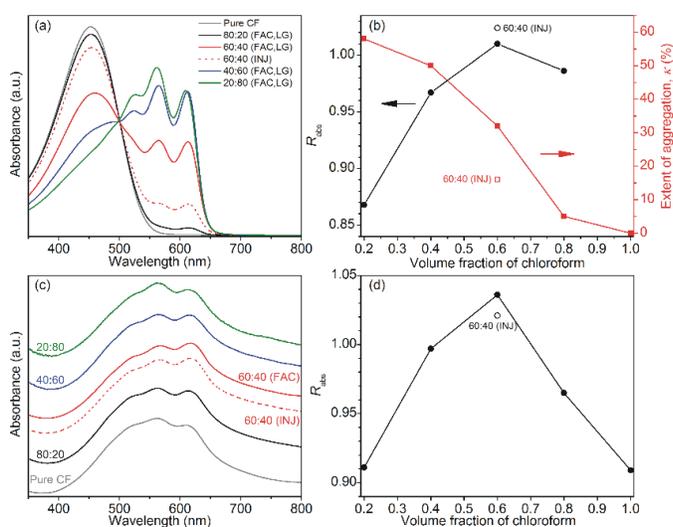


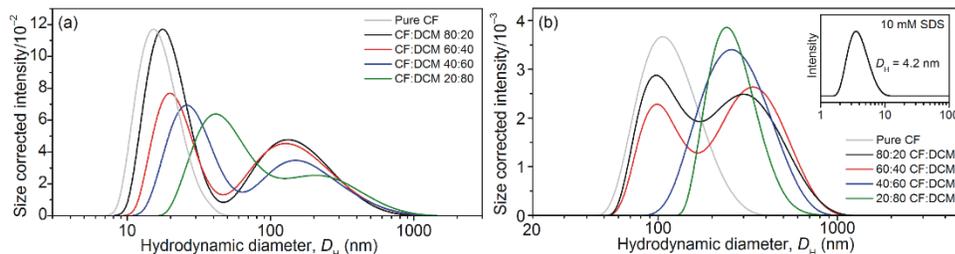
Several techniques have been developed to direct the growth of P3HT aggregates and nanostructures in the liquid phase.<sup>[1-7]</sup> Our group primarily focuses on mixed solvent systems to control the assembly of P3HT *via* the addition of poor or marginal organic solvents to a solution of well-dissolved, amorphous P3HT. Colloids of P3HT can also be generated using the *mini-emulsion method*,<sup>[8]</sup> wherein the organic solvent is removed, e.g., by heating, from a P3HT solution that has been suspended in a solvent that is immiscible with P3HT and the solvent in the solution. The resultant P3HT emulsions are typically stabilized by surfactants. Because P3HT is insoluble in water, the mini-emulsion method is particularly effective for preparing stable aqueous suspensions of P3HT.

In summer 2018 we studied the characteristics of aqueous colloids of P3HT stabilized by the sodium dodecylsulfate (SDS) surfactant. The colloids are processed from aggregate dispersions of P3HT that we fabricated in several solvent mixtures of chloroform (CF) and dichloromethane (DCM) using an interfacial (FAC) growth technique.<sup>[9]</sup> We used UV/Vis absorption spectroscopy and dynamic light scattering techniques to investigate, and compare, the properties of the P3HT aggregate dispersions in CF:DCM and the aqueous colloids. We also conducted nanoelectrochemical measurements to assess the electrophoretic mobility, zeta-potential, and conductivity of the dispersions and colloids.



**Figure 1.** (a) UV/Vis absorption spectra and (b) the extent of aggregation (red squares) and  $R_{abs}$  values (black circles) of aggregate 1 mg/mL dispersions of P3HT in CF:DCM solvent mixtures. The open symbols in (b) correspond to  $R_{abs}$  and  $\kappa$  in the 60:40 CF:DCM INJ dispersion. (c) UV/Vis spectra of the aqueous P3HT colloids prepared using the aggregate dispersions in (a). The spectra have been vertically offset for clarity. (d)  $R_{abs}$  values for the colloid dispersion in (c), where the open symbol corresponds to the colloid prepared using the 60:40 CF:DCM INJ dispersion.

The intrachain order,  $R_{abs}$ , and the extent of aggregation ( $\kappa$ ) were calculated from the UV/Vis spectra using the methods developed by Spano and co-workers.<sup>[10]</sup> Larger  $R_{abs}$  values are indicative of greater intrachain disorder, wherein  $R_{abs} > 1$  are ascribed to highly ordered *J*-type aggregates. The results for the aggregate dispersions and aqueous colloids of P3HT are shown in Figure 1. In Figure 1(a)-(b) we observe a monotonic increase in  $\kappa$  with increasing volume of the poor solvent (DCM) and a maximum  $R_{abs}$  value in 60:40 CF:DCM. In the aqueous colloidal dispersions in Figure 1(c)-(d) the  $R_{abs}$  trend is similar to that of the aggregate dispersions in Figure 1(b). Thus, in general, the intrachain characteristics of the dispersions are indeed transferred to the aqueous dispersions, but the  $R_{abs}$  values in the colloids are consistently higher than the corresponding dispersion.



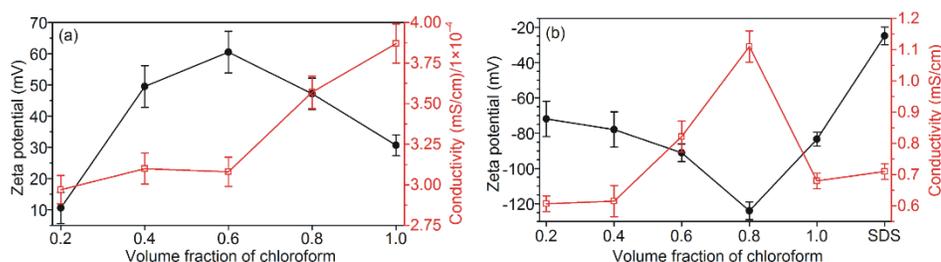
**Figure 2.** Size corrected DLS scattering intensity of (a) pure P3HT aggregate dispersions in CF:DCM mixtures and (b) aqueous P3HT/SDS colloids. The inset in (b) shows the PSD of a 10 mM SDS solution.

The size corrected (fractional) DLS scattering intensity,  $I_{corr} = I_{scatt}/D_H$ , of the dispersions and colloids are shown in Figure 2(a) and 2(b), respectively. The size distribution of the aggregate dispersions are all bimodal, wherein the band at lower  $D_H$  is consistent with residual amorphous P3HT, smaller dimers, trimers, etc., and the band at higher  $D_H$  corresponds to larger aggregates. As the amount of DCM increases the smaller  $D_H$  bands monotonically shifts to larger  $D_H$ , which is consistent with an increase in the extent of aggregation in Figure 2(b) and the growth of larger

P3HT aggregates. The behavior of PSDs of the aqueous colloids in Figure 2(b) is notably different than the dispersions in Figure 2(a). The 40:60 and 20:80 CF:DCM dispersions yield unimodal distributions, which become more narrow and shift to smaller  $D_H$  with increasing volume fraction of DCM in the mixture used to induce aggregation. These changes in the modality of the PSDs are tentatively ascribed to the effect of variations of the CF:DCM solvent composition on the formation of the colloids.

The zeta potential ( $\zeta$ ) reveals information about the electrostatic repulsive forces and surface potential of the colloids and nanoparticle dispersions.<sup>[11]</sup> Typically,  $\zeta$  is used to assess the stability of colloids, wherein larger  $\pm\zeta$  values are associated with more stable colloids, i.e.,  $\zeta$  values closer to zero are highly unstable. Because this our first attempt to apply this technique to these systems, we are primarily concerned with correlations between  $\zeta$  and conductivity and the properties of the liquid phase dispersions and colloids.

**Figure 3.** Zeta potential ( $\zeta$ ) and conductivity ( $\sigma$ ) of (a) aggregate dispersions of P3HT in CF:DCM and (b) aqueous colloids prepared using the CF:DCM dispersions in (a).



The zeta potential and conductivity of aggregate dispersions of P3HT in CF:DCM and aqueous colloids are plotted in Figure 3. The  $\zeta$  trend in Figure 3(a) is similar to  $R_{abs}$  in Figure 1(b), and indeed we find a strong linear correlation  $R_{abs}$  and  $\zeta$  in the aggregate dispersions. This trend may be interpreted in terms of (1) the relative stability of the dispersions or (2) the surface charge of the P3HT aggregates in the CF:DCM mixtures. With respect to the latter, if we interpret  $\zeta$  as measure of surface charge, the higher surface charge may be attributable to the higher structural order, i.e., lower conformational disorder, of the aggregates. In contrast to positive zeta potentials of the aggregate dispersions, the  $\zeta$  values of the aqueous colloids are all negative. The  $\zeta$  and  $\sigma$  trends are notably different for the colloids. The  $\sigma$  values are much larger in the colloids and unlike the dispersions, there is not a clear linear correlation between  $\zeta$  and  $R_{abs}$ . However,  $\zeta$  still exhibits a peak, albeit corresponding to 80:20 CF:DCM, which monotonically increases with increasing DCM in the solvent mixture used to fabricate the aggregate dispersion.

This summer the grant funded the research of three undergraduate students: two juniors and one sophomore. For all three students, the project was their first experience with independent research; thus, work on this project was a significant step in their education and development as scientists. All three students excelled in the lab and we currently have one paper under review and a second manuscript is in preparation. For me, professionally, this would make eight papers in peer-reviewed journals that resulted from work funded by the ACS-PRF grant. In October 2018 the students will be presenting their work at Southeast Regional Meeting of the American Chemical Society (SERMACS) in Savannah, GA. The project was instrumental in advancing the students understanding, appreciation and interest in scientific research, as well as their skills in the lab. Two of the students are continuing research in the lab during the 2018-2019 academic year, and they are currently applying to graduate programs to pursue their Ph.D.s in chemistry. Undoubtedly, their work on this project, involvement in the writing process, and oral dissemination of results at the SERMACS conference, will be beneficial to these students in their future educational and professional endeavors.

## References

- [1] Oosterbaan, W., Vrindts, V., Berson, S., Guillerez, S., Douheret, O., Ruttens, B., D'Haen, J., Adriaenssens, P., Manca, J., Lutsen, L., Vanderzande, D., *J. Mater. Chem.* **2009**, *19*, 5424-5435.
- [2] Roehling, J. D., Arslan, I., Moule, A. J., *J. Mater. Chem.* **2012**, *22*, 2498-2506.
- [3] Martin, T. P., Wise, A. J., Busby, E., Gao, J., Roehling, J. D., Ford, M. J., Larsen, D. S., Moulé, A. J., Grey, J. K., *J. Phys. Chem. B* **2012**, *117*, 4478-4487.
- [4] Baghgar, M., Labastide, J., Bokel, F., Dujovne, I., McKenna, A., Barnes, A. M., Pentzer, E., Emrick, T., Hayward, R., Barnes, M. D., *J. Phys. Chem. Lett.* **2012**, *3*, 1674-1679.
- [5] Scharsich, C., Lohwasser, R. H., Sommer, M., Asawapirom, U., Scherf, U., Thelakkat, M., Neher, D., Köhler, A., *J. Polym. Sci. Pol. Phys.* **2012**, *50*, 442-453.
- [6] Zhao, K., Xue, L., Liu, J., Gao, X., Wu, S., Han, Y., Geng, Y., *Langmuir* **2010**, *26*, 471-477.
- [7] Potai, R., Kamphan, A., Traiphol, R., *J. Polym. Sci. Pol. Phys.* **2013**, *51*, 1288-1297.
- [8] Tan, B., Li, Y., Palacios, M. F., Therrien, J., Sobkowicz, M. J., *Colloids Surf., A* **2016**, *488*, 7-14.
- [9] Marni, S., David, B., *J. Polym. Sci. Pol. Phys.* **2018**, *56*, 999-1011.
- [10] Clark, J., Chang, J.-F., Spano, F. C., Friend, R. H., Silva, C., *Appl. Phys. Lett.* **2009**, *94*, 163306.
- [11] Bhattacharjee, S., *Journal of Controlled Release* **2016**, *235*, 337-351.