STM JOURNALS

Journal of
Polymer & Composites

ISSN: 2321-2810 (Online)
ISSN: 2321-8525 (Print)
Volume 13, Special Issue 6, 2025
DOI (Journal): 10.37591/JoPC

https://journals.stmjournals.com/jopc

Review JoPC

Polymer Chemistry of Ion-Selective Membranes and Hydrogels for Clinical Sodium Sensing: Advances and Perspectives

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Abstract

Accurate and timely monitoring of serum sodium levels is critical in diagnosing and managing hyponatremia, a common and potentially life-threatening electrolyte disorder. Recent advances in polymer chemistry have driven the development of ion-selective membranes and hydrogels tailored for clinical sodium sensing, bridging the gap between material science and biomedical diagnostics. This review critically examines the design and synthesis of polymeric materials—focusing on block copolymers, conductive polymers, and stimuli-responsive hydrogels—used to fabricate ion-selective electrodes (ISEs) and biosensors for sodium detection. Emphasis is placed on polymerization strategies, functional group modification, and crosslinking methods that enable tunable ion selectivity, mechanical stability, and biocompatibility. Fabrication techniques such as electrospinning, layer-by-layer assembly, and solvent casting are discussed in relation to membrane morphology and sensor performance. Furthermore, emerging smart polymers capable of responding to pH, temperature, or enzymatic triggers show promise for real-time and non-invasive sodium monitoring. Current translational challenges—including calibration drift, biofouling, and regulatory hurdles—are highlighted, alongside future research directions integrating polymer chemistry with flexible electronics and wearable diagnostics. By mapping the interplay between chemical structure and sensing function, this review aims to guide the rational design of next-generation polymer-based sodium sensors to improve patient care in electrolyte disorders such as hyponatremia.

Keywords: Polymer chemistry, ion-selective membrane, sodium sensing, hydrogels, block copolymer, hyponatremia monitoring, biomedical sensor, stimuli-responsive polymers, electrolyte detection, conductive polymers

INTRODUCTION

Hyponatremia, defined as serum sodium concentration below 135 mEq/L, represents the most common electrolyte disturbance in hospitalized patients, affecting nearly 20% of inpatients and leading to considerable morbidity if not effectively monitored and managed [1,2]. Conventional laboratory-based measurement methods, such as flame photometry and ion-selective electrode (ISE) analysis, though accurate, require venous blood sampling and centralized equipment, limiting their suitability for continuous monitoring or point-of-care (POC) applications [3,4].

Advances in polymer chemistry have enabled the development of ion-selective membranes and smart hydrogels tailored for Na^+ detection. Membrane-based ISEs often employ polymeric matrices such as poly(vinyl chloride) (PVC) or polyurethane to host ionophores, enhancing selectivity and mechanical

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Received Date: July 09, 2025
Accepted Date: July 23, 2025
Published Date: September 23, 2025

Citation: Virendra C. Patil, Yogesh R. Chavan. Polymer Chemistry of Ion-Selective Membranes and Hydrogels for Clinical Sodium Sensing: Advances and Perspectives. Journal of Polymer & Composites. 2025; 13(Special Issue 6): S895–S901p.

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stability [5,6]. More recently, conductive polymers like PEDOT:PSS and polyaniline have been introduced as solid-contact layers, improving charge transfer and preventing water layer formation—key to stable and miniaturized sensors [7,8].

Furthermore, hydrogel-based sensors, including ionic hydrogels and ionogels, offer promising flexibility and biocompatibility for wearable or minimally invasive devices [9,10]. A recent paper-based potentiometric sensor integrated with a polymeric hydrogel demonstrated near-Nernstian Na^+ detection (10^{-7} to 10^{0} M) with applications in urine analysis, highlighting the translational potential of polymer chemistry in electrolytic diagnostics [9].

Clinically, institutions like the Krishna Institute of Medical Sciences (KIMS), Karad, with significant experience in managing hyponatremia (personal communication, 2024), may benefit from point-of-care sodium sensors—especially in rural or resource-limited settings. Integrating polymer chemistry innovations into simple, robust POC devices could significantly improve monitoring in such environments.

This review focuses on recent polymer chemistry approaches to sodium sensing—including ion-selective membranes, conductive polymer interfaces, and hydrogels—analyzing their design, fabrication, and potential for clinical deployment in hyponatremia management.

POLYMER CHEMISTRY FOUNDATIONS IN ION SENSING

The functionality and performance of ion-selective sensors for sodium detection are deeply rooted in polymer chemistry—particularly in the development of ion-selective membranes (ISMs) and polymer-assisted interfaces that enhance ion recognition, selectivity, and signal transduction. ISMs are typically composed of polymer matrices such as poly(vinyl chloride) (PVC), polyurethane, polymethyl methacrylate (PMMA), and amphiphilic block copolymers with distinct hydrophobic and hydrophilic segments [11,12]. These matrices serve as hosts for sodium-selective ionophores, plasticizers, and selective additives. The plasticizers, such as dioctyl phthalate (DOP), play a crucial role in adjusting the membrane's dielectric constant, promoting ion mobility, and enhancing mechanical flexibility [13].

Recent innovations in polymerization techniques—like ring-opening polymerization (ROP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT)—have allowed for precise control over molecular weight distribution, chain architecture, and functional group positioning [14,15]. Such control is essential for customizing membrane thickness, porosity, and surface properties, all of which influence sensor sensitivity and response time.

Moreover, crosslinking strategies—both physical (e.g., chain entanglement) and chemical (e.g., UV-curing or click chemistry)—are employed to stabilize polymer hydrogels and nanocomposite membranes. These networks resist dissolution while maintaining sufficient water content for rapid ion transport [16]. Block copolymers like PEG–PLA and PEG–PCL are particularly attractive for sodium sensor interfaces because they offer tunable hydrophilicity, swelling behavior, and mechanical strength. These materials facilitate sensor integration with aqueous biological environments, ensuring consistent signal transduction even in dynamic conditions [17]. Collectively, the synergy of polymer design, synthetic control, and structural tailoring underpins the advancement of highly selective, responsive, and biocompatible sodium sensors.

Ion-Selective Membranes for Sodium Sensing

Polymeric ion-selective membranes (ISMs) are foundational components in modern sodium sensing technologies. These membranes are commonly fabricated via solvent-casting techniques using blends of polyvinyl chloride (PVC) or other polymers combined with ionophores—such as sodium ionophore X—which provide selectivity toward sodium ions. Plasticizers like dioctyl phthalate (DOP) are included to impart flexibility and facilitate ion transport, while selective additives such as lipophilic salts enhance membrane stability and electrochemical performance [11]. Recent advancements in nanotechnology have enabled the integration of nanostructured materials like carbon nanotubes (CNTs),

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graphene, and metal–organic frameworks (MOFs) into ISMs. These additives increase membrane surface area and improve ion flux, thereby enhancing sensitivity, selectivity, and detection speed [18].

A particularly promising method for membrane fabrication is the layer-by-layer (LbL) assembly technique. This approach allows for the deposition of ultrathin, highly uniform films with nanometer-scale control over thickness and composition. When LbL-assembled membranes are applied to the tips of ion-selective electrodes (ISEs), they enable faster response times, lower detection limits, and more reproducible performance due to improved analyte accessibility and signal stability [19].

Furthermore, the development of patentable, biodegradable polymeric membranes is gaining momentum, especially for short-term or disposable sodium sensors. Polymers like polylactic acid (PLA), when blended with polyvinylidene fluoride (PVDF), yield mechanically robust yet degradable composites suitable for transient biomedical applications. These PLA–PVDF membranes are particularly advantageous in ambulatory and point-of-care contexts, where biocompatibility, disposability, and environmental sustainability are critical [20]. Overall, the evolution of ISMs toward more sophisticated, nanostructured, and biodegradable designs holds promise for next-generation wearable and implantable sodium sensing devices.

Conductive Polymers as Solid-Contact Layers

To improve the long-term stability and performance of polymer-based sodium sensors, conductive polymers (CPs) are increasingly employed as solid-contact layers between the electrode substrate and the ion-selective membrane (ISM). These CP layers facilitate efficient ion-to-electron transduction and help mitigate common issues such as signal drift and water layer formation. Among the most widely utilized CPs are poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS), polyaniline (PANI), and polypyrrole (PPy), owing to their excellent redox properties, mechanical flexibility, environmental stability, and ease of processing [21,22].

Solid-contact electrodes incorporating PEDOT: PSS have demonstrated particularly favorable outcomes, including reduced potential drift and enhanced reproducibility. One of the major advantages of PEDOT: PSS is its ability to prevent the formation of aqueous interlayers between the membrane and the underlying electrode—one of the primary causes of instability and eventual sensor failure in polymer membrane-based systems [23]. Furthermore, the nanostructuring of CPs significantly improves their electrochemical performance. For instance, fabricating PEDOT: PSS in the form of nanofibers, or integrating it with conductive fillers such as carbon black, graphene, or carbon nanotubes, increases the effective surface area, improves charge transfer resistance, and enhances double-layer capacitance at the membrane interface [24].

Table 1. Representative polymer systems, synthesis strategies, and their functional roles in sodium sensing.

Polymer / composite	Polymerization / fabrication method	Application in sensor	Key functional advantage
Poly (vinyl chloride) (PVC) + ionophore	Solvent casting	Ion-selective membrane (ISM)	High selectivity and stability
PLA–PVDF blend	Solvent casting	Biodegradable membrane	Short-term Na^+ sensing, flexible format
PEDOT: PSS	Oxidative polymerization	Solid-contact layer	Reduced drift, improved electron transfer
Polyaniline / polypyrrole	Chemical polymerization	Conductive interface	Flexibility and redox stability
PEG–PLA / PEG–PCL hydrogels	Ring-opening polymerization (ROP)	Hydrogel electrolyte / ionogel	Biocompatibility, tunable swelling
PEDOT: PSS–hydrogel composite	Blending	Mixed ionic–electronic conductor	Enhanced transduction, flexibility
Nanostructured PVC–graphene	Solvent casting + nanofiller	ISM with increased surface area	Faster response, lower detection limit
Layer-by-layer (LbL) assembled membrane	Sequential deposition	Thin ISM	Precise thickness, improved sensitivity

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These enhancements not only stabilize the sensor signal over prolonged operation but also improve sensitivity and response time in dynamic physiological environments such as sweat or interstitial fluid. Table 1 below summarizes representative conductive polymer systems, their respective synthesis approaches—such as electrochemical polymerization or chemical oxidative methods—and their specific functional contributions toward high-performance sodium sensing. As sensor technologies continue to evolve, integrating nanostructured CPs within flexible, miniaturized platforms holds significant promise for next-generation wearable and point-of-care diagnostic devices.

Hydrogel-Based and Smart Polymer Sensors

Hydrogels, composed of three-dimensional, crosslinked polymer networks with the capacity to absorb significant amounts of water, have garnered increasing attention as promising materials for developing flexible and skin-conformal sodium sensors [25]. Their intrinsic high-water content closely mimics the ionic and mechanical environment of biological tissues, which enhances both biocompatibility and ion transport efficiency (26). This makes them particularly well-suited for continuous, non-invasive monitoring applications. Biodegradable hydrogels derived from polymers such as polyethylene glycol (PEG), polyvinyl alcohol (PVA), and block copolymers like PEG–polylactic acid (PLA) or PEG–polycaprolactone (PCL) can be chemically engineered to include sodium-ion-binding ligands. These functional modifications significantly enhance sensor selectivity and sensitivity toward sodium ions [27].

Emerging studies have introduced ionic hydrogels and ionogels that act as solid electrolytes in wearable or implantable sodium sensing devices [28]. Conductive hydrogel composites, such as poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS), have demonstrated mixed ionic and electronic conductivity, allowing efficient transduction of ionic signals into electronic outputs [29]. These composite materials bridge the gap between the biological and electronic domains, making them ideal for real-time biosensing platforms.

Moreover, stimuli-responsive hydrogels—capable of responding to changes in pH, enzymatic activity, or temperature—are under active investigation for next-generation sensing applications [30]. These materials can dynamically alter their swelling behavior or conductivity in response to specific physiological cues. Such smart hydrogel systems offer the potential to not only detect sodium levels passively but also actively respond to pathological events such as acute hyponatremia or dehydration. As a result, they hold significant promise for integration into advanced wearable biosensors that deliver continuous, real-time health monitoring in both clinical and remote settings.

Biomedical Applications and Translational Perspectives

The integration of polymer-based membranes, conductive polymers, and hydrogels into point-of-care (POC) and wearable sodium sensors represents a transformative step forward in the proactive monitoring of hyponatremia, particularly in both hospitalized and ambulatory populations [31]. These polymeric platforms allow for the development of soft, conformal, and miniaturized devices with superior biocompatibility, water retention, and ion selectivity—making them well-suited for continuous, non-invasive electrolyte monitoring. Recent advancements include flexible sodium sensors embedded in wristbands, skin-adherent patches, and smart textiles that can analyze sweat in real-time, serving as proxies for systemic sodium levels [32]. These systems offer real-time feedback, enabling early detection of sodium imbalances before clinical symptoms arise, particularly benefiting vulnerable groups such as older adults, athletes, and individuals with chronic heart or kidney conditions.

The potential of these sensors to revolutionize patient care is significant; however, key technical and translational challenges remain. Sensor calibration drift over prolonged use can reduce measurement reliability, while biofouling from skin lipids, proteins, and microbial contaminants can interfere with signal quality. Mechanical durability is also critical, as wearable devices must endure repeated flexing, compression, and exposure to moisture without compromising function [33]. In addition, regulatory frameworks for wearable medical devices are stringent, demanding comprehensive validation of sensor safety, accuracy, and reproducibility before clinical deployment.

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Overcoming these barriers requires a multidisciplinary approach. Polymer chemists can design advanced materials with antifouling and self-healing properties; materials scientists and engineers can enhance structural resilience; and clinicians can provide insights into user needs and medical relevance. By bridging these domains, future generations of wearable sodium sensors may offer not only real-time diagnostics but also integration with telemedicine platforms for continuous remote monitoring. Ultimately, these technologies promise to shift the paradigm of electrolyte assessment from reactive to preventive, advancing personalized healthcare.

Future Perspectives

Looking ahead, the field of polymer-based sodium sensors is poised for transformative advancements that will significantly enhance diagnostic precision and therapeutic responsiveness. One promising direction involves the development of multi-analyte polymeric sensors capable of simultaneously detecting key electrolytes such as sodium, potassium, and chloride. These sensors could provide a more comprehensive electrolyte profile, enabling early detection and better management of imbalances such as hyponatremia and hyperkalemia [34].

Another exciting innovation is the integration of bioactive polymers that not only detect changes in electrolyte concentrations but also respond autonomously by releasing therapeutic agents when critical thresholds are crossed. Such smart materials could facilitate closed-loop feedback systems for real-time intervention, particularly in critical care settings.

Additionally, the adoption of sustainable, bio-derived polymers is gaining traction. These materials offer the dual benefits of environmental sustainability and enhanced biocompatibility, supporting long-term implantation or biodegradation without adverse effects. This shift is especially important as healthcare systems prioritize eco-friendly practices.

Furthermore, advances in 3D printing and microfabrication are enabling the creation of highly customized, patient-specific device geometries. These tailored sensors can conform to unique anatomical sites, improving comfort, accuracy, and long-term wearability.

Collectively, these innovations—driven by the intersection of cutting-edge polymer chemistry and clinical needs—are expected to elevate the standard of care in electrolyte monitoring. Especially in resource-limited settings, such next-generation polymer-based sodium sensors could prove invaluable in enhancing hyponatremia management and improving overall patient outcomes.

CONCLUSION

Recent advances in polymer chemistry have profoundly influenced the development of next-generation sodium sensing technologies, particularly in the realm of biomedical diagnostics. Sophisticated polymer-based systems—such as ion-selective membranes, solid-contact conductive polymer interfaces, and soft, stretchable hydrogel sensors—are now capable of detecting sodium ions with enhanced precision and reliability. Innovations in controlled polymerization techniques, site-specific functionalization, and the creation of smart crosslinked polymer networks allow for tailored physicochemical properties including high selectivity, optimal biocompatibility, and tunable degradation rates. These features are especially vital in clinical settings where stability, sensitivity, and safety are paramount. Moreover, the field is moving toward the development of multi-analyte platforms that can simultaneously detect sodium alongside other critical electrolytes or biomarkers, offering a more comprehensive picture of a patient's physiological status. Bioresponsive polymers that change their properties in response to fluctuations in sodium concentration, as well as integration with flexible electronics and wireless data transmission, are pushing the boundaries toward wearable and continuous monitoring devices. These advancements promise to shift sodium monitoring from infrequent laboratory measurements to real-time, patient-centric diagnostics. Such polymer-based sodium sensors have the potential to revolutionize the management of electrolyte imbalances like hyponatremia by enabling earlier detection, more accurate tracking, and personalized interventions. As polymer chemists

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continue to align material design with clinical functionality, these innovations are poised to significantly enhance diagnostic accuracy, therapeutic monitoring, and ultimately, patient outcomes across a range of healthcare applications.

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