

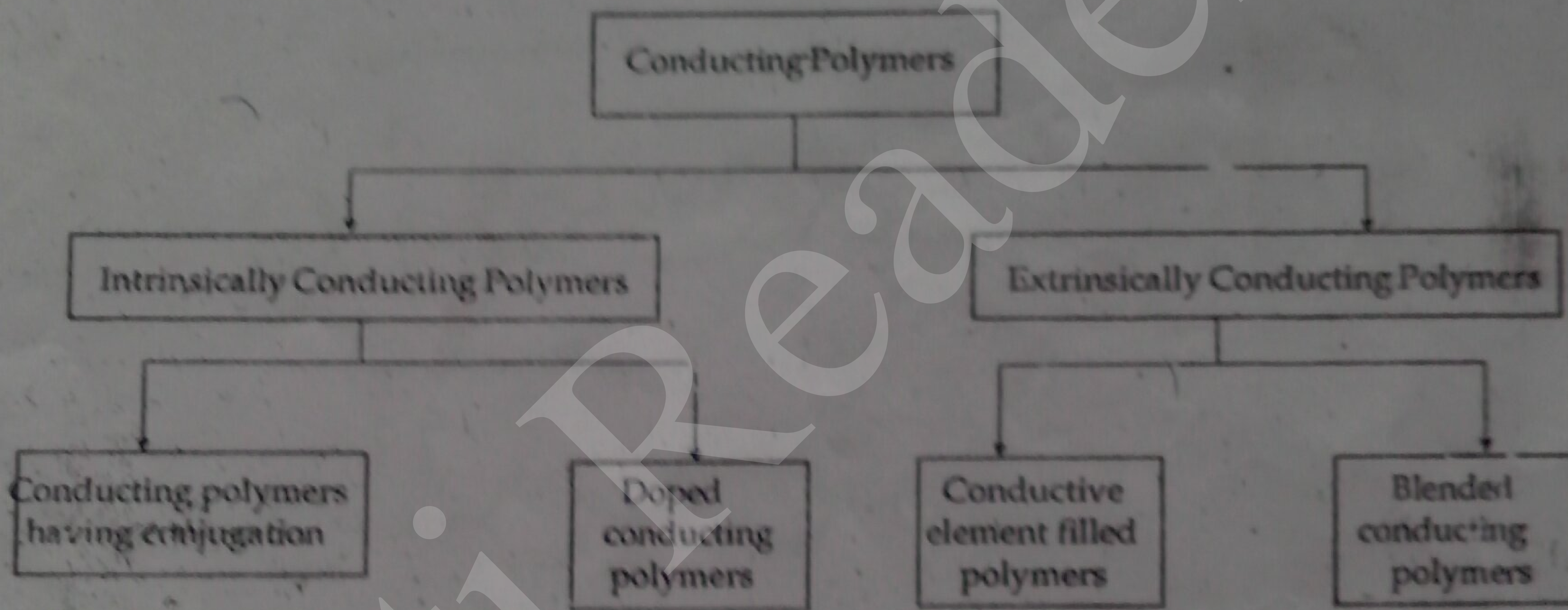
*Properties.* Polyacrylonitrile softens only slightly below its decomposition temperature of about 300 °C so it found little use as a plastic material. Moreover, it does not dissolve in its monomer so it cannot be shaped by bulk casting.

As it dissolves in solvents such as dimethylformamide and tetramethylenesulphone so it found wide use as fibers. *Orlon* is the trade name of polyacrylonitrile. Orlon fibers are resistant to water and are quick drying. These are more resistant to acid, gases than nylon.

*Applications.* Orlon fibers are used for manufacturing window shades. It can also be used as wool-like fiber for suits, bathing suits, sweaters etc.

### 3 CONDUCTING POLYMERS

A polymer which can conduct electricity is termed as conducting polymer. Conducting polymer can be classified into following types :



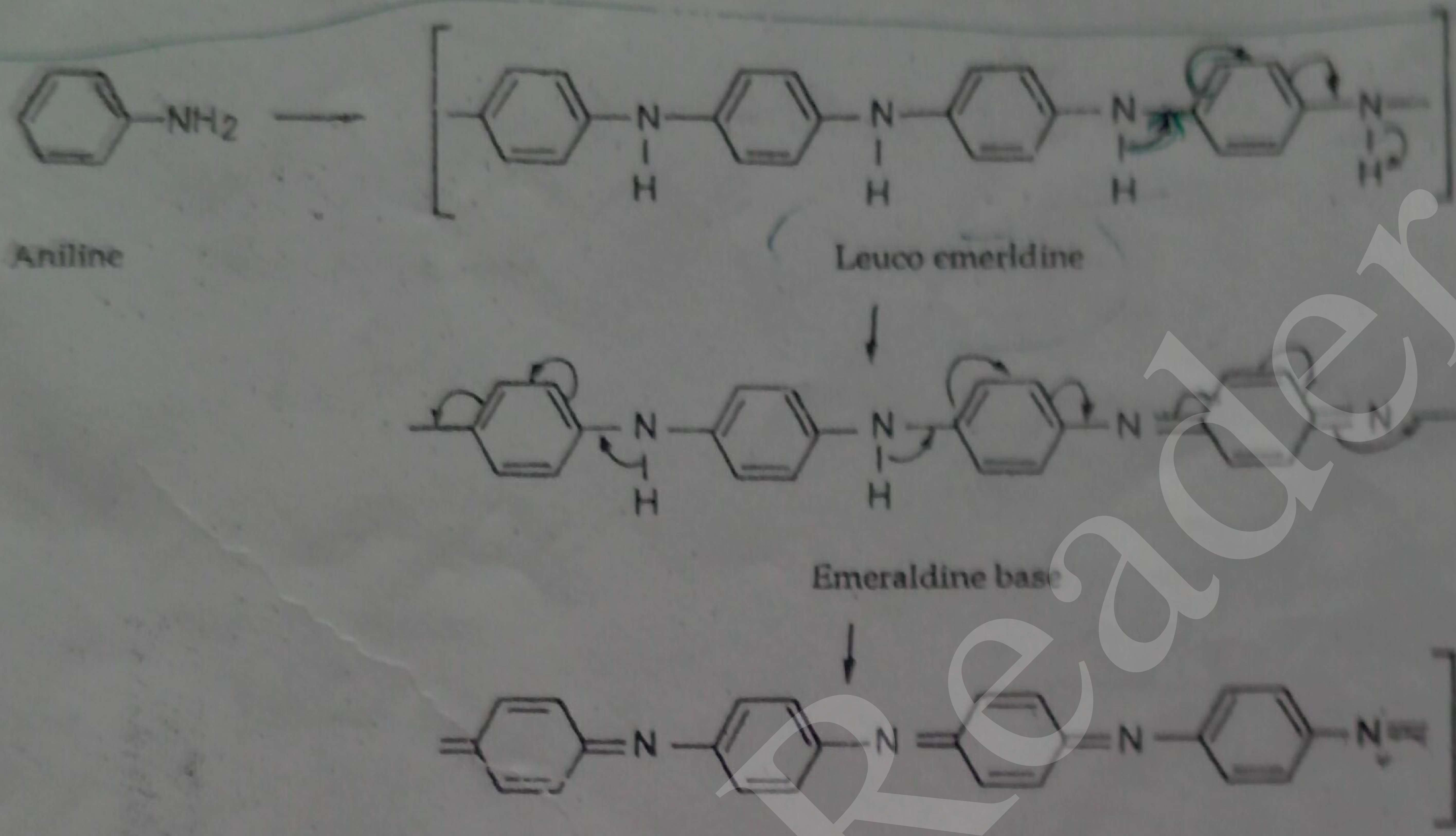
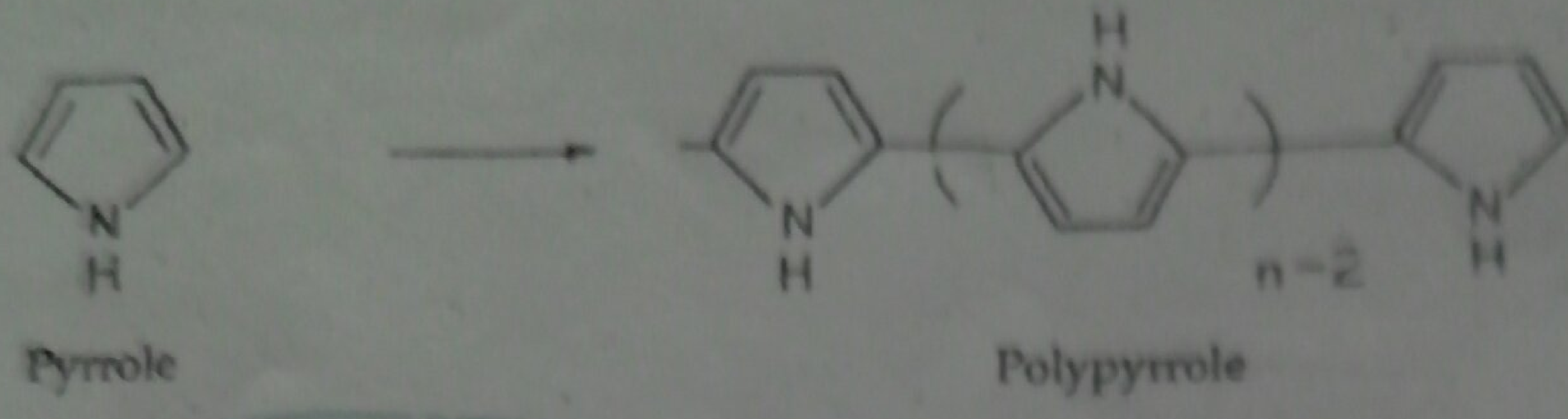
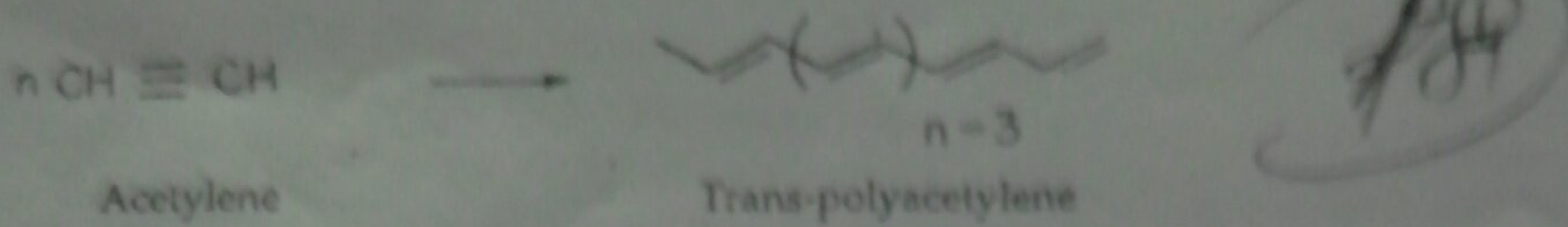
These are briefly discussed below :

(i) Intrinsically conducting polymers. These polymers have extensive conjugation in the backbone which is responsible for conductance. These are further of two types :

(a) Conducting polymers having conjugated  $\pi$  - electrons in the backbone.

Such polymers contain conjugated  $\pi$  - electrons in the backbone which increases their conductivity to a large extent. This is because, overlapping of conjugated  $\pi$  - electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction could occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

Examples :

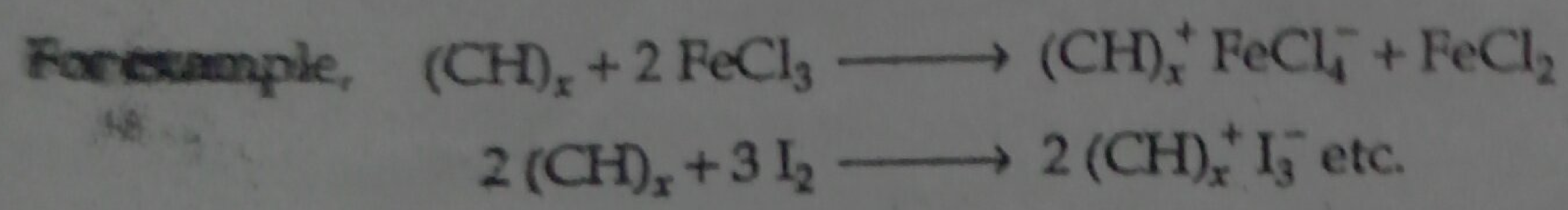
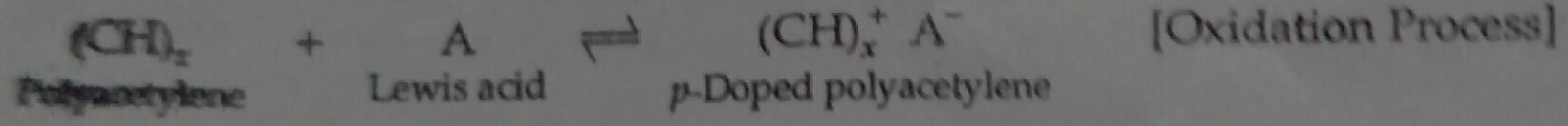


All the three forms of polyanilines have conductivities of the orders of  $10^{-10} \text{ S cm}^{-1}$ . Conductivity of these polymers, having conjugated  $\pi$ -electrons in the backbone is not sufficient for their use in different applications.

(b) *Doped conducting polymers.* In comparison to conventional polymers, the conducting polymers of type (a) can be easily oxidized or reduced as they have low ionization potentials and high electron affinities. Their conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction.

By analogy with semiconductor technology, it is referred to as **Doping** and is of following two types

**p-doping.** It is done by oxidation process. Conducting polymer of type (a) is treated with Lewis acids (A) or with iodine vapour or iodine in  $\text{CCl}_4$ .



In *p*-doping, conducting polymer of type (a) is partially oxidised using a suitable oxidising agent (that's why it is also called as oxidative doping). This oxidation process (i.e., removal of an electron from the polymer pi-back bone) leads to the formation of delocalised radical ion called polaron. A second oxidation of this polaron, followed by radical recombination yields two positive charge carriers on each chain which are mobile. Thus, these delocalised positive charges are current carriers for conduction (refer Fig. 3)

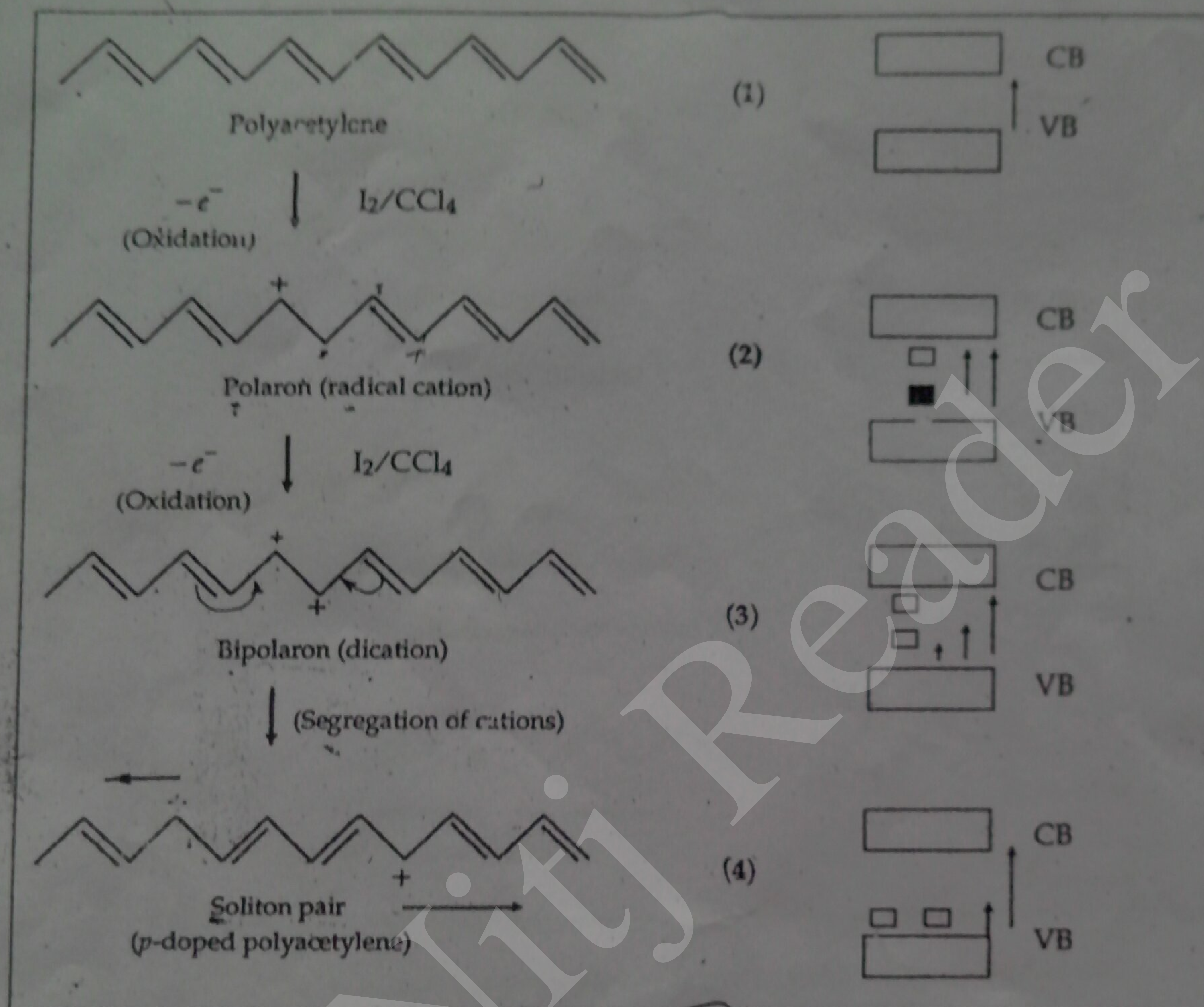
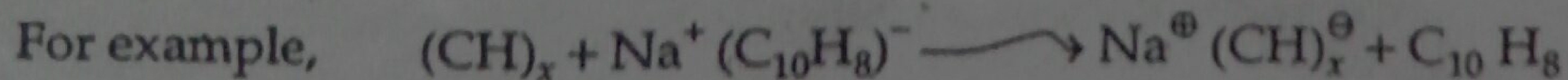
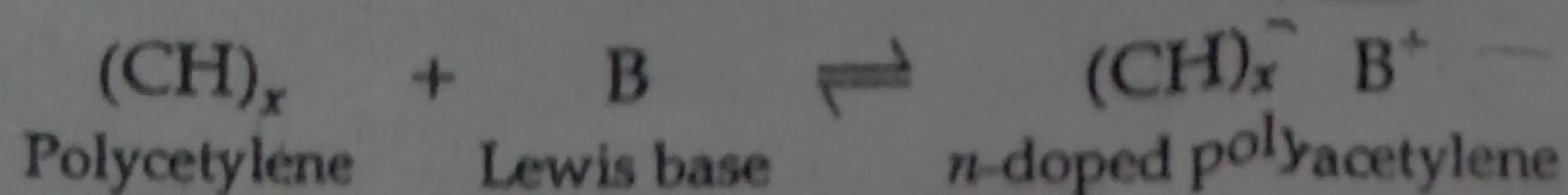


Fig. 3. *p*-doping of polyacetylene to give a polaron, a bipolaron, and a soliton pair.

[Here, VB = Valence band ; CB = Conduction band ; □ = Acceptor level]

***n*-doping.** It is done by reduction process. For this, conducting polymer of Type (a) is treated with lewis bases (B) like sodium naphthalide.



In *n*-doping (or Reductive doping), the reduction process (i.e., the addition of an electron to the polymer backbone using a reducing agent like sodium naphthalide,

$\text{Na}^{\oplus}(\text{C}_{10}\text{H}_8)^{\ominus}$  leads to the formation of polaron and bipolaron: in two steps. This followed by recombination of radicals yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction. (refer Fig. 4)

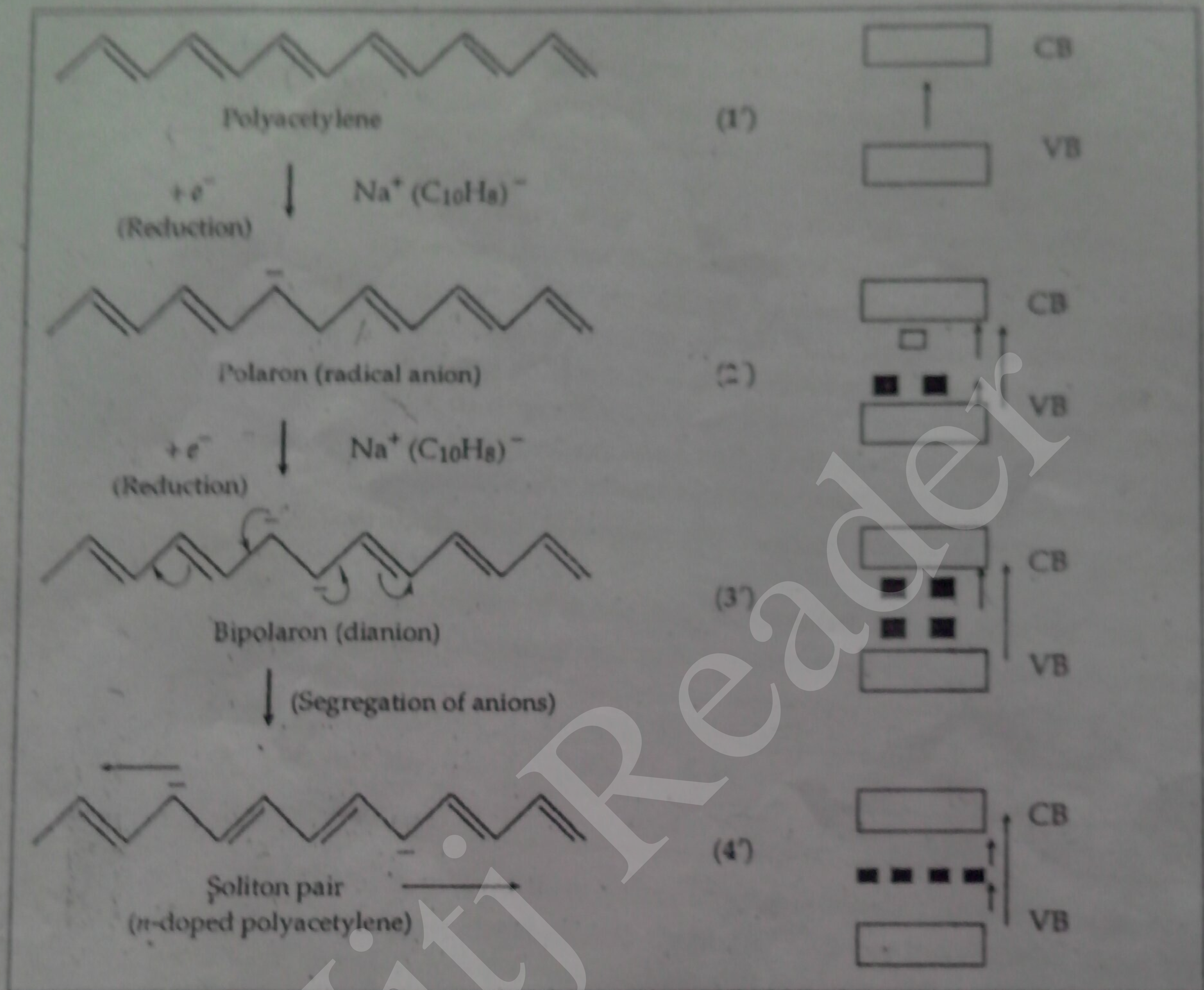


Fig. 4. n-doping of polyacetylene to give a polaron, a bipolaron, and a soliton pair.

[Here, VB = Valence band ; CB = Conduction band ;  $\blacksquare$  = Donor level]

**Interpretation of conductivity in conjugated polymers through band theory :**

- (1) Valence band (VB) and conduction band (CB) in conjugated polymers like trans polyacetylene are separated by a significant band gap, thus conductivity of undoped polymer is not very high.
- (2) Electron removed from polyacetylene by oxidation will lead to the formation of radical cation (or polaron). It has a hole in between VB and CB.
- (2) The electron added to polyacetylene by reductive doping does not go into the conduction band but into an intermediate electronic state within the band gap of radical anion (or polaron).

- (3) Further oxidation will lead to the formation of Bication (or Bipolaron) with two holes in the VB and CB.
- (3') Further reduction will lead to the formation of Bianion (or Bipolaron). It contains electrons in the energy levels residing in the band gap
- (4) Bication lowers its energy by segregating into two positive solitons *i.e.*, two holes in the mid gap energy levels. The presence of holes in the band gap allows facile jumps of electrons from the VB into this holes. Then holes thus created in the VB conduct electricity. As a consequence, conductivity increases significantly.
- (4') Bianion lower its energy by segregating into two negative solitons at the midgap energy levels. Current could then be carried as the charged solitons and the defect sites move along the chain. The position of dopant level in the band gap allows facile jumps of electrons into the conduction band. This lead to the generation of conduction pathways. As a consequence, conductivity increases significantly.

In general, doping increases the surface conductivity of polymer to a large extent.

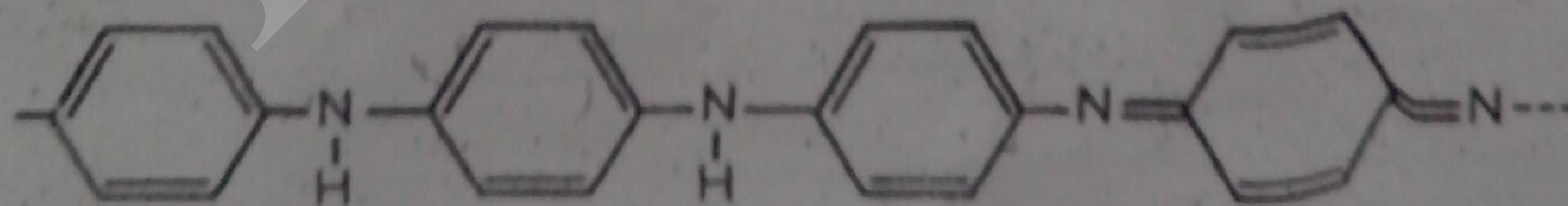
The conductivities of some polymers after doping is tabulated below :

Table : Dopants and conductivities of conducting polymers.

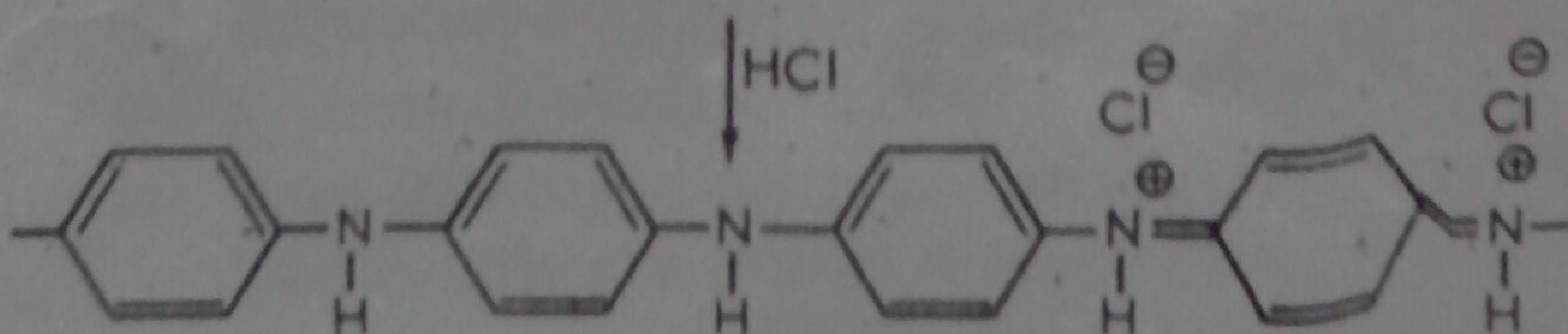
Conducting Polymer	Trans-polyacetylene	Polyaniline	Polypyrrole
Dopants (s)	I <sub>2</sub> , Br <sub>2</sub> , Li, AsF <sub>5</sub> , Na	HCl	BF <sub>4</sub> <sup>⊖</sup> , ClO <sub>4</sub> <sup>⊖</sup>
Conductivity (S cm <sup>-1</sup> )	10,000	1,000	500-7500

For instance, polyaniline exists in several oxidation states with electrical conductivities varying progressively from 10<sup>-11</sup> S per cm to more than 10<sup>5</sup> S per cm. Only one form, called the emeraldine salt is electrically conducting. Mechanically flexible dark-blue films of conductive polyaniline are made by protonic doping (*i.e.*, protonation of imine nitrogen atoms in the backbone) of emeraldine films either by dipping in acid or passing gaseous acid over it. Doping is reversible process as deprotonation can also be done by treatment with aqueous alkali.

Emeraldine salt is also known as 'synthetic metal'. It has conductivity like metals, metallic lusture and metallic sound.



Emeraldine base  
(Conductivity = 10<sup>-10</sup> S cm<sup>-1</sup>)



Emeraldine salt  
(Conductivity ~ 10<sup>3</sup> S cm<sup>-1</sup>)

### Factors Influencing the Conductivity of Organic Polymers

The conductivity of organic polymers is influenced by various factors. These are briefly discussed below :

(a) *Conjugation length of the polymer chain* : With the increase in the extent of conjugation in a given polymer, its conductivity increases.

(b) *Doping level* : Generally with increase in the doping level of the polymer, conductivity is found to increase but after some time, it becomes saturated.

(c) *Temperature* : In contrast to metals, the conductivity of conducting polymer is found to increase with increase in temperature. At some high temperature, conductivity becomes constant.

(d) *Frequency of current* : The conductivity of these materials also depend on the frequency of current because the transport mechanism of most of these materials is hopping.

Interesting range of properties offered by intrinsically conducting polymers (ICP's) are :

- (a) Conductivity ;
- (b) Ability to store a charge ;
- (c) Ability to ion exchange ;
- (d) Absorption of visible light to give coloured products ;
- (e) Transparency to X-rays.

Successful application depends on achieving the following features :

- (a) Advantage in processing ;
- (b) Excellent properties in products ;
- (c) Economy ;
- (d) Good product stability ;
- (e) More efficient recycling and
- (f) Demonstration of ecological advantages.

Limitations of Intrinsically conducting polymers (ICP's) :

- (a) Their conductivities are inferior to metals.

For example,

Material	Conductivity
Polyacetylene	400,000 S cm <sup>-1</sup>
Cu	600,000 S cm <sup>-1</sup>

But on the basis of weight, situation is reversed.

- (b) Improcessability ;
- (c) Poor mechanical strength ;
- (d) Poor stability under exposure to common environmental conditions, particularly at elevated temperatures ;
- (e) Poor storage stability leading to loss in conductivity.

(ii) *Extrinsically conducting Polymers*. These polymers owe their conductivity due to the presence of externally added ingredients in them. These are of following two types :

(a) **Conductive element filled polymer.** In this, the polymer acts as the binder to hold the conducting element (such as carbon black, metallic fibers, metallic oxides, etc.) together in the solid entity.

Minimum concentration of conductive filler which should be added so that polymer starts conducting is known as *percolation threshold*. Because at this concentration of filler, a conducting path is formed in polymeric material. Generally, special conducting grade C-black is used as filler which has very-high surface area ( $1000 \text{ m}^2/\text{gm}$ ), more porosity and more of a filamentous properties.

These polymers possess reasonably good bulk conductivity; are generally low in cost; light in weight, mechanically durable and strong and are easily processable in different forms, shapes and sizes.

Such compounds have been important, for example, in hospital operating theatres where it was essential that static charges did not build up, leading to explosion involving an aesthetics.

But it is to be noted that addition of as little as 10% carbon black will drastically reduce the tensile strength, elongation at break and impact strength of polypropylene mouldings. This problem can be easily overcome by blending a conventional polymer with a conducting polymer. The resultant blended conducting polymers are discussed below:

(b) **Blended Conducting Polymers.** These polymers are obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and they can be easily processed.

For example, up to 40% of polypyrrole will have little effect on tensile strength and also give a much higher impact strength than obtained with a carbon-black filled compound at only 10% loading.

Such compounds are of interest in electromagnetic shielding.

#### Applications of conducting polymers

(a) **In Rechargeable batteries.** These batteries are small in size (button type), longer lasting and can produce current density upto  $50 \text{ mA}/\text{cm}^2$ . Moreover, these rechargeable batteries have ecological advantage as they do not involve heavy metals so they do not appear to have any serious toxicological problems.

(b) **In Analytical sensors.** Conducting polymers are also used for making sensors for pH,  $\text{O}_2$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{NH}_3$  and glucose.

(c) **For making Ion-exchangers.** Membranes made up of them can show boundary layer effects with selective permeability for ions, gases, etc. Hence, they are useful for ion-exchangers and controlled release of drugs.

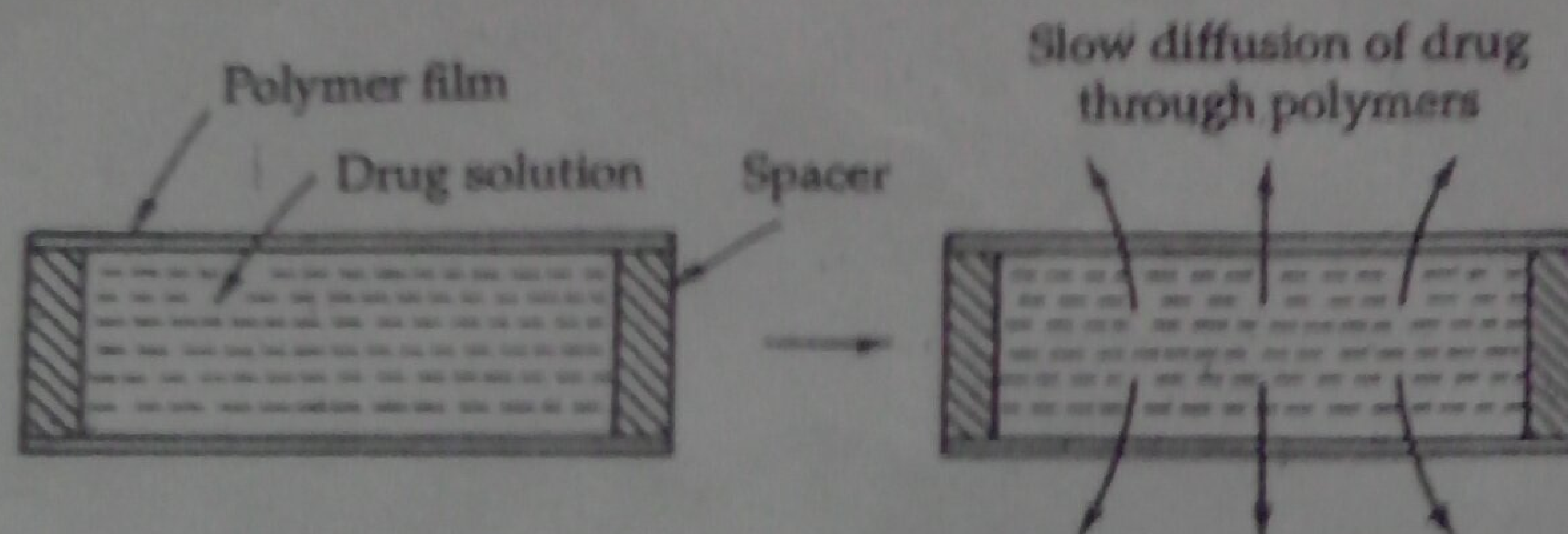


Fig. 5. Slow controlled release of a drug by diffusion through a polymer membrane.

Diffusion of the drug from the polymer matrix permits a continuous (for a period of weeks or months) and controlled release. With this, regular injection or oral ingestion of the drug is no longer needed. This technique has been used for the slow release of birth control drugs and it has potential to be used for cancer chemotherapy.

(d) *In electrochromic displays and optical filters.* ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters (with adjustable transparency). Thus, conducting polymers can be used as electrochromic materials (i.e., the materials which change colour reversibly during the electrochemical processes of charge and discharge).

(e) *In photoresistive.* Photostructural lacquers based on ICP's are useful for lithography, LED's and Data storage.

A base form of polyaniline is used as a resist for lithography. Its solution in DMF (1-methyl-2-pyrrolidone) mixed with triphenylsulphonium hexafluorophosphate has been used to spin coat thin films on quartz and silicon. The blue film on exposure to UV radiation of 240 nm turns green, characteristic of conducting state of polyaniline. Conducting lines as small as 0.5  $\mu\text{m}$  can be obtained by using this technique.

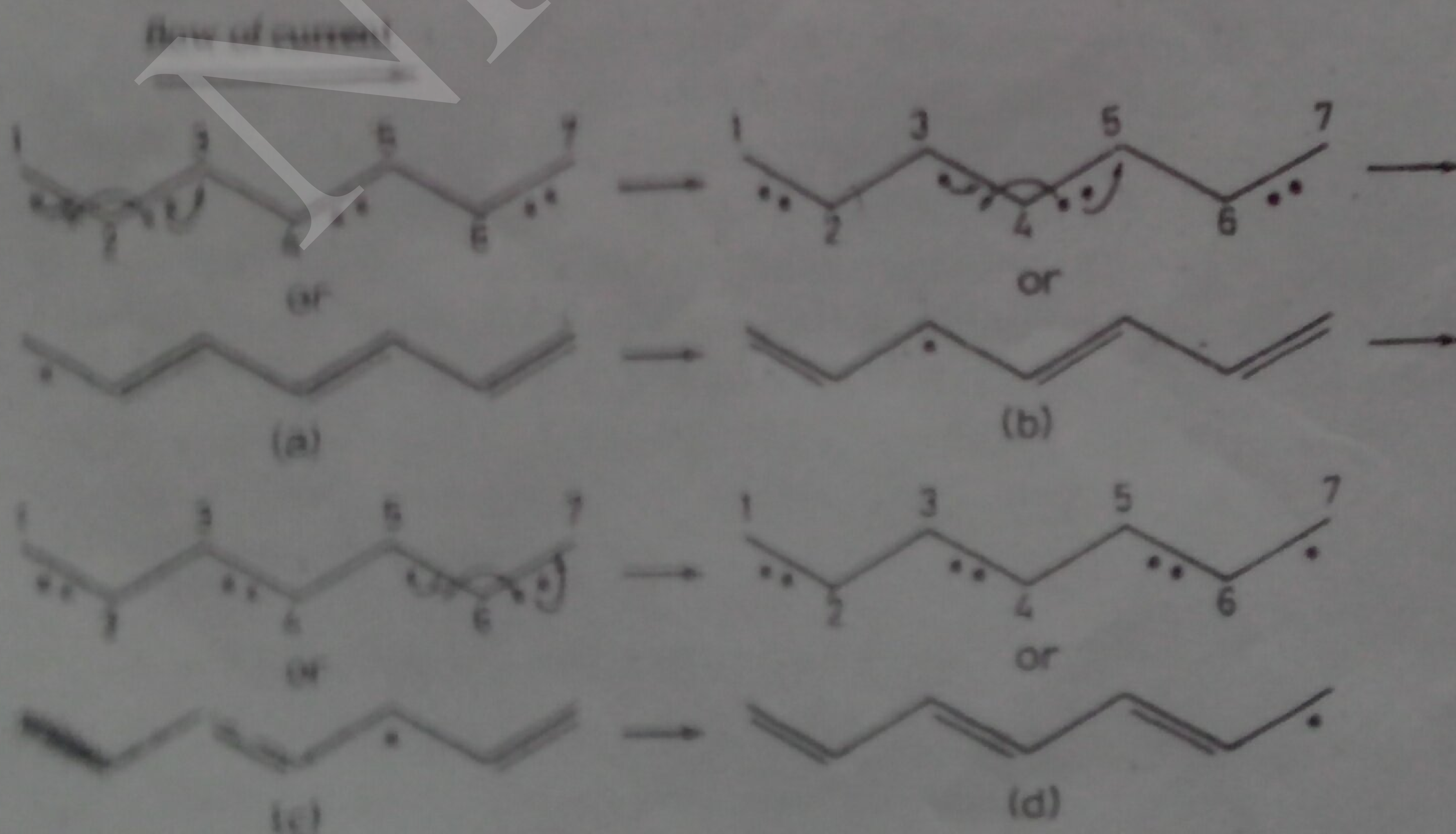
(f) *In photovoltaic devices.* For example, Al | conducting polymer | Au Photovoltaic cells.

**Example 1.** Illustrate the conductivity mechanism in polyacetylene.

**Solution.** Polyacetylene  $(\text{CH})_n$  has long chain of atoms in which each carbon atom is  $sp^2$  hybridized.



From an external source, when an electron enters an unhybridized  $p$  orbital of a C atom in the polyacetylene molecule, it moves down the chain of C—C bonds as shown in the illustration:





Suppose the electron enters the chain at carbon atom 1, the breakage of the  $\pi$  bond between carbon atoms 2 and 3 can be easily visualized (a); then one of the broken  $\pi$  bond's electrons pairs with the lone electron to form a new  $\pi$  bond between C atoms 1 and 2, thereby leaving an unpaired electron on C atom 3 (b). Then, the  $\pi$  bond between carbon atoms 4 and 5 is broken, one electron pairing with the lone electron on C atom 3 and forming a new  $\pi$  bond between C atoms 3 and 4. The lone electron now appears on carbon atom 5 (c). By the same sequence of events, the additional electron can move to C atom 7 (d). The process continues, down the chain of the molecule, thereby turning it into a conducting path.

**Example 2.** Give one example each of the practical applications of the following conducting polymers: (a) polyaniline, (b) polypyrrole.

**Solution.** (a) Polyaniline is used to make rechargeable batteries in the shape as flat buttons or as laminated rolled films.

(b) Polypyrrole is used in 'smart' windows. These smart windows can change their colour in response to changes in temperature or amount of sunlight. The colour change is from a transparent yellow-green to blue-black.

**Example 3.** It is being said that 'one day conducting polymers may be used in place of metals in electrical wiring'. Can you think of one advantage of using conducting polymers in place of metals?

**Solution.** Conducting polymers are lighter & they do not corrode.

**Example 4.** Give the synthesis of polyaniline.

**Solution.** A 0.1 M aniline hydrochloride solution is made in 1.0 M aqueous HCl. To this, an aqueous solution of 0.1 M ammonium persulphate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is slowly added with stirring. Polymerisation reaction is exothermic and hence the temperature rises. To maintain the polymerisation temperature of 3 - 4°C, the reaction vessel is placed in an ice bath for one to two hours with constant stirring. During the polymerisation, colour changes in the following sequence:

Light blue → blue green → copper tint → green

Polyaniline finally gets precipitated in the green form. The precipitate is filtered, washed several times with distilled water followed by methyl alcohol or acetone washings until the washings are colourless. The residue is then transferred to a beaker containing 1.0 M aqueous HCl and allowed to stand overnight. The precipitate is filtered, and dried under vacuum at 60 - 80°C for eight hours. A green coloured salt, called emeraldine salt is obtained. This salt is stirred with 0.1 M  $\text{NH}_4\text{OH}$  for six hours at a pH of 9. It is then filtered, washed first with distilled water and then with methanol. Final washings are done with diethylether. The resulting solid, p-doped polyaniline (i.e., conducting polyaniline) is dried at 60 - 80°C under vacuum.

#### 4 MANUFACTURE OF PLASTIC ARTICLES

It is done by processing of polymers. Polymer processing embraces the technology of making articles from polymer compounds.