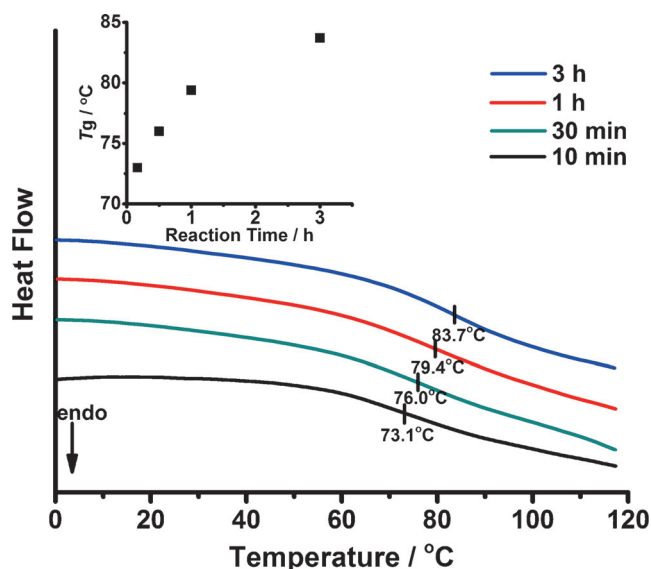
to 1.0 h, the $T_g$ of the supramolecular polymers increased from 73.1°C to 79.4°C. This could be due to the elongation of the supramolecular polymer chains with the extension of polymerization time. It is noteworthy that when the interfacial reaction was further prolonged to 3.0 h, the $T_g$ of the supramolecular polymers slightly increased from 79.4°C to 83.7°C, suggesting that the increase of supramolecular polymer chain became slow when the reaction time was longer than 1.0 h. This result indicates that the $T_g$ of the supramolecular polymers can be well-modulated by tuning the reaction time of the supramolecular interfacial polymerization.
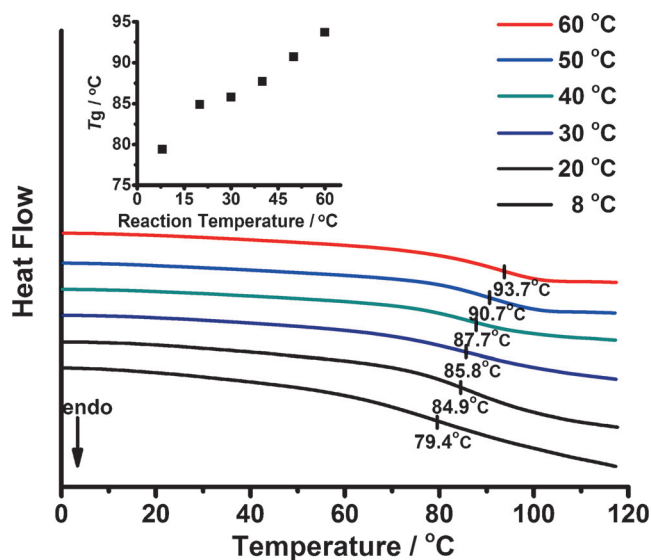


**Figure 4.** DSC curves and $T_g$ of the supramolecular polymers prepared at different reaction temperatures while keeping the reaction time at 1.0 h.

We also wondered whether the $T_g$ of the supramolecular polymers could be controlled through tuning the reaction temperature. To answer this question, the supramolecular polymers were prepared at different temperatures. As shown in Figure 4, the $T_g$ of the supramolecular polymers increased from 79.4°C to 93.7°C when increasing the reaction temperature from 8°C to 60°C while keeping the same reaction time of 1.0 h. It seems as if the higher temperature accelerates the interfacial reaction rate, thus leading to the formation of supramolecular polymers with longer chains. We can therefore conclude that the $T_g$ of the supramolecular polymers fabricated by supramolecular interfacial polymerization can be well-controlled by simply changing the reaction time and temperature.

An additional advantage of this method for fabricating supramolecular polymers is that the supramolecular polymeric films could be formed at the water–oil interface with different concentrations of MA-C12 (for example, $0.05 \, mol \, L^{-1}$ to $0.40 \, mol \, L^{-1}$) and (UPy-SH)$_2$ ($0.05 \, mol \, L^{-1}$ to $0.40 \, mol \, L^{-1}$). Furthermore, the supramolecular polymeric films could be successfully fabricated with the molar ratios of MA-C12 and (UPy-SH)$_2$ from 8:1 to 1:8, suggesting the molar ratios of monomers need not to be strictly equal in the supramolecular interfacial polymerization. Moreover, the supramolecular polymeric films can be depolymerized by destroying the quadruple hydrogen bonds in DMSO.

In conclusion, we have demonstrated that supramolecular interfacial polymerization is a facile and controllable method for fabricating supramolecular polymers. Supramolecular interfacial polymerization was here employed to fabricate supramolecular polymers through thiol–maleimide click reaction; many other mild and highly efficient reactions are expected to be applicable to this approach. By marrying supramolecular polymer chemistry to conventional interfacial polymerization, this line of research enriches the method of supramolecular polymerization to polymerize immiscible monomers in a controlled manner. It is anticipated that this facile strategy could be utilized in fabricating supramolecular materials with controllable properties, structures, and functions.

### Acknowledgements

### Conflict of interest

The authors declare no conflict of interest.

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