**[Illuminating the rigid amorphous fraction of semiconducting polymers, and its pivotal influence on Optoelectronic Performance](https://acs.digitellinc.com/acs/live/22/page/677/6?eventSearchInput=&eventSearchDateTimeStart=&eventSearchDateTimeEnd=&eventSearchTrack%5b%5d=201" \l "sessionCollapse394101)**

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Nearly all semicrystalline polymers possess two types of amorphous domains, the mobile amorphous fraction (MAF) and the rigid amorphous fraction (RAF), which exhibit distinct glass transition phenomena and govern material performance. Yet, for semiconducting polymers, there is little information about the morphological landscape surrounding these transitions at device relevant thickness and hence their identity and the role they play in device performance is obscured and of great debate. Here, we not only elucidated the identity of these transitions (backbone Tg and RAF Tg) but also the mechanism by which they control material performance in four representative semiconducting polymers (P3HT, DPPT-C8C10, N2200, and PFFBT-4T). This was first achieved through temperature dependent *in-situ* ellipsometry, whereby, the thermal expansion, optical profile, and conformation were all assessed. The contribution of RAF to the thermal expansion was observed to be 20% for P3HT and 75% for the remaining high-performance polymers. This was attributed to their high rigidity and paracrystalline disorder which promote crystalline-amorphous connectivity associated with RAF. The conformation and optoelectronic behavior were further assessed utilizing temperature dependent DFT simulation, GIWAXS, solid-state NMR, and OFET charge mobility, thus providing the 1st holistic picture of the influence of RAF on the performance of semiconducting polymers. Our work demonstrates that the RAF is a critical component governing polymer connectivity and subsequently optoelectronic and mechanical behavior.

