Investigation of the Morphology of Conducting Polymers Using SAXS

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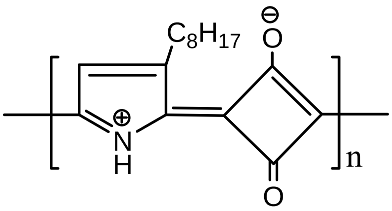
Polymers with extended π-electron conjugation have unique intrinsic conductivity and are classified as conjugated polymers or conducting polymers (CP). Like semiconductors, CP can produce novel electrical, optical and magnetic phenomena and be translated into various useful devices in optoelectronic, sensor, and biomedical applications; CP thus attract attention and remain at the forefront in many areas of development, but CP differ from semiconductors in many respects, such as charge transport, structure etc. An important point to note about conventional semiconductors is that they generally have a rigid structure stemming from four-fold or higher coordination of a central metal atom. The removal or addition of electrons in rigid semiconductors leads to charge transport. The electrical conductivity in a CP is interpreted to originate from extended overlap of the π–orbitals intrinsic to these organic materials. As an important difference, the polymeric nature and two-fold coordination of CP allows for greatly increased flexibility and, hence, susceptibility to structural distortion; such distortion might influence its intrinsic conductivity. Development of a CP requires an understanding of the detailed morphology and its variation under manipulation. This topic has hence become a focus of research from both scientific and practical points of view. In this work, we investigate the morphology of CP using the small angle X-ray scattering (SAXS) technique.

The target ppolymer in this work is poly(3-n-octylpyrrole)squaraine; which was produced from polycondensation of squaric acid and 3-n-octylpyrrole in an azeotropic solution of 1-butanol and benzene. This polysquaraine possesses a zwitterionic repeating unit, as illustrated in Scheme 1. For the formation of squaraine with squaric acid, the derivatives of pyrrole effects the polycondensation process and determine the backbone structure in polysquaraine. Thus, it is interesting to study the derivative effect in morphology structure for this polysquaraine condensation.



Scheme 1: Representative repeating unit of poly(3-n-octylpyrrole)squaraine

The morphology of the target polymer in solution can be controlled as the linear and folding structures. The morphology of this zwitteionic CP can be distinguished by SAXS. The SAXS curve of the linear polymer in solution, displayed as the blue line in Fig. 1; whereas, the folding polymer appeared as the red curve in Fig. 1. The radius of gyration (*Rg*) of the polymer can be determined from the plot of $\ln I(Q)$ versus Q^2 in low Q range; the value of *Rg* can thus be extracted from the slope ($-Rg^2/3$) of this plot. By this means, we obtained the *Rg* values of the linear and folding polymers to be 22±2 nm and 16±2 nm, respectively. The result ambiguously demonstrates that two conformers might be present in solution for this zwitterionic polymer.

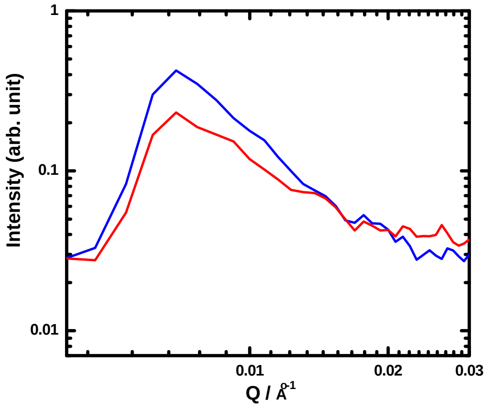


Fig. 1: Small angle X-ray scattering curves of poly(3-n-octylpyrrole)squaraines in trichloromethane: the free zwitterionic polymer in solution is present in an almost linear form (blue curve) and the polymer is exist as a folded form (red curve).