

Advances in Polymer Chemistry for Coronary Artery Disease

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Abstract

Coronary artery disease (CAD) remains the leading cause of morbidity and mortality worldwide, driving ongoing innovation in therapeutic materials and device design. Polymer chemistry has emerged as a cornerstone in the development of advanced cardiovascular interventions, offering versatile platforms to improve the safety, efficacy, and functionality of implantable devices. This review explores recent advances in the synthesis and application of biodegradable and biostable polymers, focusing on their roles in drug-eluting stents (DES), bioresorbable scaffolds, and polymer-based drug delivery systems. Tailored polymer architectures, including block copolymers, smart and stimuli-responsive polymers, and surface-functionalized composites, have enhanced drug release kinetics, reduced thrombogenicity, and improved endothelialization. Advances in polymer molecular design—such as incorporating hydrophilic segments, functional side chains, or bioactive molecules—have further improved biocompatibility and mechanical performance, addressing clinical challenges like in-stent restenosis and late thrombosis. The review also highlights emerging trends, including shape-memory polymers and electroactive composites that respond dynamically to physiological cues. Finally, translational challenges, including biodegradation kinetics, scale-up synthesis, and regulatory considerations, are critically discussed. By integrating polymer chemistry insights with clinical perspectives, this paper underscores the transformative potential of polymer-based biomaterials in reshaping the prevention, diagnosis, and treatment of CAD, ultimately advancing patient care.

Keywords: Coronary artery disease (CAD), polymer chemistry, drug-eluting stents (DES), bioresorbable scaffolds, biodegradable polymers, smart polymers, surface functionalization

INTRODUCTION

Coronary artery disease (CAD) remains the leading cause of morbidity and mortality worldwide, creating a critical need for innovative therapeutic strategies that improve patient outcomes [1]. In recent decades, polymer chemistry has emerged as a transformative force in CAD treatment, particularly through the development of drug-eluting stents (DES), bioresorbable vascular scaffolds (BVS), nanoparticle carriers, and bio functional coatings [2–3].

The versatility of polymers stems from their tunable chemical structures, which allow fine control over properties such as degradation rate, drug release kinetics, mechanical strength, and hemocompatibility [4]. By modifying molecular architecture and

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functionalizing polymer surfaces, scientists have developed materials that reduce thrombosis, promote endothelialization, and match the dynamic mechanical environment of coronary arteries [5–6].

This review explores recent advances in polymer chemistry applied to CAD, focusing on key applications in DES, BVS, and surface-functionalized materials. We discuss the evolution from first-generation permanent polymer devices to next-generation bioresorbable and smart polymer systems. We also highlight the challenges and future directions needed to translate these innovations from laboratory synthesis to clinical practice.

Polymer Chemistry in Cardiovascular Applications

Polymers used in cardiovascular devices can be broadly categorized into biodegradable and biostable materials [3]. Biodegradable polymers—such as poly (L-lactic acid) (PLLA), polycaprolactone (PCL), and poly (lactic-co-glycolic acid) (PLGA)—degrade into non-toxic byproducts, reducing long-term complications associated with permanent implants [7]. Biostable polymers like polyurethane (PU) and polytetrafluoroethylene (PTFE) offer durable mechanical support but carry risks of chronic inflammation and late thrombosis [8].

Recent advances in copolymerization techniques, including block and graft copolymers, have enabled researchers to combine desirable properties, such as flexibility, strength, and controlled degradation [9–10]. Tailoring the molecular architecture—adjusting crystallinity, crosslinking, and hydrophilic segments—has allowed for precise control of drug release and scaffold resorption rates [11].

Surface functionalization is another critical strategy. By grafting bioactive molecules (e.g., heparin, nitric oxide donors, or endothelial progenitor cell-capturing ligands), researchers have developed polymers that reduce platelet adhesion and accelerate endothelialization, directly addressing the primary causes of late stent thrombosis [12–13].

Drug-Eluting Stents (DES) and Polymeric Coatings

Drug-eluting stents revolutionized CAD treatment by combining metallic scaffolds with polymer-based coatings that release antiproliferative drugs, dramatically reducing restenosis rates compared to bare-metal stents [14]. First-generation DES employed non-biodegradable polymers like poly(ethylene-co-vinyl acetate) (PEVA) and poly(n-butyl methacrylate) (PBMA), which controlled drug release but triggered late thrombosis due to persistent inflammation [15].

To overcome these challenges, second- and third-generation DES adopted biodegradable polymers such as PLLA and PLGA, which degrade safely after drug release, improving long-term biocompatibility [16]. Recent innovations have included dual-layer polymer coatings, which separate the drug-release function from the hemocompatibility function, and smart coatings responsive to pH or enzymatic activity for on-demand drug delivery [17–18].

Surface modifications, including heparinization and NO-releasing layers, have been shown to further reduce thrombogenicity and improve endothelialization rates, leading to safer and more durable clinical outcomes [19–20].

Bioresorbable Vascular Scaffolds (BVS)

Bioresorbable vascular scaffolds were developed to provide temporary mechanical support before gradually degrading, thereby restoring natural vessel function and reducing long-term risks associated with permanent implants [21]. The most widely used material, PLLA, offers a balance of strength and controlled degradation [22].

Table 1. Polymer Types and Applications in CAD.

Polymer type	Examples	Applications	Advantages	Challenges
Biodegradable polymers	PLLA, PLGA, PCL	BVS, drug carriers	Resorbable, reduced chronic inflammation	Mechanical strength, degradation byproducts
Biostable polymers	PU, PTFE	Non-degradable stents, grafts	Long-term support	Chronic inflammation risk
Copolymers & blends	PLLA/PCL, PEG-based copolymers	DES coatings, nanocarriers	Tunable flexibility and degradation	Complex synthesis
Smart polymers	Shape-memory, stimuli-responsive	Responsive drug delivery systems	Dynamic adaptation to physiological cues	Regulatory hurdles, reproducibility
Functionalized polymers	Heparinized PLLA, NO-releasing polymers	Anti-thrombogenic coatings	Enhanced endothelialization	Stability and large-scale production

Key challenges in BVS design include ensuring sufficient radial strength to prevent acute vessel recoil, while achieving predictable biodegradation within two to three years to minimize inflammatory responses [23]. Recent strategies have combined PLLA with PCL or incorporated inorganic fillers like magnesium hydroxide to enhance flexibility and reduce strut thickness, addressing complications linked to earlier thick-strut designs [24–25].

Surface functionalization—such as hydrophilic coatings and NO-releasing functionalities—further enhances endothelialization and reduces neointimal hyperplasia [26]. Despite mixed clinical results with early devices, ongoing improvements in polymer crystallinity, molecular weight, and composite structure hold promise for safer and more effective next-generation BVS [27]. In the Table 1 different polymer types and its applications in CAD is listed.

Smart and Stimuli-Responsive Polymers

Beyond conventional biodegradable polymers, recent advances in polymer chemistry have led to smart or stimuli-responsive polymers that adapt their behavior under physiological triggers such as temperature, pH, mechanical stress, or enzyme presence [26,27]. These materials open new avenues for personalized and dynamic CAD therapies.

For instance, shape-memory polymers (SMPs) can expand or contract in response to temperature changes, enabling minimally invasive delivery and self-deployment of stents and scaffolds [28]. SMP-based scaffolds have demonstrated controlled recovery forces suitable for maintaining arterial patency while gradually degrading [29].

Other systems utilize pH- or enzyme-sensitive linkages within polymer chains, triggering drug release specifically in diseased vascular regions where local pH or enzyme concentrations differ from healthy tissue [30]. Such selective delivery minimizes systemic side effects while improving therapeutic efficacy.

Emerging designs integrate conductive or electroactive polymers (e.g., polypyrrole or polyaniline derivatives), potentially allowing real-time modulation of drug release under external electrical stimuli [31]. These systems could provide on-demand therapy based on patient needs or external clinician input.

While promising, challenges remain: ensuring biocompatibility of responsive moieties, achieving predictable behavior in complex biological environments, and scaling up synthesis to reproducible clinical-grade materials [32].

Surface Functionalization and Bioactivity Enhancement

Surface properties of polymer-based devices are critical in modulating biological responses such as thrombosis, inflammation, and endothelialization [33,34]. Advanced surface functionalization strategies directly address these challenges.

Heparinization — covalent attachment or layer-by-layer deposition of heparin — imparts anticoagulant properties, reducing platelet adhesion and early thrombus formation on stent surfaces [35]. Studies have shown that heparin-functionalized PLLA scaffolds achieve faster endothelial coverage compared to unmodified controls [36].

Nitric oxide (NO)-releasing polymers represent another innovation: NO inhibits platelet aggregation and smooth muscle proliferation while promoting endothelial cell migration [37]. NO donors, such as diazeniumdiolates or S-nitrosothiols, can be chemically linked to polymer backbones or blended into coatings for sustained release [38].

Beyond antithrombotic strategies, biofunctionalization with peptides or antibodies that capture circulating endothelial progenitor cells (EPCs) accelerates reendothelialization [39]. Common ligands include vascular endothelial growth factor (VEGF) and antibodies targeting CD34 or CD133 surface markers [40]. These techniques increasingly use site-selective conjugation and click chemistry to achieve stable and oriented attachment of bioactive molecules, improving both efficacy and reproducibility [41]. While successful at preclinical stages, the translation of these surface-engineered polymers faces hurdles including long-term stability, potential immunogenicity, and process scalability [42].

Polymeric Nanoparticles and Drug Delivery Systems

Beyond structural scaffolds and stents, advances in polymer chemistry have enabled the development of polymeric nanoparticles and micelles for targeted drug delivery in coronary artery disease (CAD) [43]. These systems aim to deliver therapeutic agents—such as anti-inflammatory drugs, anticoagulants, or growth factors—directly to atherosclerotic plaques, enhancing efficacy while reducing systemic side effects [44]. Common materials include biodegradable polymers like poly (lactic-co-glycolic acid) (PLGA), polycaprolactone (PCL), and PEGylated copolymers, chosen for their controlled degradation profiles and established safety records [45]. Through copolymerization and surface functionalization, researchers have improved particle stability, circulation time, and plaque-targeting specificity [46].

Stimuli-responsive nanoparticles, designed to release drugs in response to changes in pH or enzymatic activity within plaques, offer more precise therapy [47]. For instance, Zhang et al. (2023) developed pH-sensitive PLGA nanoparticles releasing statins specifically in inflamed vascular regions, resulting in localized therapeutic effects [48]. Polymeric micelles and dendrimers further enable encapsulation of hydrophobic drugs, improving solubility and controlled release kinetics [49]. Meanwhile, nanocomposites combining polymers with inorganic nanoparticles, like iron oxide or gold, introduce imaging capabilities for theranostic applications—simultaneous therapy and diagnosis [50]. Although still largely in preclinical stages, polymer-based nanoparticles show promise for minimally invasive, plaque-targeted treatment and could complement existing interventions such as stents and scaffolds [51]. Translational challenges include scaling up synthesis, ensuring reproducible particle size distribution, and confirming long-term safety [52].

Emerging Composite and Hybrid Materials

To overcome the limitations of single-component polymers, recent research has focused on composite and hybrid materials that integrate polymers with inorganic fillers, bioactive molecules, or metals [53]. These materials aim to combine the flexibility and processability of polymers with the mechanical strength

and functional properties of additives. For example, adding magnesium hydroxide nanoparticles to PLLA scaffolds neutralizes acidic degradation byproducts, enhancing biocompatibility and reducing local inflammation [54]. Similarly, blending PLLA with polycaprolactone (PCL) improves flexibility and reduces brittleness without sacrificing radial strength [55].

Nanocomposite coatings, incorporating graphene oxide, titanium dioxide, or hydroxyapatite, have been explored to improve mechanical reinforcement and add bioactivity [56]. In drug-eluting stents (DES), dual-layer composite coatings separate drug release control from hemocompatibility layers, offering more precise therapeutic modulation [57]. Researchers have also investigated electroactive polymer composites, where conductive polymers such as polypyrrole are integrated with biodegradable matrices, enabling potential applications in electrically controlled drug delivery or tissue regeneration [58]. Despite encouraging preclinical results, composite and hybrid materials face challenges such as uniform dispersion of fillers, interfacial compatibility, and maintaining biodegradability alongside added functionality [59]. Further optimization of synthesis methods, alongside rigorous in vivo evaluation, is essential for clinical translation.

CONCLUSION

Advances in polymer chemistry have profoundly transformed the management of coronary artery disease (CAD), offering safer, more effective, and increasingly personalized therapeutic solutions. Through careful control of molecular architecture, copolymer design, and functionalization strategies, researchers have developed drug-eluting stents with improved drug release kinetics, bioresorbable vascular scaffolds that safely degrade after vessel healing, and smart polymer systems capable of dynamic, stimulus-responsive behavior. Surface engineering approaches—such as heparinization, nitric oxide release, and endothelial progenitor cell capture—have further enhanced hemocompatibility and accelerated reendothelialization, addressing key clinical challenges like late thrombosis. The integration of biodegradable polymers with nanoparticles, nanocomposites, and electroactive materials has extended polymer applications beyond structural support to targeted drug delivery and even theranostics. Despite remarkable progress, significant challenges remain before next-generation polymeric devices can reach routine clinical practice. These include ensuring reproducible large-scale synthesis, long-term safety validation, and navigating complex regulatory pathways. Collaborative efforts across polymer chemistry, bioengineering, and clinical research will be crucial to translate these laboratory innovations into tangible improvements in patient care. Overall, the convergence of polymer chemistry and cardiovascular medicine holds great promise. As new materials and fabrication strategies emerge, polymer-based devices and delivery systems are expected to play an increasingly central role in the prevention, treatment, and long-term management of CAD—ultimately improving both survival and quality of life for millions of patients worldwide.

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