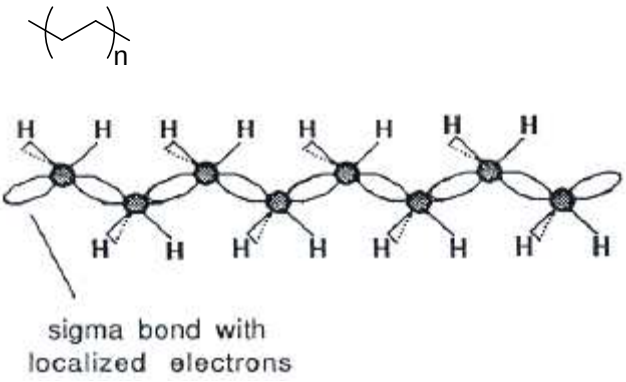
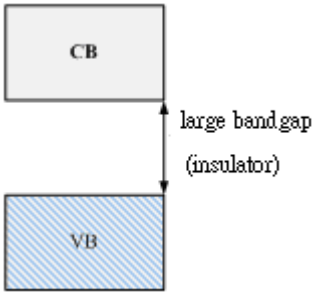
1. (a) From the point of view on chemical structure and electronic structure, please describe why polyethylene and polyacetylene are insulator and semiconductor, respectivyly.(10 points) (b) Explain why conjugated polymers always have color?
(5 points)
Ans：

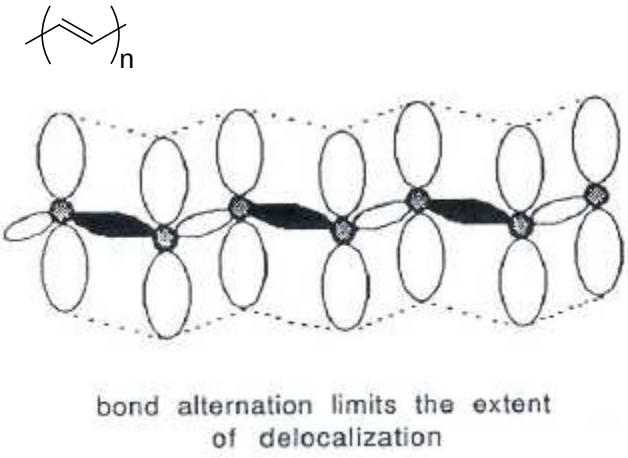
Polyethylene (2pts)

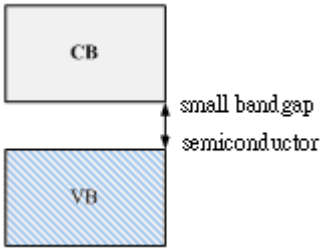




因爲 C 和 C 之間電子被”定域化(localiezd)”無法移動且是一個 sp^3 結構，故爲絕緣體。(3pts)

Polyacetylene (2pts)





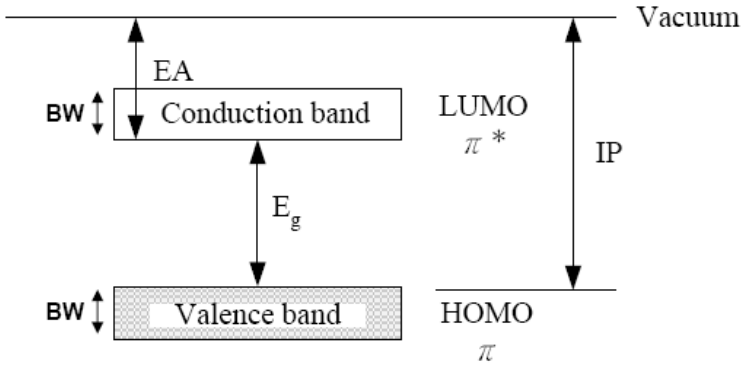
因爲 C 和 C 之間的 π 電子“未被定域化(delocalized)”且藉由 π 電子軌域的重疊因而降低了導帶與價帶之間的能量差，所以只要較小的能量就可以移動電子，所以是半導體。(3pts)

(b).

一般而言，幾乎所有的 conjugated polymers 的 band gap 都大於 1.5eV，而 valence band 與 conduction band 之間的能差(band gap)符合可見光能量範圍，因此 Visible spectrum absorption 會導致 conjugated polymers 有顏色。(5pts)

2. Please describe the definitions of ionization potential, electronic affinity, and bandwidth and draw the energy diagram fro them. (20 points)

Ans：



(Figure 11pts)

IP： ionization potential; 將電子從價帶頂層移到無窮遠處所需能量。(3pts)

EA：electronic affinity; 電子從無窮遠處到傳導帶所需能量。(3pts)

BW：band width; 價帶底層到價帶頂層的能量差。(3pts)

3. Please explain why conjugated polymers require high levels of doping to achieve high conductivity and compare with inorganic semiconductors, such as Si.(15 points)

Ans：

$\sigma = e \cdot n \cdot \mu$

σ : conductivity (S/cm)

n: carrier (e or h) density (cm^{-3})

μ : mobility (cm^2/VS)

e =1.6×10^{-19} C

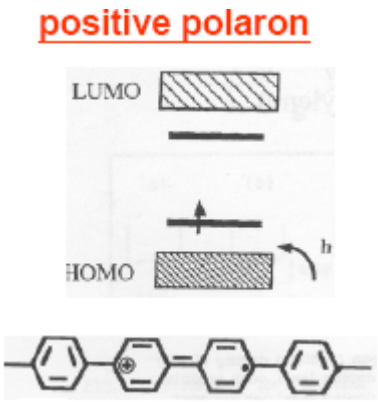
因爲無機物半導體 silicon (Si)具 3D 排列規則的結構，電荷很容易移動傳導(mobility 高)(5pts)，所以只需少量摻雜就可提高導電度；有機高分子通常是amorphous，電荷的傳遞只能透過 intrachain、interchain、和 intradomain 三種形式，基本上 mobility 不高(5pts)，所以必須要大量的摻雜才能提高導電度(5pts)。

4. (a) Please describe the definitions of soliton, polaron, and bipolaron. (10points) (b) If polyphenylene is doped by I_2, please describe the doping mechanism using polaron and bipolaron by chemical structures as well as by energy diagram. (20 points)

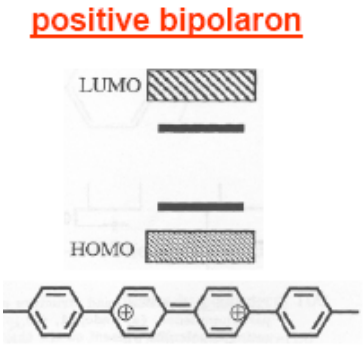
Ans：

(a). Take oxidation doping of a conjugated polymer for example:

polaron：The combination of a charged site coupled to a free radical via a local lattice distortion is called a polaron.(3pts)

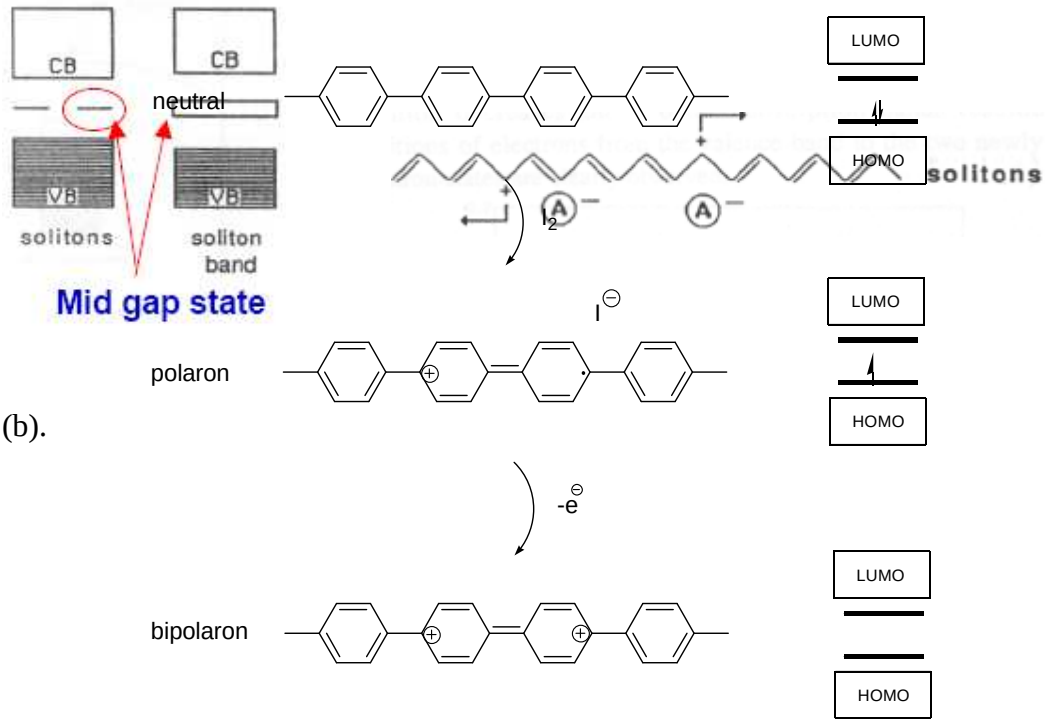


bipolaron：Upon further oxidation, an electron can be removed form the polaron, thus the free radical of the polaron is removed to create a dication which is comprised of two positive charges coupled through the lattice distortion. This dication is called bipolaron.(3pts)



Soltion: In the case of conjugated polymers with degenerated ground state (ex. Polyacetylene), further oxidation of polarons creates dications which are not bound to each other and can freely separate along the chain. This is called soliton.(4pts)

(b).



5. Describe the development of conjugated polymers (including discovery, synthesis, properties and applications). You can describe your answer as complete as possible. (20 points).

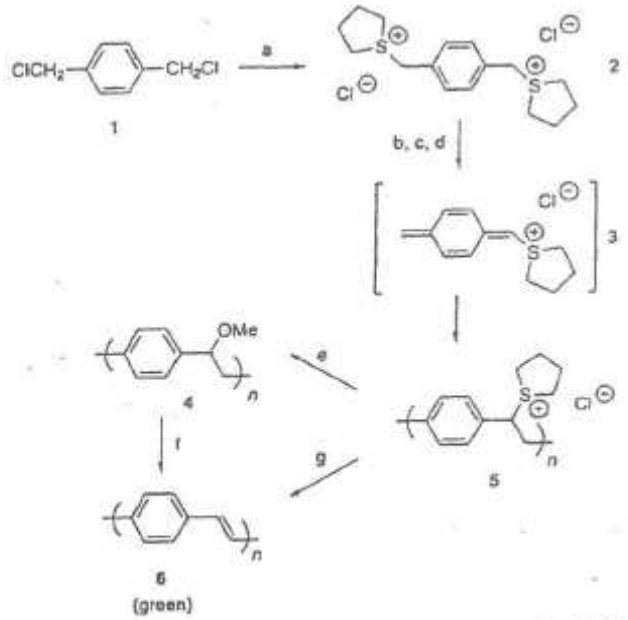
Ans：

Discovery：

對Conjugated polymers對大貢獻者2000年拿到Nobel prize的日本教授Shirakawa (白川英樹)、美國教授Heeger、MacDiarmid等三人。Shirakawa的研究團隊在一次的實驗中不小心把catalyst加入過量超過1000倍，使得本來該得到黑色粉末聚乙炔（順式聚乙炔），卻變成了銀白色的薄膜（反式聚乙炔），1976年與美國教授Heeger、MacDiarmid討論後發現經由dopping (I_2)後，polyacetylene 可以導電(增高了十億倍)，因此開啓conjugated polymer的研究。(5pts)

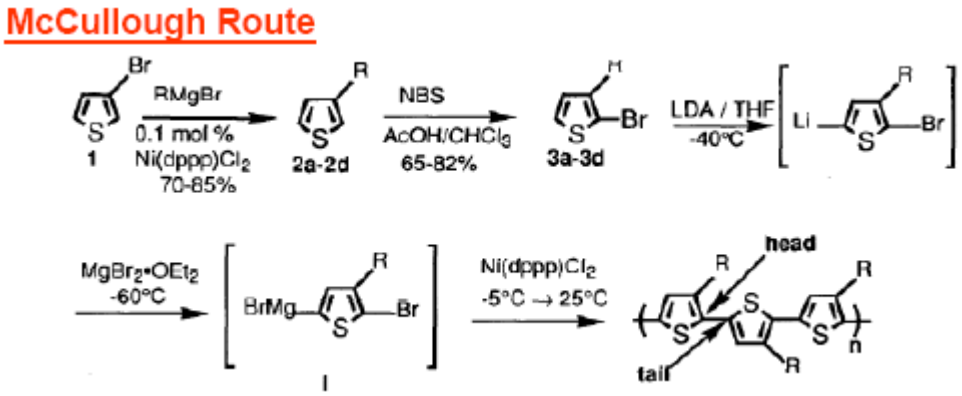
Synthesis：

(1). precursor method：以 PPV 爲例，先聚好 precursor polymer 後再以化學合成方法修飾，如下圖：(1pts)

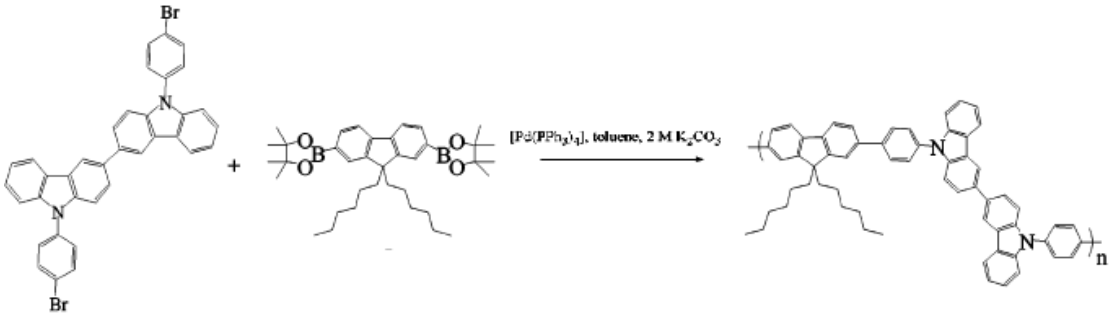


Scheme 1. Synthesis of PPV (6): a) tetrahydrothiophene, MeOH, 65 °C; b) NaOH, MeOH/H_2O or Bu_4NOH, MeOH, 0 °C; c) neutralization (HCl); d) dialysis (water); e) MeOH, 50 °C; f) 220 °C, HCl(g)/Ar, 22 h; g) 180–300 °C, vacuum, 12 h.

(2). Chain growth (addition)：以 P3HT 爲例，完成單體後再加入催化劑起始化單體，之後單體是一個一個慢慢的接上去，如下圖：(2pts)



(3). Step growth (condensation)：以 Suzuki coupling 爲例，兩種(或兩種以上)不同的單體之雙官能基雙溴及雙硼酯宰加入催化劑反應，會先得到 oligmer，oligmer 再與 oligmer 之間反應如此循環下去而得到高分子，如下圖：(2pts)



Properties：(每寫出一個就 1pts 共 5pts)

(1). Optical absorption spectra (UV-Vis)：conjugated polymers 在 ground state 的電子結構由 UV-Vis 照射後電子會從 $\pi \rightarrow \pi^*$ 因此會產生吸收峰。

(2). Photoluminescence spectra (PL)：當 conjugated polymers 的 ground state 電子被激發到 excited state 後，此時的有 1/4 的電子會以 singal 的形式以輻射衰退方式

回到 gorund state，而輻射衰退方式時間極快(約 10^{-9} 秒)因此可以觀察到螢光。

(3). Molecular weight：分子量回隨著聚合時間慢慢增長，但達一定程度時就不會再增長亦有可能會形成 gel。

(4). Viscosity：隨著分子量增大其 viscosity 會慢慢增加(也與分子本身的 rigid 有關，越 rigid 其 viscosity 越高)。

(5). Thermal：如 TGA，當熱裂解溫度越高其熱穩定性越好；DSC，越 rigid 或是分子量越高其 Tg (glass transition temperature)越高。

(6). Morphology：藉由 electron microscopy，如 AFM 可以觀察到 conjugated polymers 會有不同的型態(amophose、fiber...and so on.)。

Application：(每寫出一個就 1pts 共 5pts)
Solar cell、PLED、Biosensor、transistor、electrochromic、Nonlinear、memory、質子傳導模。