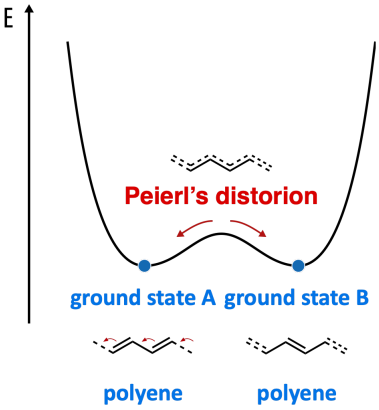
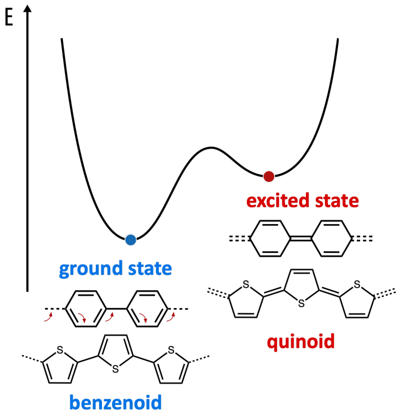
School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Organic Electronic Materials 2025 Exercise 5

Solutions

1. Using qualitative energy diagrams, represent the energy landscapes of polyacetylene and polythiophene, and draw the molecular structures corresponding to their different states. What is the difference between the ground states of these two polymers?

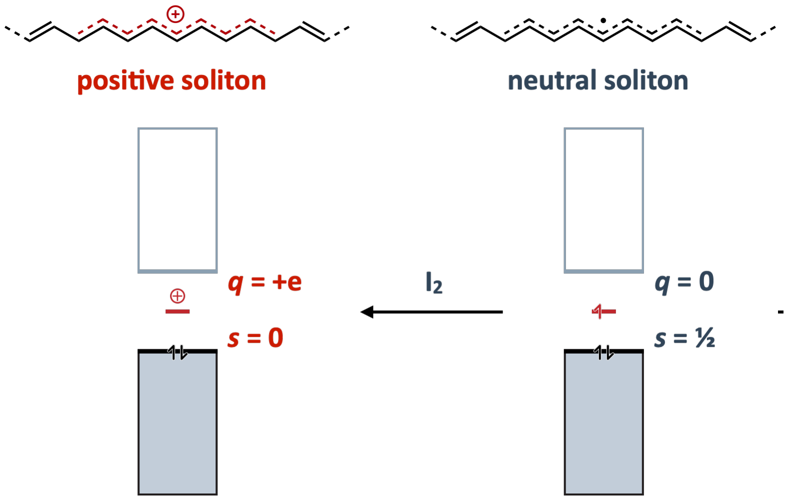




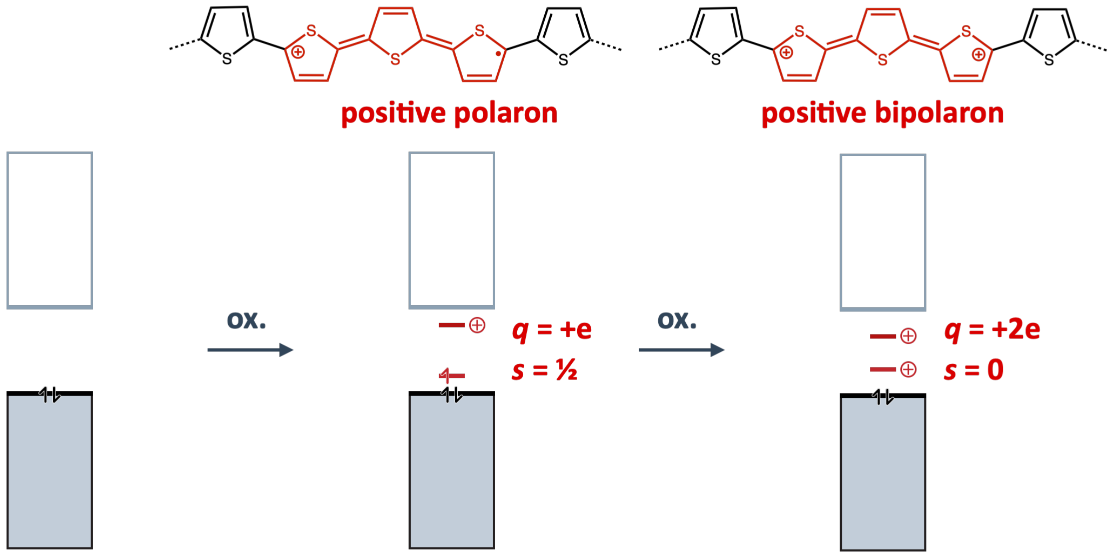
Compared to other π-conjugated polymer semiconductors, polyacetylene has two energetically and geometrically equivalent, degenerate ground states.

2. Draw the MO energy level diagrams of both polymers of question 1 when doped with a very small amount of an oxidant, and name the species formed in both cases. Draw their chemical structures and define what they are from an organic chemistry perspective.

Polyacetylene case: *Formed species: positive soliton (chemistry view: carbocation)*



Polythiophene case: *Formed species: positive polaron or bipolarons (chemistry view: radical cation or dication)*



3. Describe with your own words the Peierls’ distortion and what this causes in polyacetylene.

Peierls' distortion is a phenomenon in which a one-dimensional crystalline structure becomes distorted due to the presence of an odd number of electrons per unit cell. This distortion occurs because the electrons are unable to pair up, leading to a spontaneous shift in the positions of the atoms in the crystal lattice.

In polyacetylene, Peierls' distortion causes the carbon-carbon double bonds in the polymer chain to alternate in length, with some being longer and some being shorter than the average bond length. This results in a zigzag pattern in the chain, where each carbon atom is bonded to two different types of neighboring carbon atoms. This alternating pattern of bonds creates a band gap in the electronic *structure of the material, which makes it a semiconductor. This unique electronic structure is responsible for many of the interesting properties of polyacetylene, such as its high conductivity and potential applications in electronic devices.*

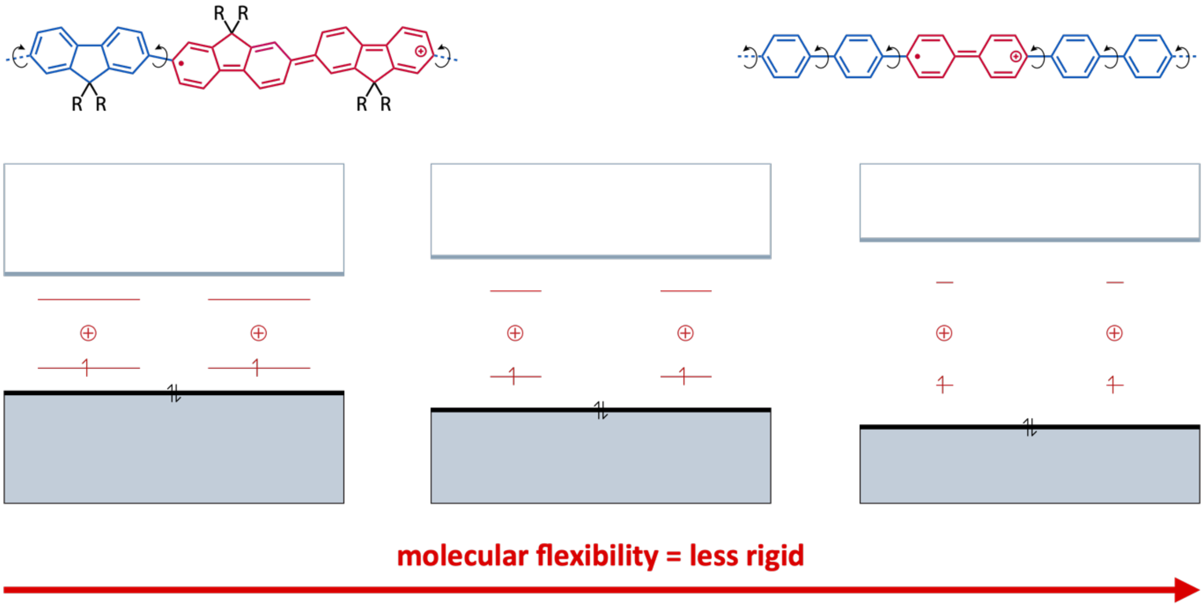
4. What are the characteristics of a soliton? What experimental technique provides strong evidence for its presence, and how does it work?

Neutral solitons are radicals with spin s = 1/2 and charge q = 0. ESR (electron spin resonance) spectroscopy can give evidence for the presence of this particle since it probes the unpaired spins.

5. What different factors may influence the correlation length of polarons/bipolarons?

The correlation length, which corresponds to the distance over which a polaron or bipolaron remains delocalized along a conjugated polymer chain, is influenced by temperature, crystallinity, steric substituents, and molecular rigidity as they can all influence the probability to have twists in the polymer chain.

6. Molecular flexibility affects the dynamic disorder in organic semiconductors which can in turn limit the delocalization of charge carriers. With the help of energy band diagrams and example molecular structures, explain why this happens.

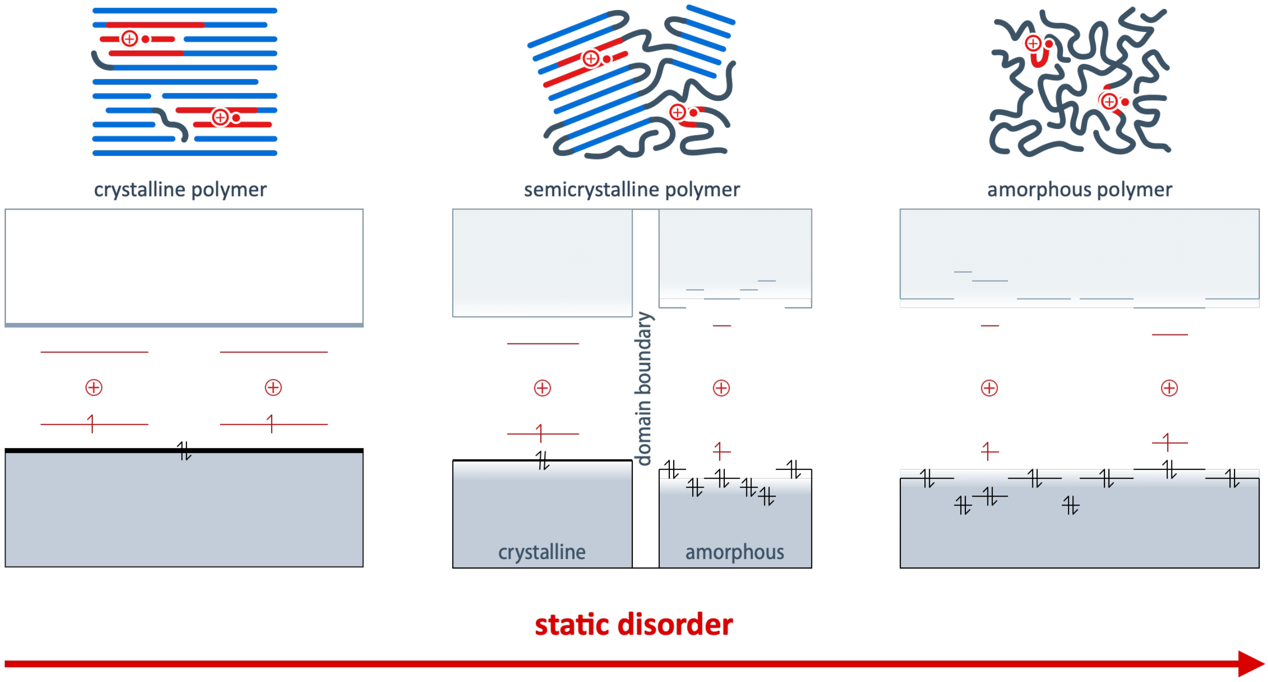


Molecular flexibility leads to dynamic disorder, meaning that the molecular conformations are constantly fluctuating due to thermal motion. These fluctuations cause variations in the π–π stacking distances and angles, as well as in the orbital overlap between neighboring molecules.

- *Rigid molecules like planar fused-ring systems (ex: pentacene) tend to show better delocalization and mobility. Energy bands are relatively narrow and ordered, facilitating delocalized band-like transport.*
- *Flexible molecules with long side chains or single bonds that allow rotations (ex: polythiophenes with flexible alkyl side chains) show more disorder and localization.*

Greater molecular flexibility introduces dynamic energetic disorder, reduces effective conjugation lengths, and increases localization of the charge carriers.

7. Draw the energy band diagrams of (i) a highly doped crystalline organic semiconductor and (ii) a highly doped amorphous organic semiconductor. Explain why you would expect the overall conductivity of the amorphous system to be lower than the crystalline system (assuming the same molecule and same operating temperature in both systems).



(i) Highly doped crystalline organic semiconductor:

- *Energy band diagram: Shows a broad, well-defined conduction band and valence band.*
- *Fermi level lies inside the conduction band (n-type doping) or valence band (p-type doping).*
- *Delocalized charge carriers allow for band-like transport, leading to high mobility.*

(ii) Highly doped amorphous organic semiconductor:

- *Energy band diagram: Shows localized states ("band tails") extending into the gap due to disorder.*
- *Fermi level lies among localized states rather than true extended bands.*
- *Transport is dominated by hopping between localized sites.*

Conductivity in the amorphous system is lower because:

- *Delocalization is reduced in disordered materials: carriers cannot move freely in extended states.*
- *Charge transport occurs mainly via thermally activated hopping, which is slower than band transport.*
- *The percolation paths for charge carriers are more tortuous and inefficient compared to the direct paths in a crystal.*

Reading suggestions:

- Electronic Processes in Organic Semiconductors: An Introduction (A. Köhler and H. Bässler, Wiley VCH 2015), Chapter 3.3: **Charge Carrier Transport**.
- Organic Electronics II (H. Klauk, Wiley VCH 2012), Chapter 3: **Charge Transport Theories in Organic Semiconductors** (R. Noriega, A. Saleo).
- V. Coropceanu *et al.*, *Chem. Rev.* **107**, 926, (2007); **Charge Transport in Organic Semiconductors**.