

## Synthesis of Polyesters Using Surfactant Catalysts in Microemulsions: The Role of Micelle Shape

Eloi Silva\*, Vadilson Malaquias Santos, Rayanne Penha Wandenkolken Lima and Fabrício Uliana

Chemistry Department/Federal University of Espírito Santo (UFES)/Brazil

### ABSTRACT

In this study, we explored traditional methods commonly found in the literature to analyze how surfactants and polymers interact during the synthesis of polyester in emulsion systems. The study justifies its focus on micellar catalysis by exploring its effectiveness and suggesting methods for enhancing the synergy among surfactants, reactants, and catalysis. We looked at factors such as surface tension, critical micelle concentration, micelle shapes, aggregation numbers, and interfacial phenomena in the process of macromolecular packing in emulsion polycondensation. A surfactant-water system consisting of dodecylbenzene sulfonic acid (DBSA) and sodium dodecyl sulfate (SDS) was employed. Polyesters were prepared from glycerol (GLY), ethylene glycol (EG), diethylene glycol (DEG), and dicarboxylic acids in a surfactant-water system under mild conditions ranging from 70–150°C. FTIR and <sup>1</sup>H NMR confirmed the esterification. Differential scanning calorimetry indicated no crystallinity and a glass transition temperature range of –53 to –46°C, typical of soft matter. The resulting polymers had molecular weights ranging from 1180–6800 g/mol. We found that these polymer aggregate shapes can respond by changing their sizes, both in bulk and at the air-solution interface, when the concentration of surfactants is increased above the critical micelle concentration. The results showed narrow spherical and ellipsoidal polymer aggregates.

### \*Corresponding author

Eloi Silva, Chemistry Department/Federal University of Espírito Santo (UFES)/Brazil.

**Received:** April 15, 2026; **Accepted:** April 22, 2026; **Published:** April 30, 2026

**Keywords:** Interfaces, Polyesters, Surfactants, Micellization

### Introduction

In the present work, polyesters were prepared from Adipic Acid (AD), Glycerol (GLY), and Ethylene Glycol (EG) in a surfactant system of (DBSA) and (SDS) in microemulsions of water/surfactants. The experimental results of polyester synthesis revealed polymer aggregates that were relatively narrow, spherical, and ellipsoidal, including prolate ellipsoidal ( $R_a > R_b = R_c$ ) and tri-axial ellipsoidal ( $R_a \neq R_b \neq R_c$ ) structures. The molecular dynamics (MD) technique is used in this paper to investigate the interaction of an anionic SDS and DBSA micelle with a polymer, poly (ethylene adipate), and polyethylene glycol (PEG), an aliphatic polyester synthesized from a polycondensation reaction between ethylene glycol and adipic acid. The density functional theory (DFT) method was used to characterize the electronic structure of SDS and DBSA. The main proposition put forth by this study is that the synthesis of polyesters through the use of surfactant catalyst systems is strongly influenced by micelle shapes, aggregation numbers, and H-bonds.

### Materials and Methods

#### Materials

Adipic acid, ethylene glycol, diethylene glycol, polyethylene glycol, SDS and DBSA were used as received. Deionized water was employed in all experiments.

#### Polymerization Procedure

Polymerizations were conducted in aqueous media with surfactant (SDS or DBSA). After surfactant dissolution, adipic acid and the

selected diol or triol were added, followed by acid or Lewis acid catalysts. Reactions occurred at 40–95°C for up to 20h. Products were precipitate with methanol, filtered, washed, and dried.

#### Characterization Techniques

Surface tension and conductivity measurements determined critical micelle concentration (CMC) and micellization thermodynamics. FTIR and NMR confirmed ester formation. DSC provided thermal properties. Molecular weights were estimated via intrinsic viscosity using the Mark-Houwink-Sakurada relationship.

#### Computational Methods

Molecular structures were optimized using DFT (B3LYP functional). Force-field parameters were derived from OPLS-AA. Micellar systems with SDS or DBSA were constructed with experimentally consistent aggregation numbers. MD simulations analyzed micelle stability, radius of gyration, hydrogen bonding, and polymer–micelle interactions.

### Results and Discussion

#### Polymer Characterization

FTIR and NMR spectra confirmed successful polyesterification. DSC analysis indicated amorphous materials with low glass transition temperatures (–53 to –46 °C). Molecular weights ranged from 1,200 to 6,800 g/mol. The polymers exhibited soft-matter behavior and low hardness. Morphology varied from gels to spherical and ellipsoidal aggregates, depending on surfactant system and monomer composition.

### Interfacial and Thermodynamic Properties

Surface tension measurements revealed typical micellization behavior. Ethylene glycol or polymeric species reduced the CMC, indicating strong polymer surfactant interactions. Conductivity enabled estimation of micellization enthalpy, entropy, and Gibbs free energy. Increasing cosolvent content decreased aggregation numbers and altered micelle ionization, influencing polymer aggregation and precipitation.

### Molecular Dynamics Simulations

MD simulations showed SDS forms stable spherical micelles, while DBSA micelles are more flexible and larger due to aromatic stacking and hydrogen bonding. Polymer insertion into SDS micelles often led to micelle rupture, while DBSA systems accommodated polymer chains at the micelle–water interface. Radius of gyration and eccentricity parameters revealed micelle shape transitions affect polymer stability and aggregation. Hydrogen bonding analysis confirmed micellar head groups facilitate esterification and polymer binding.

### Electronic Structure Analysis

DFT calculations showed DBSA has a smaller HOMO–LUMO gap than SDS, indicating higher reactivity and catalytic efficiency. Electrostatic potential maps highlighted regions favorable for hydrogen bonding and proton transfer, supporting the superior catalytic role of DBSA.

### Conclusions

Surfactant-assisted microemulsions provide an efficient and environmentally friendly platform for polyester synthesis under mild conditions. Micelle shape, aggregation number, and interfacial hydrogen bonding control polymer formation, aggregation, and stability. DBSA micelles offer enhanced catalytic performance due to structural flexibility and electronic properties. Combining experimental techniques with MD and DFT simulations offers a comprehensive framework for understanding micellar polymerization mechanisms [1-18].

### References

1. Rabnawaz M, Wyman I, Auras R, Cheng S (2017) A roadmap towards green packaging: the current status and future outlook for polyesters in the packaging industry. *Green Chem* 19: 4737-4753.
2. Feghali E, Tauk L, Ortiz P, Vanbroekhoven K, Eevers W (2020) Catalytic chemical recycling of biodegradable polyesters. *Polym Degrad Stab* 179: 109241.
3. Diaz C, Mehrkhodavandi P (2021) Strategies for the synthesis of block copolymers with biodegradable polyester segments. *Polym Chem* 12: 783-806.
4. Tanaka H, Kurihashi T (2003) Synthesis of Polyesters by Emulsion Polycondensation Reaction in Water. *Polym J* 35: 359-363.
5. Takasu A, Takemoto A, Hirabayashi T (2006) Polycondensation of Dicarboxylic Acids and Diols in Water Catalyzed by Surfactant-Combined Catalysts and Successive Chain Extension. *Biomacromolecules* 7: 6-9.
6. Benítez JJ, García-Segura R, Heredia A (2004) Plant biopolyester-cutin: a tough way to its chemical synthesis. *Biochim. Biophys. Acta (BBA)* 1674: 1-3.
7. Fan Z, Zhao Y, Preda F, Clacens JM, Shi H, et al. (2015) Preparation of bio-based surfactants from glycerol and dodecanol by direct etherification. *Green Chem* 17: 882-892.
8. Lovell PA, Schork FJ (2020) Fundamentals of Emulsion Polymerization. *Biomacromolecules* 21: 4396-4441.

9. Santos MS, Tavares FW, Biscaia Jr EC (2016) Molecular Thermodynamics of micellization: Micelle Size Distributions and Geometry transitions. *Braz J Chem Eng* 33: 515-523.
10. Larsson J, Sanchez-Fernandez A, Leung AE, Schweins R, Wu B, et al. (2021) Molecular structure of maltoside surfactants controls micelle formation and rheological behavior. *J Colloid Interface Sci* 581: 895-904.
11. Stubbs S, Yousaf S, Khan I (2022) A review on the synthesis of bio-based surfactants using green chemistry principles. *DARU J Pharm Sci* 30: 407-426.
12. Hendrikse RL, Bayly AE, Jimack PK (2022) Studying the structure of sodium lauryl ether sulfate solutions using dissipative particle dynamics. *J Phys Chem B* 126: 8058-8071.
13. Goddard ED (2002) Polymer/surfactant interaction: Interfacial aspects. *J Colloid Interface Sci* 256: 228-235.
14. La Mesa C (2005) Polymer surfactant and protein–surfactant interactions. *J Colloid Interface Sci* 286: 148-157.
15. Cabane B, Duplessix R (1987) Decoration of semi dilute polymer solutions with surfactant micelles. *J Phys (Paris)* 48: 651-662.
16. Froehner SJ, Belarmino A, Zanette D (1998) The role of the counterion in poly (ethylene oxide) dodecyl sulfate interactions. *Colloids Surf A* 137: 131-139.
17. Haydukivska K, Blavatska V, Paturej J (2020) Universal size ratios of Gaussian polymers with complex architecture: Radius of gyration vs hydrodynamic radius. *Sci Rep* 10: 14127.
18. Nakamura H, Imanishi S, Sanui K, Ogata N (1979) Synthesis of aromatic polyesters by interfacial polycondensation using immiscible binary solvents. *Polym J* 11: 661-664.

**Copyright:** ©2026 Eloi Silva, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.