

Polymer Physics
Quiz 10
March 19, 2021

Liu C, Hu W, Jiang H, Liu G, Han CC, Sirringhaus H, Boue F, Wang D, *Chain Conformation and Aggregation Structure Formation of a High Charge Mobility DPP-Based Donor-Acceptor Conjugated Polymer* Macromolecules **53** 8255-8266 (2020) did SANS, SALS, and DLS on a conjugated polymer DPPDTT in chloroform (good solvent) and in 1,2-dichlorobenzene (moderately poor solvent) in order to understand the aggregation phenomena in good and moderately poor solvents. Conjugated polymers have alternating double and single bonds which lead to isomeric states (swapping double and single bonds) so that the electrons in the bond are free to conduct along the chain (when doped). The double bond is a planar and rigid structure so conjugated polymers have large persistence lengths and are generally difficult to solvate. Melt processing is impossible.

- a) Figure 1 shows SANS data for DPPDTT in deuterated chloroform, and the SANS data for another conducting polymer which is less rigid, P3HT in deuterated dichlorobenzene at room temperature. Two slopes are seen, -1 and -1.6.
 - Explain why the slopes differ between the two polymers.
 - Is it possible to measure the coil size in any of these curves?
 - Why is deuterated solvent used?
- b) Figure 2 shows two Zimm plots for DPPDTT in chloroform. The first plot is strongly impacted by the absorption which dramatically increases with concentration.
 - Explain why, in the first Zimm plot, the bottom curve decreases while the other curves increase.
 - Equation (1) is the Zimm equation. What is the origin of the term $(1 + q^2 R_g^2/3)$?
 - Is this equation appropriate for the rod-like chains shown in Figure 1b?
- c) Table 1 shows the radius of gyration measured by light scattering.
 - Explain how this was measured.
 - Should it be possible to observe the Guinier regime (knee decay) in Figure 1 for the top three curves?
 - How can you explain this?
- d) Explain the behavior shown in Figure 8.
- e) Recently it has been found that polymers with stabilized free radicals can also conduct electricity under the right conditions. Yu I, Jeon D, Boudouris B, Joo Y Mixed Ionic and Electronic Conduction in Radical Polymers, Macromolecules **53** 4435-4441 (2020) describe some of the first studies on radical polymers (Boudouris won the Dillon Medal at the American Physical Society Meeting last Tuesday for this work). Explain the difference between these radical conductors and traditional conjugated polymers. From Boudouris' paper what are the advantages of radical polymers and what are the disadvantages?

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- a) *Figure 1 shows SANS data for DPPDTT in deuterated chloroform, and the SANS data for another conducting polymer which is less rigid, P3HT in deuterated dichlorobenzene at room temperature. Two slopes are seen, -1 and -1.6.*
-Explain why the slopes differ between the two polymers.
-Is it possible to measure the coil size in any of these curves?
-Why is deuterated solvent used?

These are power-law regimes. There are two options, the power, $P = -d_f$, the mass fractal dimension since $I \sim \text{mass}$ and $q \sim 1/\text{size}$ so $I \sim q^{-d_f}$. The other option is $I \sim q^{-4}$ which reflects surface fractals, if it is -4 it is a smooth sharp interface and the prefactor is S/V . If it is less steep than -4, like -3.8, it is a surface fractal of surface fractal dimension 6-slope. So for 6-4 the surface is 2D. For 3.8 it is 2.2 dimension, a rough surface.

Here we have -1 so $d_f = 1$ and it is a rod. The other is $d_f = 1.6$ which is close to 1.7 for a good solvent.

For the size of the coil you are looking for Guinier's Law so $G \exp(-q^2 R_g^2/3)$. That is a Gaussian, bell-shaped region. In a log-log plot this looks like a knee. One of these curves has such a knee the other doesn't. So you can get size in only one of the curves. The high- q knee reflects the primary structure, Kuhn length for instance, not the coil size.

You use deuteration for contrast in neutrons. D and H have the widest difference in contrast of any two elements. They are chemically almost identical. D isn't radioactive, you can drink D_2O with no ill effects, except you will weigh a bit more.

- b) *Figure 2 shows two Zimm plots for DPPDTT in chloroform. The first plot is strongly impacted by the absorption which dramatically increases with concentration.*
-Explain why, in the first Zimm plot, the bottom curve decreases while the other curves increase.
-Equation (1) is the Zimm equation. What is the origin of the term $(1 + q^2 R_g^2/3)$?
-Is this equation appropriate for the rod-like chains shown in Figure 1b?

The first curve is for $c = 0$, so the x-axis is just q^2 . Normally the intensity always decreases with q , so $1/I$ would increase with q , but the $c = 0$ curve is an extrapolated curve from each of the other q values with different concentrations. So it wasn't measured. Because the scattered intensity increases linearly with concentration but the absorption also increases with concentration and the intensity decreases with q but the absorption remains almost flat, the net effect is that at higher q measured intensity increases for the extrapolated $c = 0$ curve. Here, $1/I$ decreases. For the other curves the normal behavior of intensity decreasing with q ($1/\text{Intensity}$ increasing with q) is observed.

$1/\exp(-q^2Rg^2/3) = \exp(q^2Rg^2/3) \sim 1 + q^2Rg^2/3 + \dots$ at small qRg .

Since the equation reflects only Guinier's law (which applies to any object) and a Hildebrandt interaction parameter (which applies to any object) it should work for any object, including a rod.

- c) *Table 1 shows the radius of gyration measured by light scattering.*
-Explain how this was measured.
-Should it be possible to observe the Guinier regime (knee decay) in Figure 1 for the top three curves?
-How can you explain this?

Rg is obtained from Figure 2b from the extrapolated $c=0$ curve. $Rg^2/3$ is the slope of the blue square curve.

With $Rg = 20\text{nm}$ we expect to observe a Guinier regime at about $q = 2\pi/200\text{\AA} = 0.031 \text{\AA}^{-1}$. The plot in Figure 1 spans 0.006\AA^{-1} to 0.3\AA^{-1} so 0.03 should be in the middle of this plot and you should be able to easily resolve this radius of gyration in the SANS data. However, there is no indication of this size in the SANS data.

This is difficult to explain. Perhaps there is a thermodynamic difference between deuterated and hydrogenated chloroform.

- d) *Explain the behavior shown in Figure 8.*

Figure 8 demonstrates the agglomeration of DPPDTT chains in dichlorobenzene with a transition from rod like scattering (power-law decay of -1) to 3d structures with smooth interfaces (power-law decay of -4).

- e) *Recently it has been found that polymers with stabilized free radicals can also conduct electricity under the right conditions. Yu I, Jeon D, Boudouris B, Joo Y Mixed Ionic and Electronic Conduction in Radical Polymers, Macromolecules 53 4435-4441 (2020) describe some of the first studies on radical polymers (Boudouris won the Dillon Medal at the American Physical Society Meeting last Tuesday for this work). Explain the difference between these radical conductors and traditional conjugated polymers. From Boudouris' paper what are the advantages of radical polymers and what are the disadvantages?*

In conjugated polymers delocalization of the electrons allows conduction if the polymers are doped. The conjugated bonds are planar and lead to a rigid backbone which is difficult to process. They cannot be melt processed. Conduction is through pi-bonds which have homo and lumo electron states.

Radical conductors have delocalized electrons just like in a metal, so you form a conduction band above the fermi level. The trick is to have the stabilized free radical groups close enough to allow electron hopping between groups. You do not need doping. The free radical groups are

located in side groups so the main chain can be a conventional polymer such as polydimethyl siloxane or polymethylmethacrylate. The polymers are melt processed (extruded or injection molded) but require annealing for clustering of the free radical groups to form conductive pathways. The conductivity, while 9 orders higher than insulating materials, is still 3 orders lower than copper.