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Influence of the Hydroxy Functional Group on the Mechanical Strength of Amino Acid Based C_3-Symmetic Gelators

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ABSTRACT

Supramolecular gels are an important class of soft materials with intriguing potential applications and tunable properties. The self-assembly process of the gelators depends on the dynamic nature of the non–covalent interactions and the spatial orientation of the functional groups. Introducing additional functional groups will enable us to evaluate the role of specific interactions in the self-assembly process, which will help to design supramolecular gels with tunable properties. In this work, we are analyzing the role of hydroxyl functional groups on the self-assembly process of C_3-symmetic gelators based on trimesic amides. To achieve this task, we have synthesized the trimesic amide of amino acid derivative of the methyl ester of tyrosine benzene-1,3,5-tricarbonyl tyrosine (TTA) and compared the properties with a known chiral gelator (benzene-1,3,5-tricarbonyl phenylalanine (TPA), which do not have hydroxyl groups. We are evaluating the role of additional hydrogen bonding group in the self-assembly process and the mechanical strength of the supramolecular gels.

INTRODUCTION

Supramolecular gels based on low molecular weight gelators (LMWGs)[1] have witnessed tremendous growth over the last decade due to their emerging potential applications, such as dynamic gels, biological applications using gels as cell growth media, and also as a medium to control crystal growth, drug delivery, etc. The self-assembly process of the gelators depends on the dynamic nature of the non–covalent interactions and the spatial orientation of the functional groups. Introducing additional functional groups will enable us to evaluate the role of specific interactions in the self-assembly process, which will help to design supramolecular gels with tunable properties. Prof. Damodaran´s group developed a new strategy to develop supramolecular gels with tunable properties[2-3] by modifying the functional groups, which can alter specific interactions leading to gelation. The role of additional hydrogen bonding moieties, such as hydroxyl groups on the self-assembly process, has not been reported. In this work, we are analyzing the role of hydroxyl functional groups on the self-assembly process of C_3-symmetic gelators based on trimesic amides. We are evaluating the role of additional hydrogen bonding group in the self-assembly process and the mechanical strength of the supramolecular gels.

SYNTHESIS AND GELATION

We have synthesized the trimesic amide of amino acid derivative of the methyl ester of tyrosine benzene-1,3,5-tricarbonyl tyrosine (TTA) and compared the properties with a known chiral gelator (benzene-1,3,5-tricarbonyl phenylalanine (TPA), which do not have hydroxyl groups[4] by reacting the corresponding methyl ester of amino acid hydrochloride with benzene-1,3,5-tricarbonyl trichloride in dichloromethane (See **Fig. 1**).

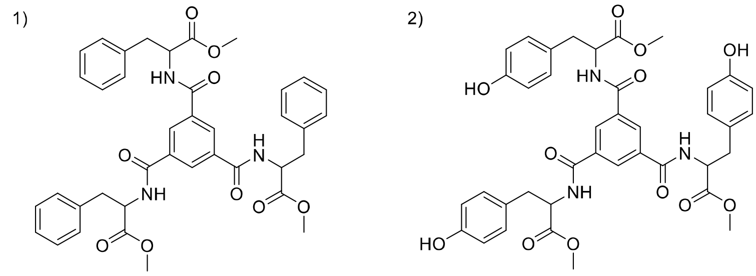

FIGURE 1: Structures of (1) TPA and (2) TTA

TPA was a versatile gelator, and gelled in a series of solvents, but TTA could form a gel in only DMF/H_2O (1:1 v/v) at an MGC of 4.5 wt/v% (See **Table 1 and Fig. 2**).

TABLE 1. MGC studies on *SSS*- and *RRR*- TTA and TPA (wt/v%)

		DMF/H_2O		DMSO/H_2O	*p*-xylene
		TTA	TPA	TPA	TPA
MGC	*SSS*	4.5	1.4	0.7	1.0
	RRR	4.5	1.4	0.7	1.0

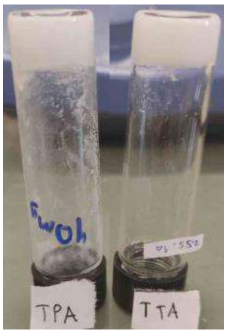

FIGURE 2: Photos of the gels of TPA (left) and TTA (right)

The TTA gels showed lower thermal strength than TPA gels (See **Table 2**). Scanning electron microscopy (SEM) was used to analyse the morphologies of the gels.

TABLE 2. *Tgel* analysis at 6.5 wt/v%. *= 3.0 wt/v%.

		DMF/H_2O		DMSO/H_2O	*p*-xylene
		TTA	TPA	TPA	TPA
T_{gel}	*SSS*	58.3	70.1	102.7*	109.1*
	RRR	60.8	68.4	105.5*	109.4*

CHARACTERISATIONS

The mechanical strength of these gels was analyzed by rheology. Two different methods of rheology were compared. The methods are as follows:

1. Syringe method: The tip of a syringe was cut off. A heated solution, containing the gelator at 6.5 wt% and 1:1 v/v DMF/water, was then poured into the syringe body, and the resulting gel was left to age overnight. The resulting gel was pressed out of the syringe onto the rheometer. Rheology of the gel was then measured.
2. Vial method: The gelator at 6.5 wt% in1:1 v/v DMF/water was heated to get a clear solution and cooled to room temperature, and the resulting gel was left to age overnight. The resulting gel was scooped out onto the rheometer using a spoon. Rheology of the gel was then measured.

The resulting amplitude sweeps showed that method 2 did damage the gel (See **Fig. 4a**), so the syringe method was used for further measurements. The TPA gel was found to be mechanically stronger than the TTA gel, presumably due to the enhanced solubility arising from the additional hydroxyl group (See **Fig. 4b**).

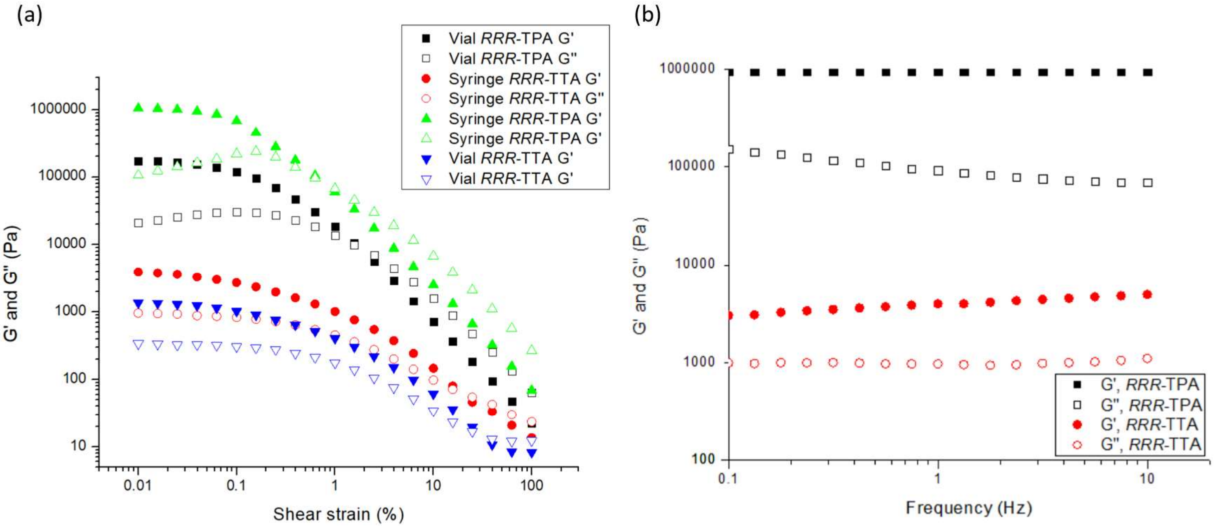

FIGURE 4: Rheological experiments with *RRR*-TTA and TPA (6.5 wt/v%); (a) amplitude sweep at a constant frequency of 1.0 Hz using the vial and syringe methods, (b) frequency sweep at a constant strain of 0.02%.

CONCLUSION

We have successfully synthesized and studied the gelation properties of the enantiomeric forms of TTA and TPA. SEM displayed that while the morphology of TPA displayed thicker fibers of diameter around 4.5 µm, the morphology of TTA revealed thinner fibers of diameter around 0.2 µm. Stability of the gels was analyzed, which revealed that the *RRR*-TPA gel was both thermally and mechanically stronger than the *RRR*-TTA gel. Currently, we are conducting anion sensing experiments on both TTA and TPA.

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