

Smart Polymeric Nanoparticles: Influence of Functional Groups on Their Structural Behavior Under Specific Physical and Chemical Stimuli

Miguel A. Hernandez-M.¹, L. R.-Virgen¹, R. Caro-B.¹⁻², G. M.-Mejía¹, J. Manuel del Río-G.³ and Monica de la Luz C.-T.¹

¹ Escuela Superior de Ingeniería Mecánica y Eléctrica, ESIME, Av. Luis Enrique Erro S/N Unidad Profesional Adolfo López Mateos, Zacatenco, Alcaldía Gustavo A. Madero, Mexico City 07738, Mexico.
² Laboratorio de Investigación en Polímeros y Nanomateriales, ESQIE, IPN, Av. Luis Enrique Erro S/N Unidad Profesional Adolfo López Mateos, Zacatenco, Alcaldía Gustavo A. Madero, Mexico City 07738, Mexico
³ Departamento de Física, Escuela Superior de Física y Matemáticas, ESFM, IPN, Av. Luis Enrique Erro S/N, Unidad Profesional Adolfo López Mateos, Zacatenco, Alcaldía Gustavo A. Madero, 07738, CDMX, México.

INTRODUCTION

Smart polymers are materials that modify their shape, size, and properties in response to various external stimuli, such as chemical, physical or biological signals. Specifically, pH-sensitive polymers contain ionizable acidic or basic groups within their structure. [1] Thermosensitive polymers, on the other hand, are characterized by a critical solution temperature (CST) that governs intra- and intermolecular interactions between the polymer and the solvent, triggering a reversible volume phase transition between swollen and collapsed states due to changes in solvation and the free energy of the polymer-solvent system. [1,2]

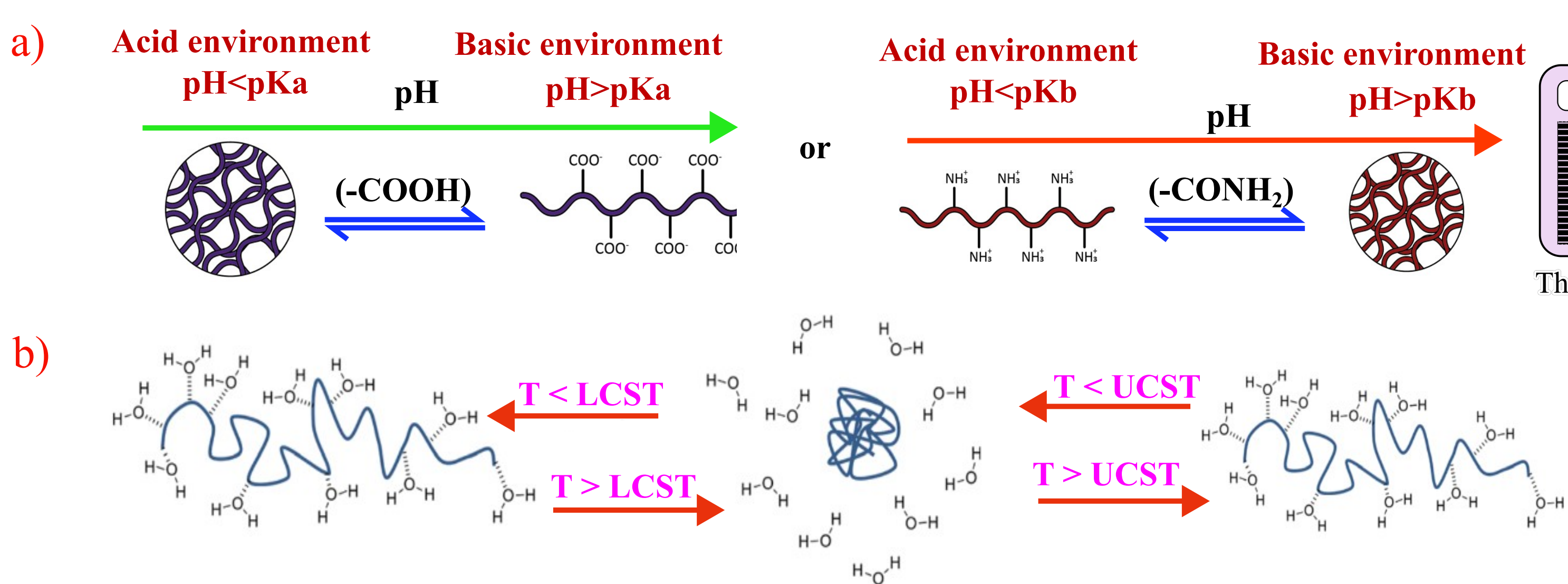


Figure 1.- a) Polymers sensitive to pH changes and b) thermosensitive polymers.

METHODOLOGY

Synthesis of materials through emulsion polymerisation.

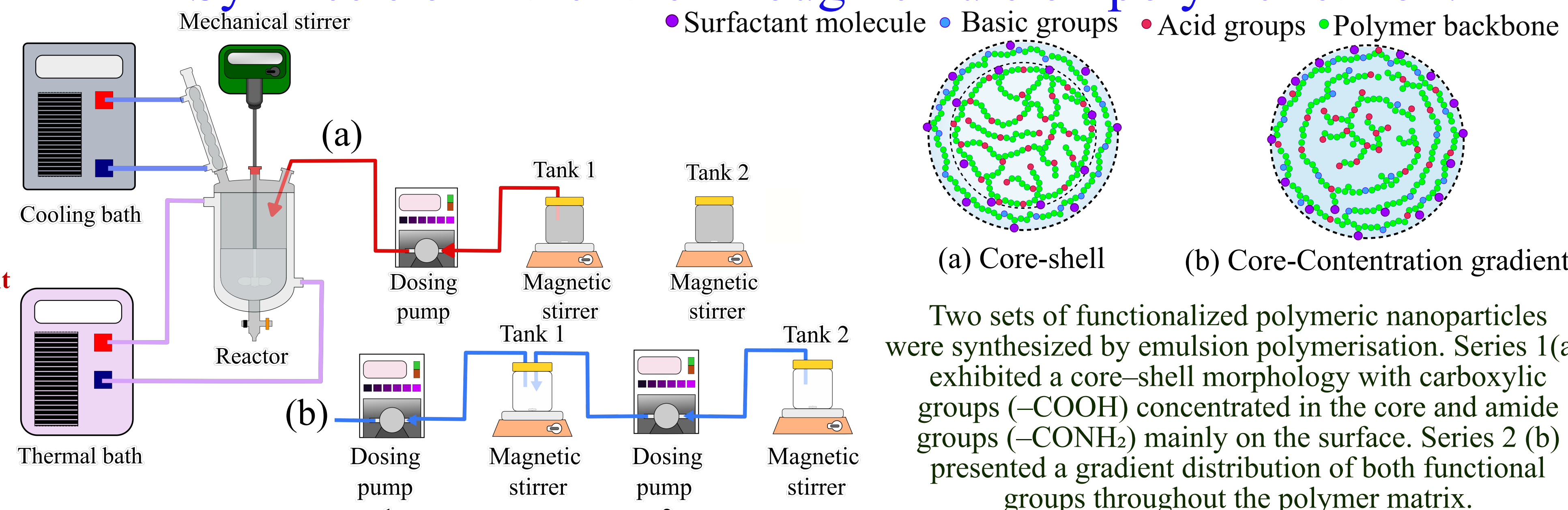


Figure 2.- a) For series 1 (core-shell nanoparticles), a two-stage semicontinuous process was employed. b) Series 2 was obtained via a power-feeding process in series.

The materials were characterised using dynamic light scattering (DLS), scanning electron microscopy (SEM) and rheometry to evaluate their conformational changes, colloidal stability, and rheological properties. In addition, the polymers were titrated with calcium chloride (CaCl_2).

RESULTS

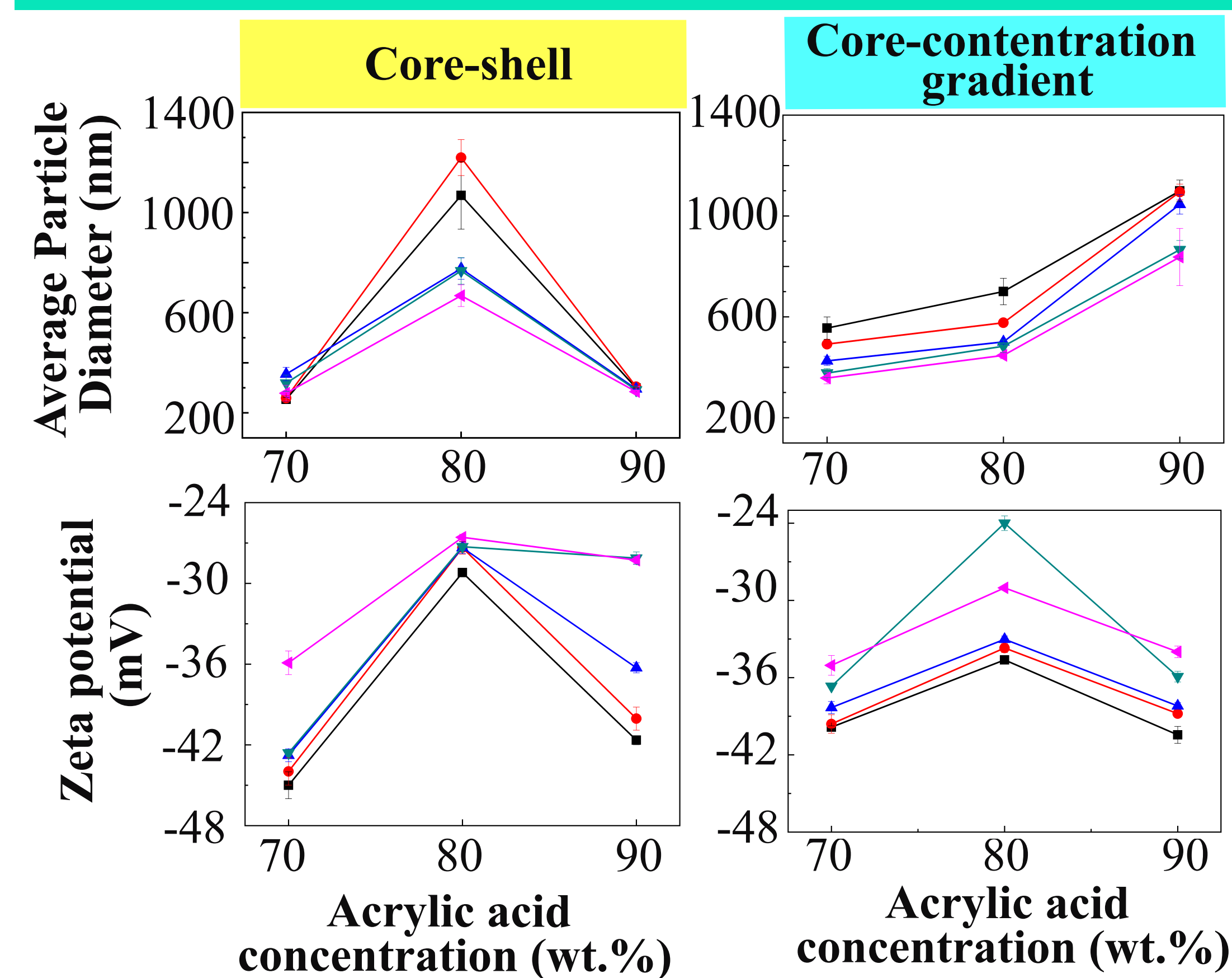


Figure 3.- Average particle diameter (nm) and Zeta potential (mV) as a function of Acrylic acid concentration (wt.%) at different temperatures (25 (■), 30 (●), 40 (▲), 50 (▼) and 60 °C (◆)).

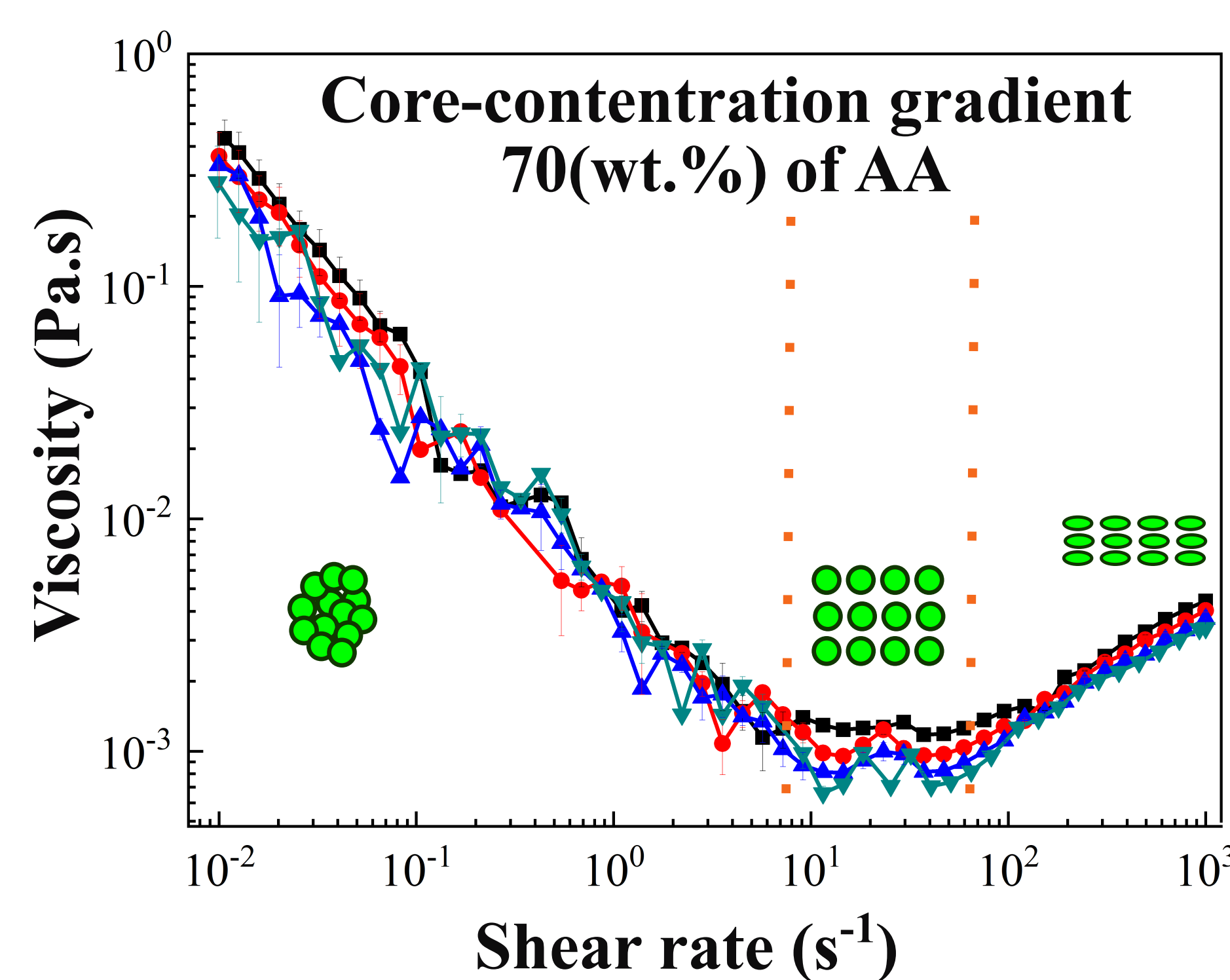


Figure 4.-Viscosity (Pa.s) as a function of Shear rate (s^{-1}) at different temperatures 30(■), 40(●), 50(▲) and 60 °C(▼)

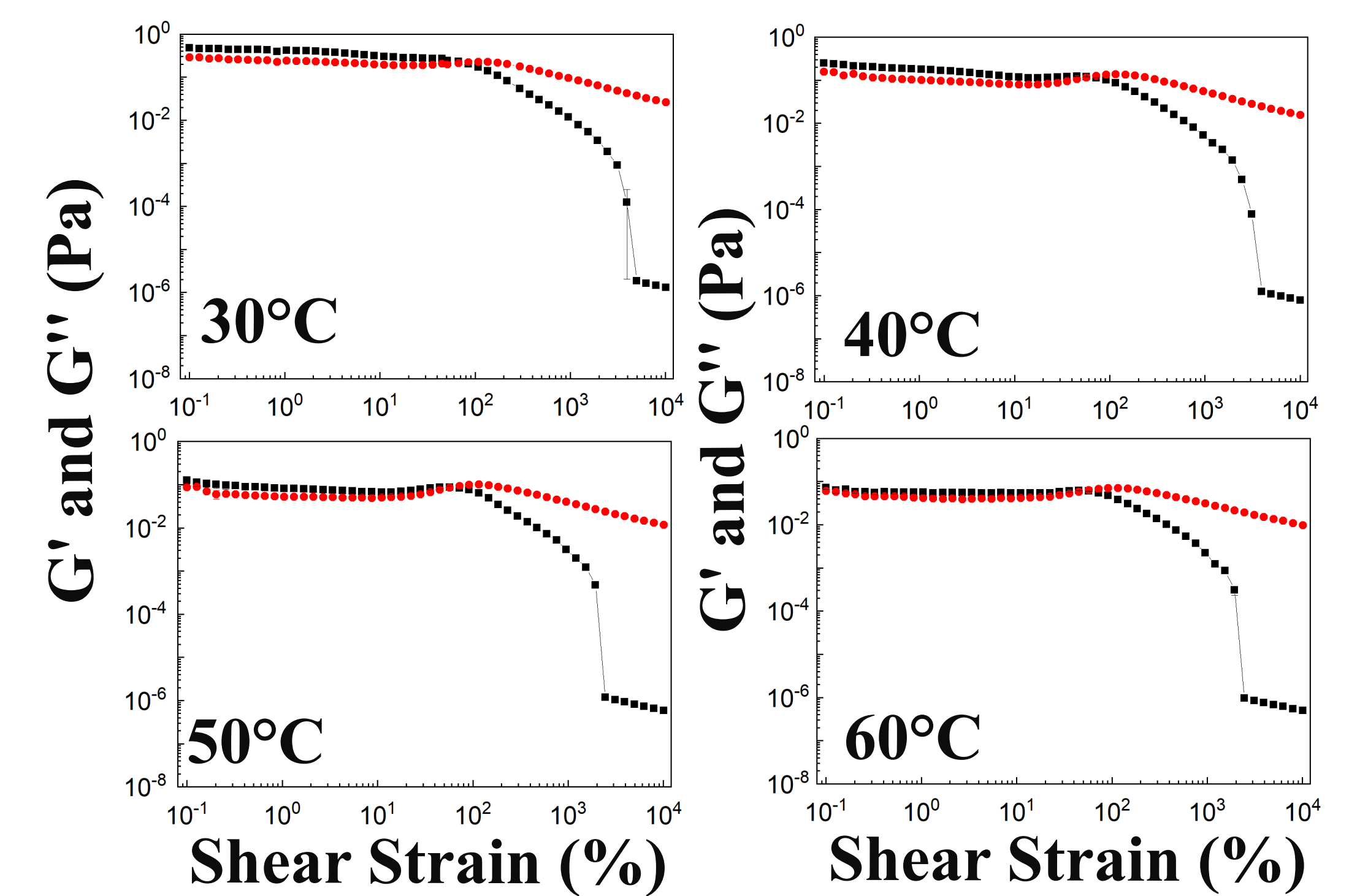


Figure 5.- Storage (G') (■) and Loss (G'') (●) moduli as a function of Shear Strain (%) at different temperatures of a material core-contentration gradient 70 (wt.%) of AA.

Series 1 particles ranged from 250–1,200 nm, showing temperature-dependent size changes linked to their two-block structure: a carboxyl-rich core and an amide-rich block with an LCST ≈ 37 °C. Above this temperature, hydrophobic collapse reduced size. Series 2 particles (300–1,100 nm) grew with higher AA content but shrank with rising temperature due to LCST-driven dehydration. Zeta potentials were negative (–46 to –22 mV) from carboxyl deprotonation. Stability declined above 40 °C as secondary interactions reduced surface charges.

Rheology showed decreasing viscosity with temperature and three regimes: shear-thinning at low shear, Newtonian at medium, and shear-thickening at high shear. $G' > G''$ within the LVR, but $G'' > G'$ at high strain, indicating structural disruption.

SEM revealed that higher AA content produced larger, rougher particles, evolving from spherical to popcorn- or cauliflower-like morphologies.

CaCl_2 addition increased particle size and zeta potential by forming complexes with carboxylic groups, inducing conformational changes and aggregation.

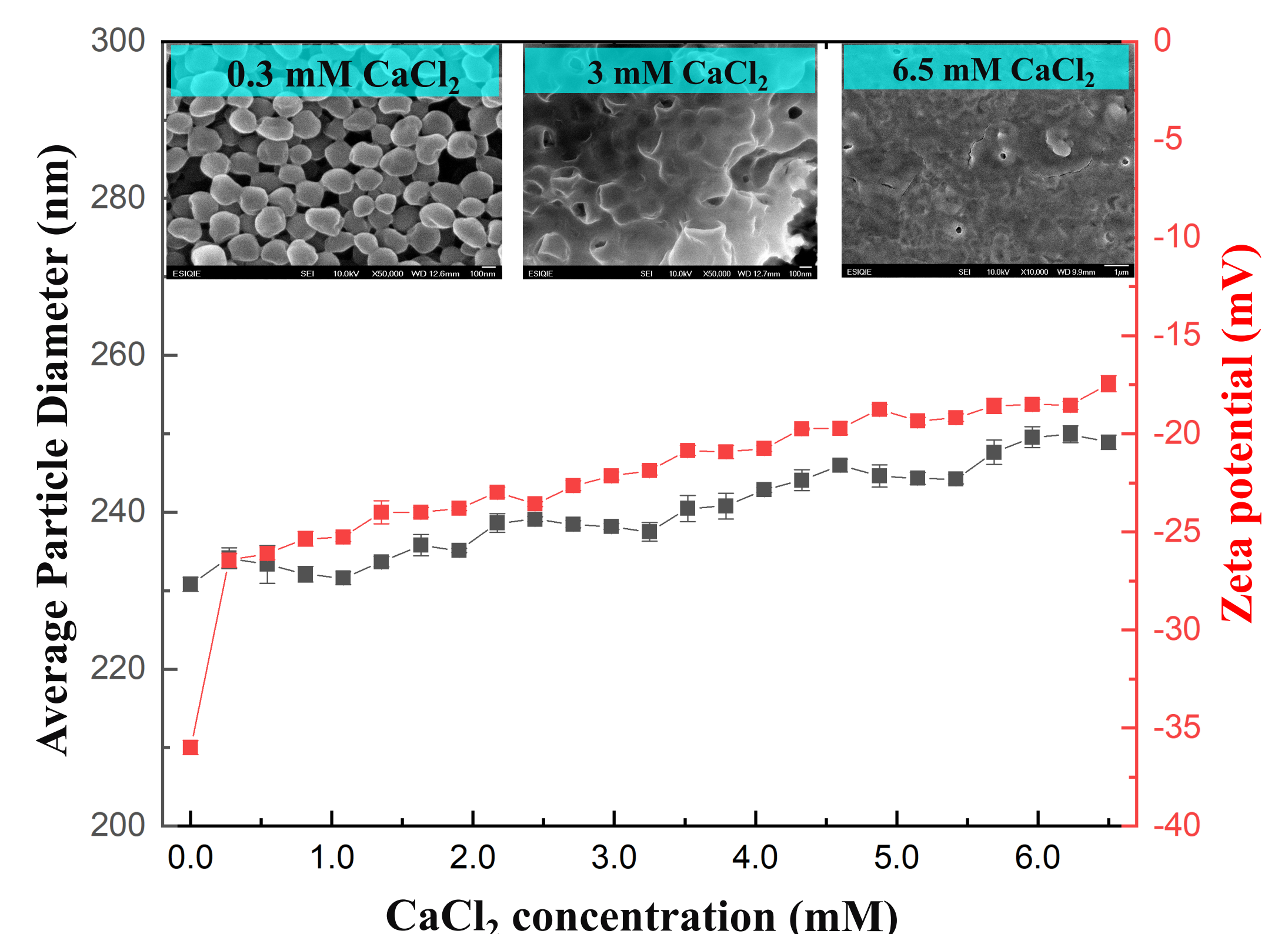


Figure 7.- Average particle diameter (nm) and Zeta potential (mV) as a function of CaCl_2 concentration (mM) for a material core-contentration gradient containing 70 wt.% AA and micrographs at concentrations of: a) 0.3 mM, b) 3.0 mM and c) 6.5 mM CaCl_2

CONCLUSIONS

Polymeric materials exhibited smart, temperature-responsive behaviour, whereby the location and content of functional groups were found to influence the boundaries of volume transition. The morphology of the particles was found to be contingent upon the acid group content, polymer chain growth, and the stabilisation of the polymer during the polymerisation process. The materials exhibited the characteristic rheology of polymeric dispersions, with viscosity decreasing as temperature increased. The complexation of acid groups with Ca^{2+} ions induced conformational rearrangements, which ultimately reduced system stability.

REFERENCES

- [1] Ruiz-Virgen; et.al. Gels 2024, 10 (8), 541. <https://doi.org/10.3390/gels10080541>.
- [2] Ruiz-Virgen; et. al. J. Solut. Chem. 2024, 53 (1), <https://doi.org/10.1007/s10953-023-01354-4>.