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# Review of polyethylenimine through ring-opening polymerization reactions and its application in $CO_2$ capture

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ABSTRACT

Despite numerous challenges and a variety of ring-opening polymerization techniques employed, polyethylenimine (PEI), either in branched or linear forms with various molecular weights, finds extensive applications. These applications include, but are not limited to, non-viral gene transfection, antimicrobial and antibacterial coatings, chelation, materials templating, and carbon dioxide ($CO_2$) capture. Nevertheless, PEI faces certain limitations, including issues related to biodegradability, non-specificity, cytotoxicity, and size constraints. Moreover, the synthesis of PEI encounters numerous challenges, such as controlling molecular weight, degree of branching, material toxicity, and sensitivity to air and impurities. The use of PEI for $CO_2$ capture has garnered significant attention; however, it still faces some limitations and drawbacks, including volatility, toxicity, corrosion, leaching, scale-up challenges, and cost. This review article delves into the different methods for synthesizing various PEI structures (both linear and branched) through diverse ring-opening polymerization techniques, such as cationic, anionic, and organocatalytic methods. The second section of this review highlights recent advancements in the utilization of PEI for $CO_2$ capture and the various categories of supported PEI sorbents, namely impregnation, grafting, and in-situ polymerization. Also discussed are the applications of these adsorbents for direct air capture (DAC) at varying process conditions. This comprehensive review of the various ring-opening polymerization techniques for PEI synthesis and its subsequent use in carbon capture establishes a good framework for the advancement of materials for $CO_2$ capture. These materials have the potential to contribute to $CO_2$ abatement technologies towards curtailing global warming challenges and provide opportunities in the quest for optimal sorbents solutions.

## 1. Introduction

Polyethylenimine (PEI) or polyaziridine is a long alkyl chain molecule consisting of repeating units of ethyleneimine (aziridine) with primary, secondary, and tertiary amine groups distributed at different positions, including chain ends, branches, or backbone [1,2]. Since the 1930s, PEI has been manufactured on an industrial scale as a cationic polymeric material and has versatile applications in various fields including water treatment, textile and paper production, biomedical, pharmaceutical and materials science, separation and purification, ink and dyes, paper processing, adhesives, cosmetics, and detergents. PEI is extensively used in gene delivery due to its ability to condense DNA into nanoparticles and protect it from degradation [3,4]. This makes it a valuable tool in gene therapy and genetic research. PEI is also applied in drug delivery systems, tissue engineering, and as a component in various biomedical devices [5]. It can be used as a wet-strength additive for

*Abbreviations:* ABDMMS, 4-Aminobutyl)dimethylmethoxysilane; ACN, Acetonitrile; AM, Acrylamide; APTES, 3-Aminopropyltriethoxysilane; APTMS, Aminopropyltrimethoxysilane; AROP, Anionic ring opening polymerization; AZ, Aziridine; BET, Brunauer-Emmett-Teller; CCS, Carbon capture and storage; CNT, Carbon nanotubes; CROP, Cationic ring opening polymerization; DAC, Direct air capture; DCM, Dichloromethane; DFT, Density functional theory; DMF, Dimethylformamide; DTG, Derivative thermogravimetric; DMSO, Dimethyl sulfoxide; GMA, Glycidyl methacrylate; GPS., 3-glycidoxypropyltrimethoxysilane.; GTMS, 3-glycidoxypropyltrimethoxysilane; HG, Hydroxylated graphene; LPEI, Linear polyethyleneimine; MOF, Metal organic framework; MPTMS, Sodium 3-mercaptopropyl trimethoxysilane; MsMAz, Methyl-N-methylsulfonyl aziridine; NHC, N-heterocyclic carbene; NMR, Nuclear Magnetic Resonance; *o*NsAz, (*o*-nitrophenylsulfonyl) aziridine; OROP, Organocatalytic ring opening polymerization; PEI, Polyethyleneimine; *p*NsAz, (*p*-nitrophenylsulfonyl)aziridine; PPI, Polypropylenimine; Ppm, Part per million; POPs, Porous organic polymers; SIPGP, Self-initiated photo-grafting and photo-polymerization; TGA, Thermogravimetric analyzer; THF, Tetrahydrofuran; TPI, 3-triethoxysilylpropyl isocyanate; TsMAz, Methyl tosyl aziridine; TsPhAz, Phenyl-N-tosylaziridines.

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