

Synthesis and characterization of highly crystalline conjugated polyparaphenylene and polythiophene conductive polymer thin films

A Mani*, P Kamaraj & K R Ramakrishnan

X-ray Diffraction Laboratory (EEI Division), Central Electrochemical Research Institute,
Karaikudi 630 006 Tamil Nadu, India
Email: ariyananmani@yahoo.com

Received 20 June 2003; revised 17 November 2003

Molecular, crystalline and morphological characteristics of polyparaphenylene (PPP) and polythiophene (PTh) conjugated polymers are reported here. Thin films of PPP and PTh exhibit molecular- and crystalline-anisotropic structures, obtained intrinsically by a single-step approach of electrochemical method. The unique advantage of controlled electrochemical polymerization/crystallization is highlighted by *ex-situ* high-temperature X-ray diffraction, morphology, luminescence, and *ex-situ* electrochemical X-ray diffraction data. Structural analysis in terms of degree of crystalline order (X_{cr}) as the crystalline-gauging parameter and X-ray diffraction profile data as molecular order probe have been reported. The electrochemical thickness effect, high degree of crystalline order ($X_{cr}=99\%$), and thin film and molecular anisotropy are highlighted in terms of supramolecular order of the highly conjugated polymer molecules.

It is commonly observed that when complexity of the polymer molecule increases, the molecular and crystalline orders decrease. However, a right choice of synthetic method and its conditions can yield better intrinsic structural order. The conjugated polyparaphenylene (PPP) and polythiophene (PTh) thin films synthesized by electrochemical method are presented to evaluate a method and its conditions that can intrinsically generate higher structural order in conjugated conductive polymers, and further improvement of crystalline order in case of crystalline conducting polymer films by high-temperature annealing. The structural characteristics of PPP and PTh thin films are investigated here by systematic analysis of X-ray diffraction, morphology and photo- and electro-luminescence data of the conjugated polymer structures.

Materials and Methods

The PPP conjugated polymer films were electrochemically synthesized as follows: benzene monomer was solubilized in conc. H_2SO_4 (~18 M) using SDS surfactant to yield an o/w type microemulsion. The optimum molar concentration ratio of benzene to H_2SO_4 was 2:5 and 0.15 g of SDS (14.3 mM) dissolved in a total volume of 70 ml of microemulsion solution. This was directly used as an electrolytic medium. The PPP films were grown on conducting ITO glass (1 cm² area) by cycling the

potential between +0.91 and -0.21V (Hg/ Hg_2SO_4 /1 M H_2SO_4 (MSE) at ambient conditions at a sweep rate of 100 mV s⁻¹. The PPP films thus obtained by potential cycling were washed using water and ethanol to remove unreacted monomer and surfactant, and dried.

All PTh films were grown on ITO glass substrate by electrochemical oxidation of thiophene monomer. Transparent ITO was used as working electrode (1 cm² area) while platinum plate (1 cm² area) and Hg/ Hg_2SO_4 (MSE) as counter- and reference-electrodes respectively. Before the electrochemical oxidation, thiophene was distilled under Ar atmosphere and the monomer was solubilized in conc. H_2SO_4 (10 M) using either SDS or Triton X-100 (14.8 mM) surfactant for a total volume of 50 ml o/w microemulsion solution. The electrochemical polymerization reaction was carried out by potentiodynamic cycling between -0.3 and +0.9V at ambient condition with a sweep rate of 100 mV s⁻¹. The homogeneous thin films were washed using water and ethanol to remove unreacted monomer and surfactant, and dried.

X-ray diffraction

Electrochemically synthesized PPP and PTh thin films were characterized using X-ray polycrystalline diffraction method. The θ -2 θ step-scan mode [JEOL (Japan) JDX 8030 computer controlled and dedicated X-ray diffraction system at a rating of 40 kV, 20 mA

and (Ni-filtered) CuK_α radiation of wavelength $\lambda = 0.15418 \text{ nm}$] were used to sensitively record the X-ray diffraction response for the systematic structural analysis.

Morphology

All the polymer samples of both powder as well as thin film forms were simultaneously subjected to scanning electron microscopic (SEM) observations (JEOL-JSM 35CF) to compliment the X-ray diffraction results as direct evidence of the crystalline conditions.

Photoluminescence

The PPP and PTh thin films were recorded for their photoluminescence characteristics using Hitachi (model 650-105) fluorescence spectrophotometer.

Electroluminescence

Trial experiments on light-emitting diode (LED) device using PPP and PTh thin films were performed in the lab to observe electroluminescence and to record I-V characteristics of the films. The preliminary results were useful to assess the structural order criteria for electroluminescence/photoluminescence.

Results and Discussion

The extent of polymer crystalline condition is measured as the degree of crystalline order $X_{cr}(\%) = [I_c \times 100]/[I_c + I_a]$ where I_c and I_a are the X-ray diffraction intensities corresponding to the crystalline and amorphous volume of the matrix, derived from earlier workers^{1,2}.

Enhanced intrinsic structural order in electrochemically synthesized conjugated polymer thin film

The X-ray diffraction patterns corresponding to PPP and PTh thin films synthesized electrochemically have been collectively shown in Figs 1 and 2 respectively; also shown are the respective morphological structures. The change in crystalline order with electrochemical growth cycles or thickness of the conjugated polymer thin films beyond certain critical thickness has been found through *ex-situ* electrochemical X-ray diffraction experiments. Initially observed [Fig. 1(a)] highly crystalline-anisotropic thin films of (001)-texture at 20 growth cycles (equivalent to the charge accumulation of 2.65 mC cm^{-2} or nearly $0.5 \mu\text{m}$ thickness) become

gradually amorphous after this critical limit due to formation of bulk characteristics³⁻⁵. This electrochemical thickness effect relating structural order and electrochemical growth cycles is reported recently⁶⁻⁸ and by us⁹⁻¹⁰ for both the PPP and PTh thin films, as is clearly gauged by X-ray diffraction profiles; and what is shown here in Fig. 1 and Table 1 is for PPP thin films. During the electrochemical growth of the polymer thin films and after 20 growth cycles, the reduction in crystalline order occurs through a narrow range of less-crystalline and less-symmetric [Fig. 1(b)] region before collapsing to highly disordered amorphous PPP films [Fig. 1(c)]. Similarly with PTh thin films, at 15 growth cycles, the structure is highly crystalline ($X_{cr}=97\%$) lamellar layered [Fig. 2(a)] while at 50 growth cycles, the phase is completely disordered ($X_{cr}=0\%$) [Fig. 2(b)]. The highly crystalline order in PTh at 15 growth cycles is directly evident from its morphology shown in Fig. 2(c) and Table 2. These data also indicate homogenous single phase structure and thin film stability even after thermal-annealing at 380°C for 30 minutes in N_2 atmosphere. From the analysis of X-ray diffraction and morphological results on PPP and PTh structures^{9,10} and similar such morphological results³⁻⁷, on the electrochemical thickness effect in PANIs and PThs, the X-ray diffraction method has become an essential means of defining the real thin film characteristics of conjugated polymer structures. In addition, the present *ex-situ* electrochemical X-ray (diffraction) analytical method has also been proved to be sensitive grouping method of "real" crystalline conjugated polymer thin films--the X-ray characterization technique has proved that electrochemical approach is an efficient method for controlled polymerization/crystallization of conjugated polymers so as to select, design and synthesize a range of structures from amorphous to highly crystalline lamellar thin films.

Another set of experimental analysis concerns the *ex-situ* high temperature X-ray diffraction results of the PTh thin films to study the post-annealing effect of the intrinsically highly ordered conjugated polymer thin films. The highly crystalline-anisotropic PTh thin films possess (h00) texture and are obtained as as-synthesized intrinsic structural order of the PTh. On post-annealing of these PTh-thin films at 300 and 380°C for 30 minutes each in N_2 atmosphere (furnace cooled), the *ex-situ* high temperature X-ray analysis has shown no change in crystal structure but a slight

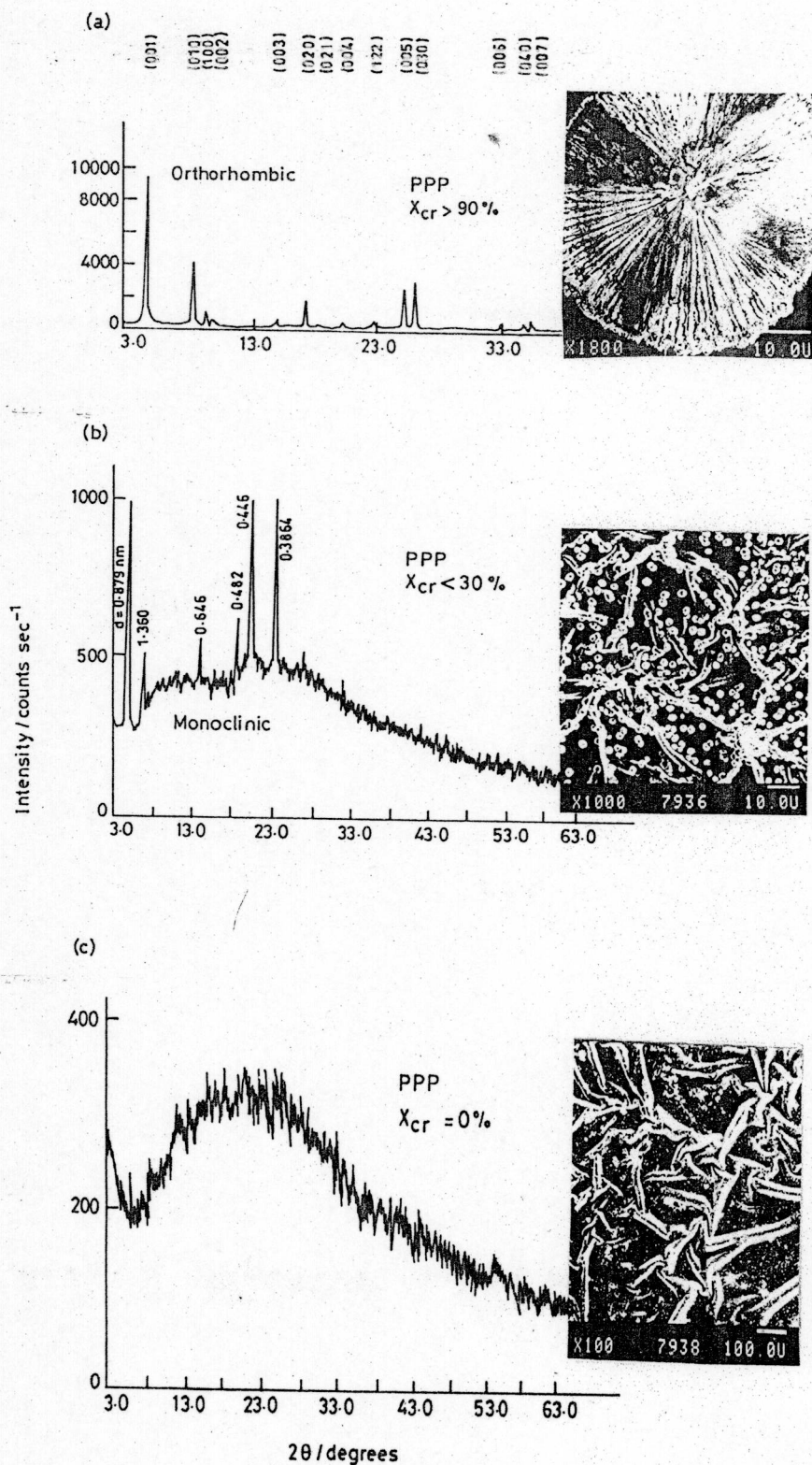


Fig. 1—The effect of crystalline order in terms of X-ray diffraction response and morphology with electrochemical growth cycles in PPP thin films: (a) 20 growth cycles (highly crystalline, $X_{cr} > 90\%$); (b) deteriorating to partially crystalline ($X_{cr} < 30\%$) on 30 growth cycles; and (c) becoming completely amorphous ($X_{cr} = 0\%$) with 50 growth cycles.

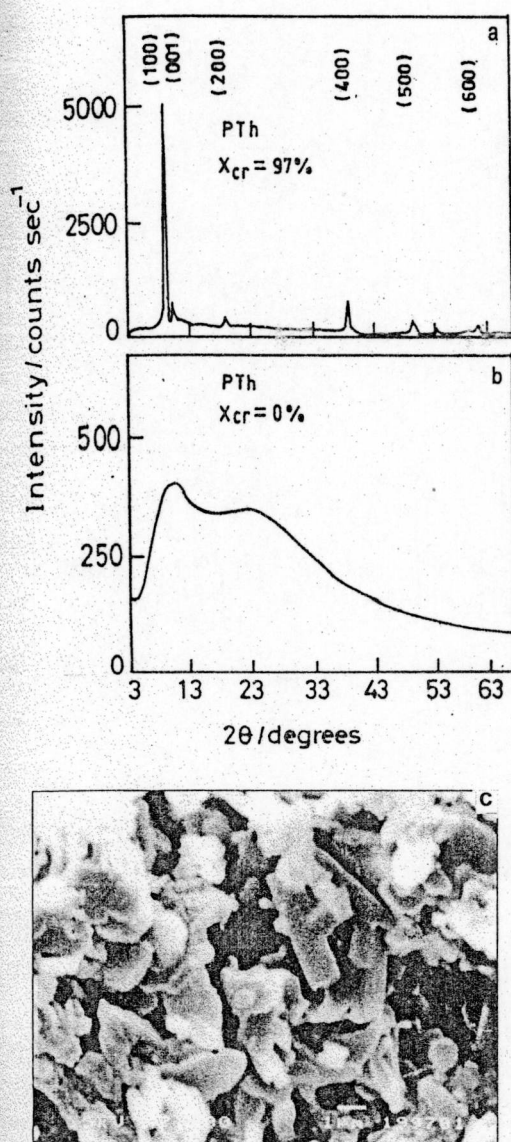


Fig. 2—Change of crystalline order on electrochemical growth cycles in PTh thin films: X-ray diffraction patterns for (a) 15 growth cycles [highly crystalline] & (b) 50 growth cycles (highly non-crystalline); (c) the corresponding SEM morphology for 15 growth cycles after heat-treatment at 380°C for 30 minutes in N₂ atmosphere.

change in the crystalline order followed by disturbance of the thin film anisotropy. These results indicate that the secondary means like post-treatment or annealing of polymer samples can also cause structural deterioration (instead of enhancement) in terms of the degree of crystalline order and crystallite orientations as well. But once highest structural order is achieved, possibly in a direct single-step approach, most treatments are not needed; such conjugated polymer thin films of intrinsically highly ordered structures are mostly suitable for the best performance of electrochemical, opto-electronic devices and other technological applications.

Table 1—Observed X-ray diffraction data of PPP thin films

d, nm	(hkl)	I/I ₀
1.7659	(001)	100
1.0273	(010)	34
0.9111	(100)	12
0.8838	(002)	05
0.5901	(003)	07
0.5151	(020)	18
0.4792	(021)	06
0.4414	(004)	06
0.3897	(122)	08
0.3545	(005)	27
0.3424	(030)	26
0.2918	(006)	05
0.2583	(040)	05
0.2527	(007)	08

The X-ray diffraction data is indexed in the orthorhombic crystal lattice of unit cell parameters: $a = 0.9104$, $b = 1.0278$ and $c = 1.7661$ nm. Intensities, $I(hkl)$ are normalized with respect to $I(001)$.

Table 2—X-ray powder diffraction data of highly crystalline PTh thin films (all observed reflections included) before and after heat treatment at 380°C for 30 min in N₂ atmosphere.

d, nm	(hkl)	I/I ₀ ^b
2.2071	(001)	08
0.9205	(100)	100
0.8007	(010)	05
0.5467	(004)	04
0.4572	(200)	09
0.4411	(005)	05
0.4249	(202)	05
0.3882	(203)	05
0.3531	(204)	05
0.2957	(302)	08
0.2568	(130)	03
0.2302	(400)	07
0.2140	(403)	03
0.1799	(510)	03
0.1606	(050)	04
0.1536	(600)	03

Indexed in orthorhombic lattice of new unit cell parameters: $a = 0.9205$, $b = 0.8037$ and $c = 2.2071$ nm.

^bIntensities, $I(hkl)$ are normalized with respect to $I(100)$ reflection.

The influence of crystalline order in crystalline conducting polymers

Electrochemical method being a better choice when compared to chemical and physical means to synthesize conjugated polymers, the surfactants have been employed in microemulsion (organized) media to have controlled electrochemical polymerization/crystallization process. The X-ray analysis correlating

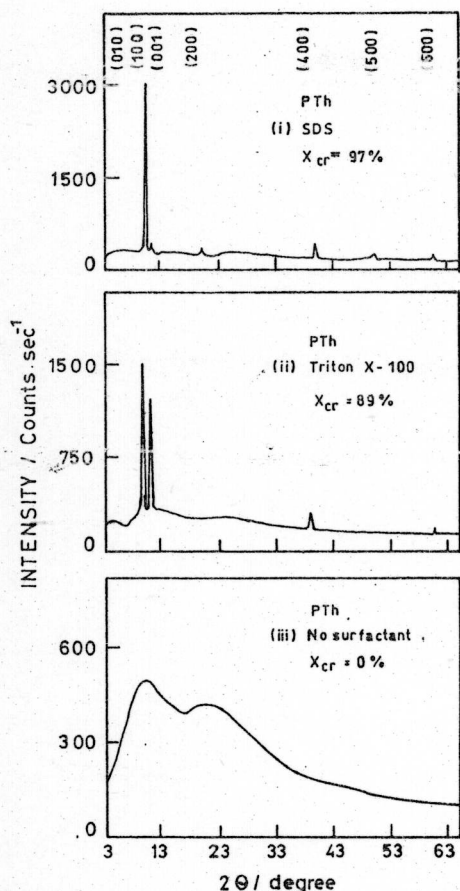


Fig. 3—X-ray diffraction patterns elucidating surfactant effect on crystalline order and its orientations in PTh thin films synthesized electrochemically in microemulsion media for 10 growth cycles: (a) SDS (anionic surfactant, $X_{cr}=97\%$); (b) Triton X-100 (neutral surfactant, $X_{cr}=89\%$); and (c) "control" experiment (no surfactant, $X_{cr}=0\%$).

degree of crystalline order, X_{cr} (%) of PTh thin films with different surfactants at 10 growth cycles is depicted in Fig. 3. Among the anionic-SDS and AOT, neutral-Triton X-100, and cationic-CTAB surfactants (results not shown), the catalytic effect of the anionic and neutral surfactants is observed to be the significant ones for the evolution of highly ordered conjugated polymer structures. The PTh thin films differ only slightly in crystalline order and crystallite orientation with SDS and Triton X-100. However, on the basis of our results on PPP and PTh thin films, the difference in structural order is found to influence the polymer properties. For example, the influence of crystalline order with luminescence properties, observed from our preliminary experiments is presented here as follows:

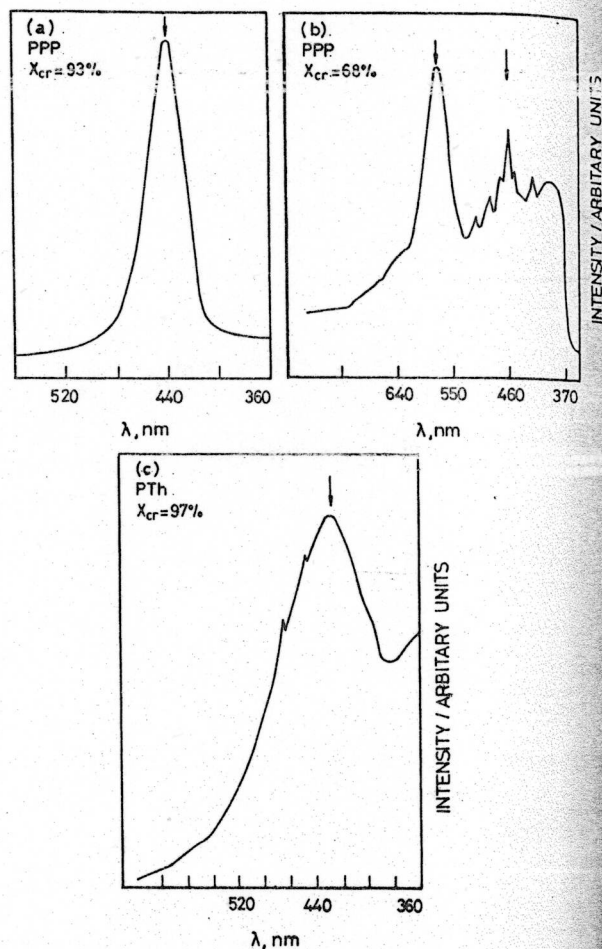


Fig. 4—The effect of crystalline order (X_{cr}) in PPP thin films as characterized by photoluminescence spectra: (a) the only intense blue emission at $\lambda_{em} = 441$ nm corresponding to $X_{cr}=93\%$; (b) intense green emission at $\lambda_{em1} = 546$ nm with a feeble blue emission at $\lambda_{em2} = 468$ nm at $X_{cr} = 68\%$; (c) the effect of crystalline order ($X_{cr} = 97\%$) in PTh thin films is the photoluminescence spectra of intense blue emission at $\lambda_{em}=430$ nm.

Photoluminescence spectra corresponding to PPP and PTh thin films are given in Fig. 4. The highly crystalline PPP of $X_{cr}=93\%$ has given a perfect (isotropic) blue emission at 441 nm for an excitation wavelength of 340 nm while partially crystalline PPP films of $X_{cr}=68\%$ has given rise to green emission at 560 nm along with a faint blue emission at 468 nm for excitation wavelength of 260 nm, as shown in Fig. 4 (a & b). Similarly, the PTh thin film of $X_{cr}=97\%$ has given an isotropic blue emission at 430 nm for an excitation wavelength of 325 nm as depicted in Fig. 4(c). The effects of crystalline order and morphology with photoluminescence characteristics are: highly

ordered and perfect crystalline morphology shows isotropic blue emission while less crystalline structure leads to multiple emission (blue and green) characteristics and the disordered (amorphous) polymer exhibits no observable photoluminescence effect. In case of light emitting diode (LED) preliminary experiments with PPP thin active layers have shown a red-yellow glow at $X_{cr}=30\%$ and an yellow glow at $X_{cr}=68\%$. The I-V characteristics of this pristine PPP active layer ($X_{cr}=68\%$) has shown (Fig. 5) less-conducting and more resistive in nature indicating the conductivity (measured using four-probe method) in the lower region ($\sim 10^{-4}$ S cm^{-1}) of the semi-conducting range when compared to an ideal active (isotropic) layer wherein a steep rise in current at low applied bias (shown schematically for comparison) characterizes the same blue emission of that of the photoluminescence spectra of PTh at $X_{cr}=97\%$. These details are depicted in Fig. 5. However, the highly crystalline-anisotropic PPP and PTh thin films are expected to be more suitable for blue laser emission, although LED experiments with these anisotropic PPP and PTh thin films ($X_{cr}=99\%$) have not been employed here as active layers and is carried over for future detailed study.

The influence of structural effects on conductive properties of partially crystalline polymers can also be realized in terms of structural order and conductive mechanism. The electrical conductivity of common conducting polymer has earlier¹¹ been explained using the charge transport mechanism of variable-range hopping (VRH) suitable for temperature-dependent, highly doped and moderately crystalline samples. However, it is basically the molecular structure, molecular conjugation, and the organization of conjugated molecules conform as crystalline structures and then to anisotropic layer structures which form the basic concept of charge transport mechanism in conductive polymers. In this case, conjugation length and chain structure of the polymers have been taken into account for the formation of anisotropic variable range hopping mechanism but it could not explain the finite conductivity in the low-temperature regime because it is the temperature-independent tunneling between the crystalline domains in doped or undoped samples has to be taken into account. Here again, the crystalline domains continue and pertain the ordered nature of structural aspects¹¹ of conjugated polymers

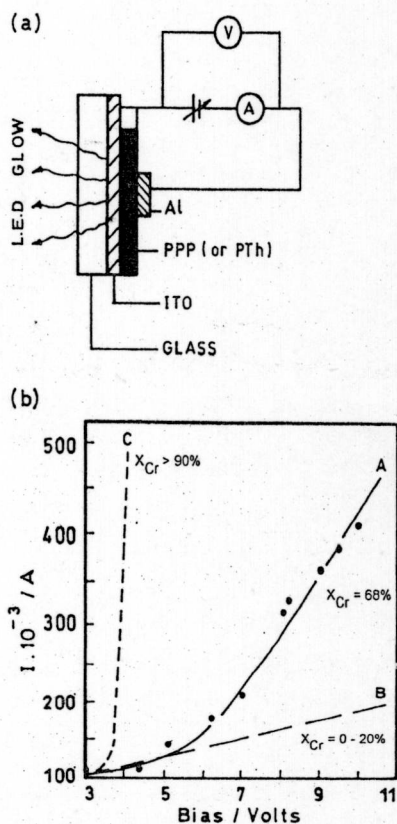


Fig. 5—The effect of crystalline order (X_{cr}) of PPP thin films as inferred from electroluminescence (LED) characteristics: (a) LED experimental set-up; (b) current—voltage plot as observed during the Al/PPP/ITO preliminary LED experiments: (A) Experimentally observed for partially crystalline ($X_{cr} = 68\%$) PPP active layer, (B) highly resistive for amorphous/less-crystalline ($X_{cr} = 0-20\%$), and (C) an ideal crystalline ($X_{cr} > 90\%$) conditions. [Curves (B) and (C) are schematic profiles].

considered to be important for the conducting mechanism.

Since the conjugation length beyond 5 nm could not have been directly observed by earlier techniques, the conjugation-break means of analysis has been considered to evaluate the conduction under VRH mechanism. This situation cannot be accepted now for the reason that (i) the concept of conjugation-sectioning immediately leads to structural disorder corresponding to very low conductivity; and (ii) rigid linear chain macromolecules of molar mass $> 10^6$ are the latest generation of the conjugated polymer candidates for which the VRH mechanism of electrical conductivity does not hold correct. Hence, a new mechanism of intrinsic (undoped) and extrinsic (doped) conductivity of the conjugated polymers must consider the actually observed^{9,10,13} higher conjugation length at least in terms of "conduction domains" and the crystallite region as a whole.

In case of conjugated polymers, it is the single covalent C—C bonds that are chemically feasible to have *trans*-fusion of monomer rings through 2,5 couplings (PPP and PTh) and not the double bonds. However, the π -conjugation sequence having alternate single and double bonds are maintained throughout the polymer backbone¹²⁻¹⁶. It is this sequence of conjugated conformations of the macromolecules and the conjugation length which are to be necessarily taken into account for more effective consideration of charge transport mechanism in conjugated polymer films. This situation becomes more sensitive in case of intrinsically highly anisotropic conjugated polymer lamellar layered structures. In the case of doped and/or functionalized conjugated polymers, more complex form of molecules occur, influencing the charge-transport properties heavily.

Conclusion

The structural analysis on collective results of *ex-situ* high temperature X-ray diffraction, morphology and luminescence of electrochemically obtained PPP and PTh thin films indicate that intrinsically high structural order of $X_{cr} > 90\%$ and high molecular and crystalline-anisotropy in the form of lamellar structure is achieved by single step controlled electrochemical synthesis in microemulsion containing anionic or neutral surfactants. Fundamental means of structural strategy to obtain ordered supramolecular assemblies of conjugated

polymers have been derived with relevance to the high-performance and longer life span of conjugated conductive polymer materials.

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