

## ALGINATE–BASED THERMO–INDUCED NETWORKS: A REMARKABLE IMPACT OF PH TO THE HYDROGEL THERMORESPONSIVENESS

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### ABSTRACT

In recent decades, hydrogels derived from natural macromolecules sourced from polysaccharides have attracted significant attention owing to their intrinsic biocompatibility, biodegradability, and nontoxicity, rendering them appropriate choices for use in biomedical applications and additional applications in healthcare <sup>[1]</sup>. Polymers which have the ability to undergo changes on their physicochemical characteristics and/or structural conformations, upon exposure to external stimuli such as pH, temperature, ionic strength, light, etc, are known as “smart” materials <sup>[2]</sup>. Many studies report the potential biomedical applications (such as drug delivery or injectable systems) of hydrogels based on stimuli–responsive derivatives of the natural polysaccharide alginate <sup>[3,4,5]</sup>.

In this research study, we explore the rheological properties of a heterograft copolymer with an alginate backbone, grafted by two different types of polymer pendant chains: (a) poly(N–isopropylacrylamide) (PNIPAM) homopolymer and (b) poly[(N–isopropylacrylamide)–co–(N–tert–butyl acrylamide)] (P(NIPAM–co–NtBAM)) random copolymer chains, displaying different Lower Critical Solution Temperatures (LCSTs).

Aqueous copolymer solutions with a polymer concentration fixed at 4 %wt. and different pH values (pH 3.5, pH 4.5 and pH 6.0) were prepared and studied through rheometry. Oscillatory as well as steady state measurements were performed. Due to its thermoresponsive side chains, the Alg–g–P(NIPAM<sub>86</sub>–co–NtBAM<sub>14</sub>)–g–PNIPAM copolymer forms hydrogels with thermo–induced sol–gel transition, above a critical temperature,  $T_{gel}$  (thermo–thickening). However, by lowering pH of the aqueous media in acidic regime, a remarkable increase of the elasticity of the polymer solution was observed in low temperatures. This effect induces significant changes in the hydrogel thermoresponsiveness, transforming the sol–gel transition to soft gel–strong gel. Moreover, the onset of thermothickening shifted to lower temperatures followed by broadening of the transition zone. This implies intermolecular interactions between the uncharged alginate backbone with the PNIPAM side chains, likely through H–bonding. The shear–thinning behavior of the soft gel in low temperatures provides injectability, which allows 3D–printing potential applications.

**KEYWORDS:** sodium alginate, heterograft copolymer, thermos–responsive, pH–responsive, rheological properties

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