

Supporting Information

Unraveling the Gallol-Driven Assembly Mechanism of Thermoreversible Supramolecular Hydrogels Inspired by Ascidians

Alexis Wolfel^a, Esteban M. Euti^a, Matías L. Picchio^{a,b}, Marcelo R. Romero^{a*},
Victor M. Galván Josa^c, Marisa Martinelli^a, Roque J. Minari^{d,e}, Cecilia I.
Alvarez Igarzabal^a*

^a Departamento de Química Orgánica, Facultad de Ciencias Químicas (Universidad Nacional de Córdoba), IPQA-CONICET, Haya de la Torre y Medina Allende, Ciudad Universitaria, Córdoba X5000 HUA, Argentina.

^b Facultad Regional Villa María (Universidad Tecnológica Nacional), Av. Universidad 450, Villa María 5900, Argentina.

^c Instituto de Física Enrique Gaviola, Facultad de Matemática, Astronomía y Física, CONICET, Medina Allende s/n, Córdoba 5000, Argentina.

^d Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), CONICET, Güemes 3450, Santa Fe 3000, Argentina.

^e Facultad de Ingeniería Química (Universidad Nacional del Litoral), Santiago del Estero 2829, Santa Fe 3000, Argentina.

Corresponding authors:

Prof. Dr. Matías L. Picchio (E-mail: mlpicchio@santafe-conicet.gov.ar)

Prof. Dr. Marcelo R. Romero (E-mail: marceloricardoromero@gmail.com)

Video S1 shows the effect of PVA degree of hydrolysis on the gelation kinetic of the supramolecular hydrogels. PVA₈₈-GA₅ solution (acetylated polymer) became a soft gel after 5 h at room temperature, while PVA₉₈-GA₅ solution (hydrolyzed polymer) solidified in 10 min at this temperature.

Video S2 shows the ability of the supramolecular hydrogels for reversibly transitioning from gel to sol states.

Video S3 shows the influence of polymer molecular weight (M_w) on the gelation kinetic of the supramolecular hydrogels. For fully hydrolyzed polymers, when M_w changed from 145 (PVA₉₈) to 85 kDa (PVA₉₉), the gelation rate varied from 10 to 4 min.

Video S4 shows the effect of GA concentration on the gelling rate of the supramolecular materials, which varied from 10 min to more than 24 h at room temperature, for 5 and 0.5% of GA, respectively.

Video S5 shows the injectability of PVA₉₈-GA₅ gelling solution, which allows writing the word “GEL”.

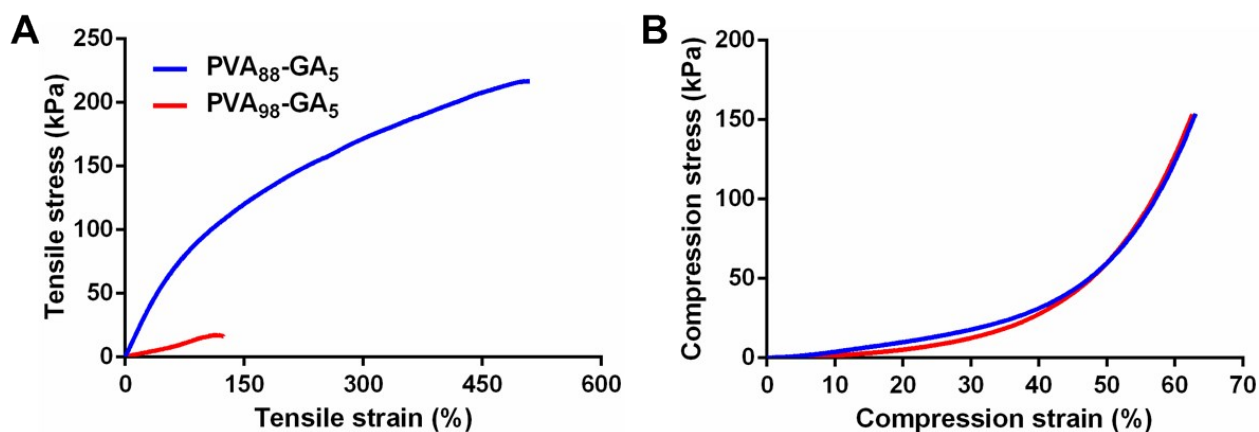


Figure S1. A) Mechanical behavior of PVA₈₈-GA₅ and PVA₉₈-GA₅ under extension (A) and compression (B) assays.

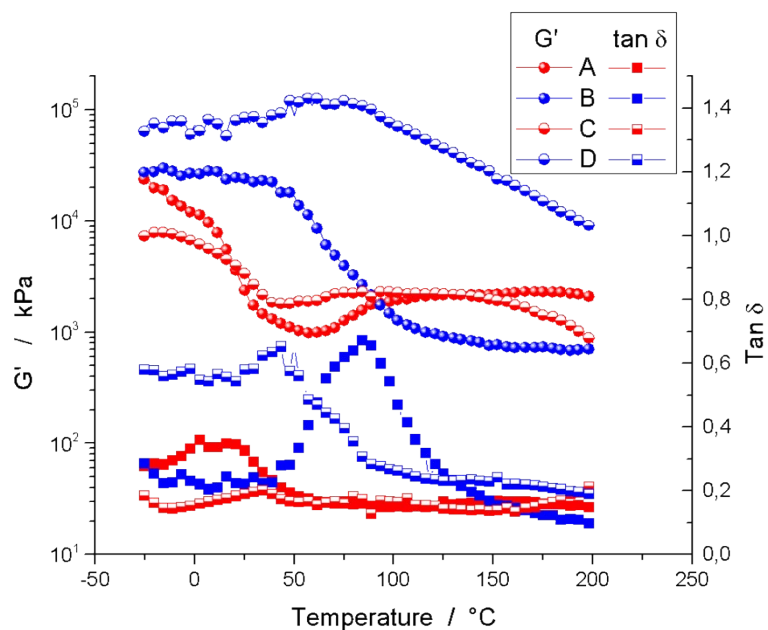


Figure S2. DMTA study of A) PVA₉₈, B) PVA₉₈-GA₅, C) PVA₈₈ and D) PVA₈₈-GA₅.

Figure S2 shows thermomechanical tests of pristine PVA's and PVA-GA supramolecular materials. As it can be observed, PVA₈₈ showed a glass transition temperature (T_g), as the maximum in $\tan \delta$, at around 20 °C. In contrast, PVA₉₈ reached its T_g at 40 °C. On the other hand, samples of PVA-GA presented notable shifting in their T_g with respect to the pure polymers, showing transitions at 40 and 80 °C for PVA₈₈-GA₅ and PVA₉₈-GA₅, respectively. The higher transition temperature in PVA₉₈-GA₅ indicates stronger interactions and in a greater extent than for the acetylated polymer/GA system.

A)

B)

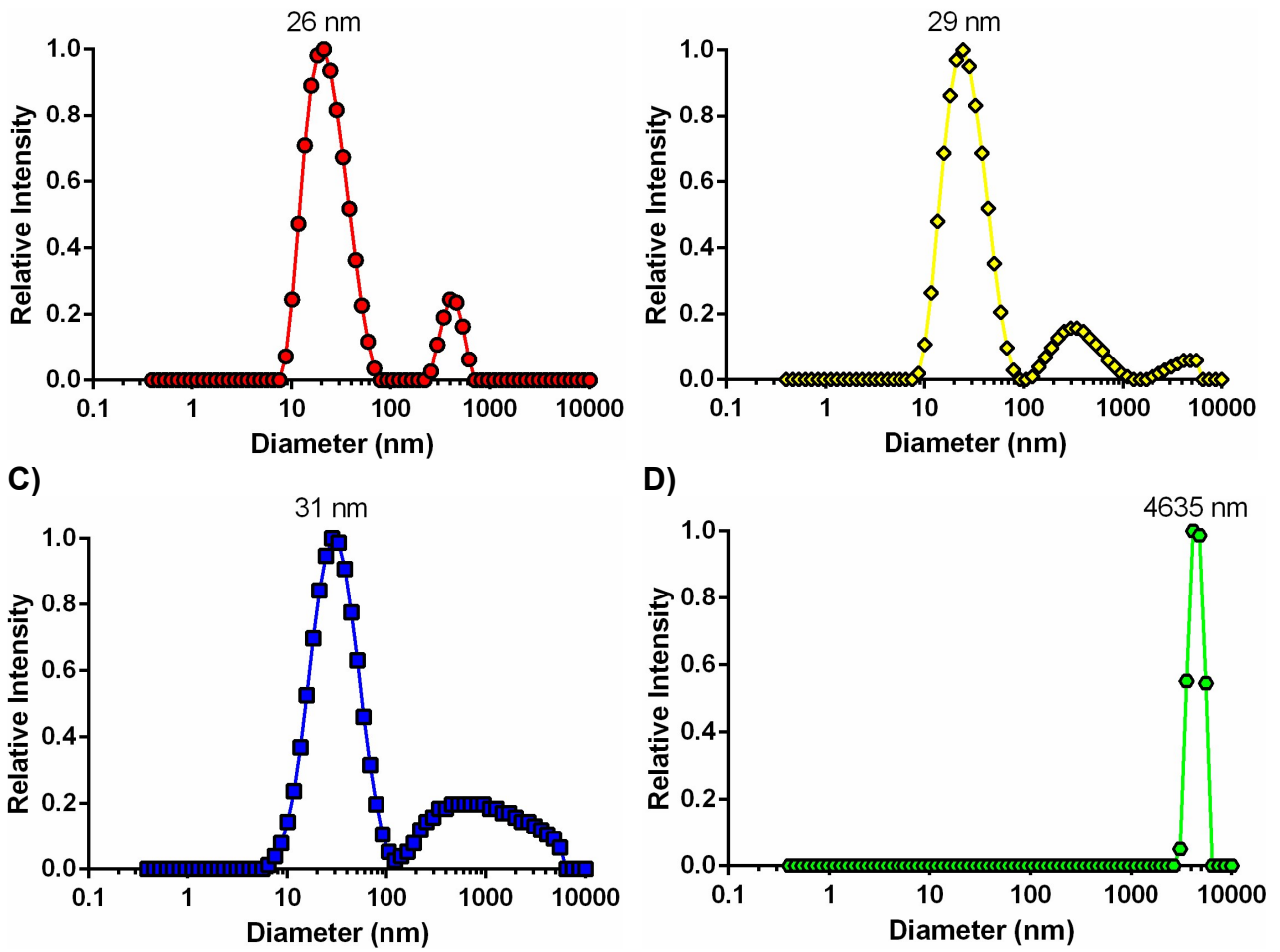


Figure S3. Intensity-based particle size distributions of A) PVA₈₈, B) PVA₉₈, C) PBA₈₈-GA, and D) PVA₉₈-GA coils under diluted conditions. [PVA] = 1.7 wt %, [GA] = 0.4 wt %.

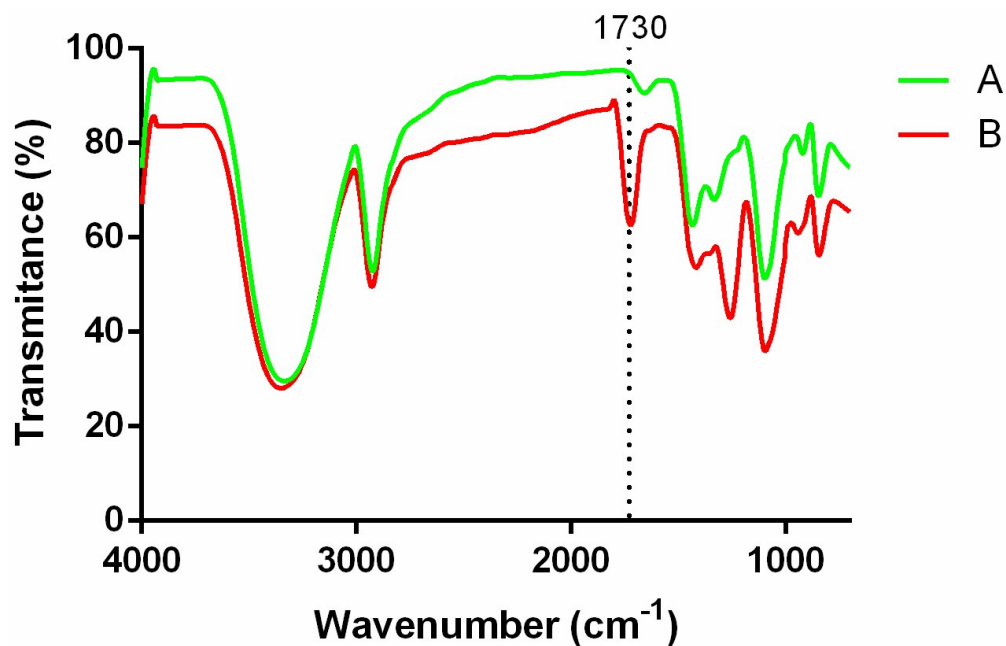


Figure S4. FTIR spectra of A) PVA₉₉ obtained from hydrolysis of B) PVA₈₈.

The signal at 1730 cm⁻¹, belonging to acetate group of PVA₈₈, almost disappears after alcoholysis process, indicating that a fully hydrolyzed polymer was obtained.

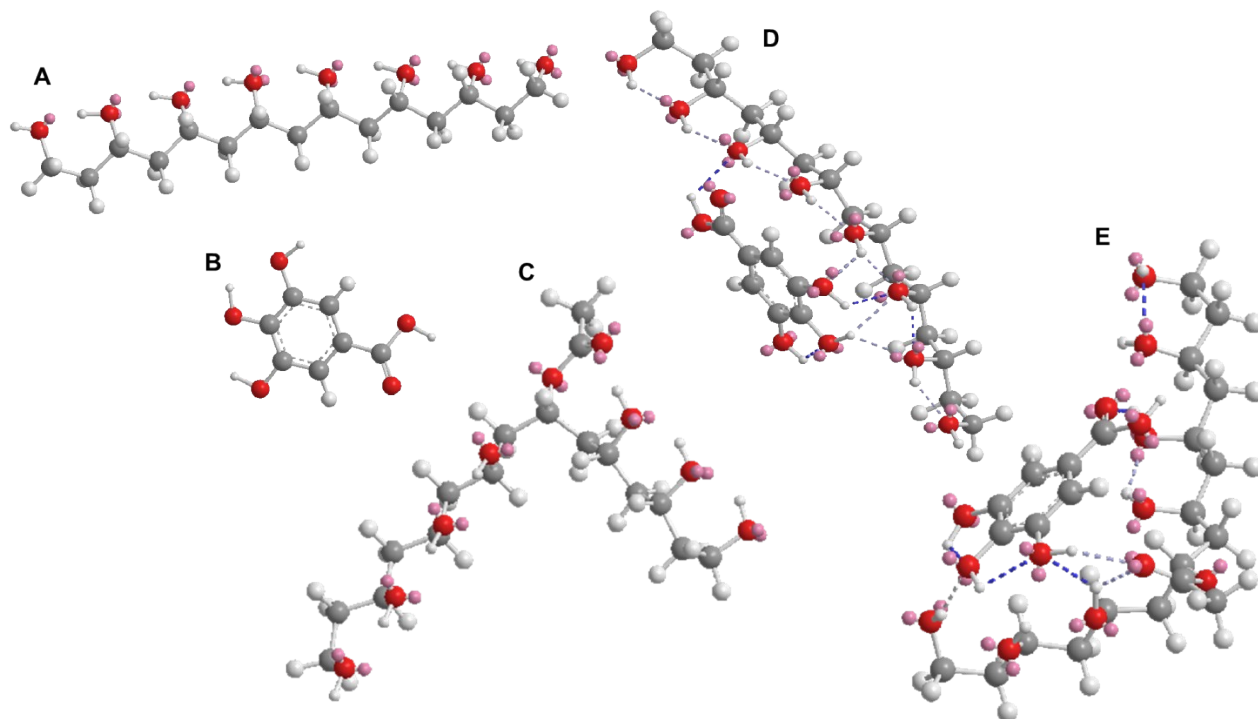


Figure S5. MMFF94 molecular dynamics simulations based on force field calculation method for A) PVA₉₈, B) GA, C) PVA₈₈, and D) PVA₉₈-GA and E) PVA₈₈-GA supramolecular complexes.

Molecular modeling and structure prediction were performed for short oligomeric PVA (8 units)/gallic acid systems at 298 °K, using MM2 force field parameterization.

Table S1. MM2 Minimization

System	Stretch	Bend	Stretch-Bend	Torsion	Non-1,4V DW	1,4 VDW	Dipole/Dipole	Total Energy kcal/mol
PVA ₉₈	1.4302	6.1348	0.6082	8.7235	-11.5562	15.0230	-26.9963	-6.6327
GA	0.5476	5.0807	-0.1250	-11.205	-4.9981	2.8678	1.2520	-6.5799
PVA ₈₈	2.0448	8.1046	0.8661	7.6015	-13.0196	18.7142	-21.9611	2.3505
PVA ₉₈ -GA	2.2676	12.9261	0.5712	-1.0932	-47.1620	18.1226	-31.6186	-45.9864
PVA ₈₈ -GA	2.7672	14.7871	0.8705	-0.9614	-48.5368	22.7681	-24.1534	-32.4588

It can be seen from Table S1, that MMFF94 molecular dynamics simulations predict stables polymer/gallol complexes for both acetylated and hydrolyzed PVA.

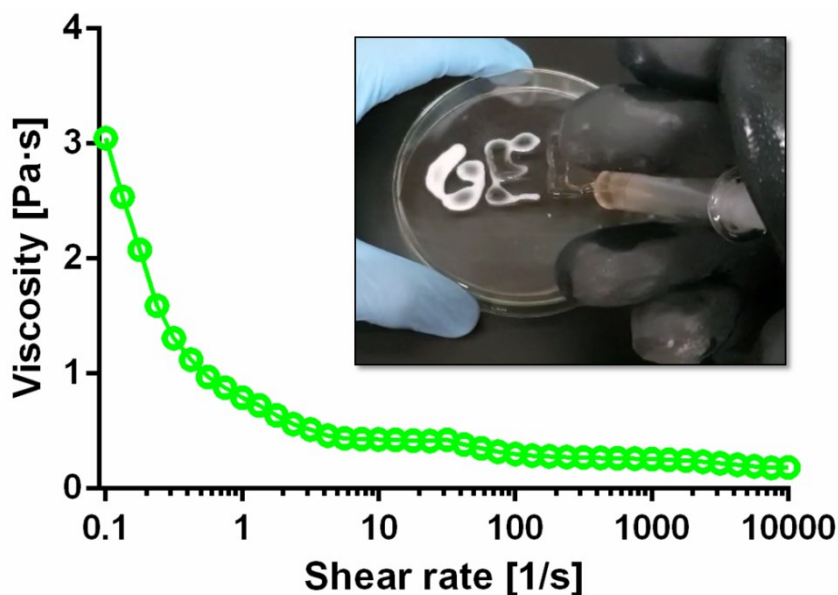


Figure S6. Changes in viscosity as a function of shear rates at 65 °C for PVA₉₈-GA₅ hydrogel. Inset: photograph showing the injectability of the PVA₉₈-GA₅ using a 10 mL syringe (plain tip inner diameter = 2 mm).