

**SYSTEMATIC STUDY OF PSS MOLECULAR WEIGHT EFFECTS ON
PEDOT:PSS THERMOELECTRIC PERFORMANCE**

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Global electricity consumption is increasing at an average annual rate of approximately 2.4%, while nearly 76% of this demand is still supplied by fossil fuels, the primary contributors to greenhouse gas emissions. Simultaneously, about 60% of the world's energy is dissipated as waste heat from industrial processes, engines, and electronic systems, representing a widely available yet underexploited energy resource. Thermoelectric generators offer a promising strategy for harvesting this waste heat, as they directly convert temperature gradients into electrical energy via the Seebeck effect.(1) However, conventional inorganic thermoelectric materials, such as tellurides and semiconductor alloys, suffer from drawbacks including high production costs, limited elemental availability, mechanical rigidity, and, in some cases, toxicity. Conductive polymers have therefore emerged as attractive alternatives due to their intrinsic flexibility, low-cost and solution-based processability, scalability, and reduced environmental impact.(2) Among them, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) stands out because of its high chemical stability, excellent aqueous processability, and

tunable electrical properties through synthetic control. Despite significant progress in PEDOT:PSS based conductive inks, the role of PSS molecular weight (Mw) in governing the thermoelectric performance of PEDOT:PSS remains insufficiently understood. Here, we systematically investigate the direct influence of PSS molecular weight on the thermoelectric properties of PEDOT:PSS, varying Mw from 23 kDa to 157 kDa during synthesis. The results clearly demonstrate that the molecular weight of PSS plays a decisive role in determining the electrical and thermoelectric behavior of the material. Increasing the PSS molecular weight promotes the formation of larger and more interconnected PEDOT-rich domains, facilitating charge transport and leading to enhanced electrical conductivity. Consequently, the power factor ($PF=S^2 \cdot s$) is significantly improved with increasing Mw. The ink synthesized using the highest PSS molecular weight (157 kDa) exhibited the best thermoelectric performance, achieving a power factor of approximately $1.32 \pm 0.03 \mu W/(K^2 m)$, an electrical conductivity (s) of $113.32 \pm 0.09 S/cm$, and a Seebeck coefficient (S) of $10.81 \pm 0.05 \mu V/K$. These findings provide clear evidence that precise control of PSS molecular weight is a key synthetic parameter directly governing the thermoelectric properties of PEDOT:PSS, reinforcing its potential as a promising material for waste heat-to-electricity conversion applications.

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Palavras-chave: pedot:pss; pss molecular weight (mw); power factor.