Ex-situ high temperature X-ray diffraction studies on partially crystalline conjugated polymers

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Molecular and crystalline structural aspects of partially crystalline conjugated polymers have been reported for polyanilines (PANis) and polythiophene (Pth). Improvement in crystalline order has been observed in chemically synthesized polymers by high-temperature annealing. This paper mainly concerns 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. A large extent of enhancement of crystalline domains up to 25% through recrystallization and crystallite growth has been obtained by high-temperature annealing of EB-and ES-PANis and Pth-dissociated hexithiophene materials (of intrinsic X_{cr} = 20 to 50 %). The mechanism of enhancement of crystalline order is given in terms of polymer molecular phenomena.

Main interest of studying conjugated polymer structures lies in clear understanding of evolution (nucleation), enhancement and control of structural order during design, synthesis, characterization and performance of the polymer materials. Since the discovery[1] of conductive polyacetylene due to its rigidly linear conjugated molecular (electronically delocalized) structure, other conjugated polymers such as polyanilines, polypyrroles, polyparaphenylenes and polythiophenes have been synthesized[2-8] as useful materials for technological applications harnessing physico-chemical properties. However, the applications[9-13] from domestic to advanced technology now demand better results and performance of the polymeric materials depending on their molecular and crystalline aspects.

The conducting polymers, particularly polyanilines, which exhibit conductivity in the lower region of semiconducting range, have been found to possess[14] amorphous or less-crystalline structures. This is basically due to slightly complex nature (quinoid type) of the polyaniline molecules compared to other simple candidates of the conjugated polymer system. 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. And to a limited extent, it is possible to further improve the structural order by post-treatment like high-temperature annealing. The structural characteristics of polyanilines (PANis), and polythiophene (Pth) are investigated here by systematic analysis of *ex-situ* high temperature X-ray diffraction and morphology.

Materials and Methods

Synthesis

(a) PANis—Water-in-oil (w/o) microemulsions with Aerosol OT(AOT) or sodium dodecyl sulphate (SDS) as surfactant were employed in the chemical synthesis of PANis (emeraldin base,EB-II and emeraline salt, ES-II). The following compositions were made: (i) 0.327 g of aniline hydrochloride in 15.1 g of water, 67.8 g of cyclohexane and 17.1 g (26.3 mM) of AOT; (ii) 0.582 g of ammonium peroxydisulphate (oxidant) in 15.1 g of water, (iii) 4 ml of 0.25 M aniline in 2 M HCl, 79.9 g of cyclohexane, 9.8 g of *n*-butanol (co-surfactant) and 4.9 g (16.8 mM) of SDS, and (iv) 3.2 ml of 0.1 M potassium peroxydisulphate (oxidant) in water. Upon mixing the two microemulsions (i) and (ii) for EB-II, and (iii) and (iv) for ES-II, polymerization of aniline occurred readily on stirring for 20 min at ambient temperature. Each microemulsion system is continuously stirred for about 12 h. The above systems are then left standing for about 24 h after stirring. Fine PANi particles obtained after centrifugation at 10000 rpm for 10 min were washed using methanol/THF and finally using water before vacuum drying in the desiccators.

(b) Pth—Chemical polymerization of Pth in an oil-in-water (o/w) microemulsion was carried out in the following steps: An aqueous oxidant solution was made up by dissolving 0.5 M ferric chloride in 25 ml

of water. This aqueous oxidant was then added to the aqueous monomer. The 50 ml microemulsion solution was stirred well for 3 hours and left standing for 18 h. Nice powder particles at the bottom of the solution after centrifugation were obtained. After filtration, powders were washed using Milli-Q water and ethanol and then dried at 50°C.

X-ray diffraction

Chemically synthesized EB- and ES-PANis and Pth powders were characterized using X-ray polycrystalline diffraction method. The θ-2θ 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$_\alpha$ radiation of wavelength λ = 0.15418 nm] was used to sensitively record the X-ray diffraction response for the systematic and reasonably accurate structural analysis.

Morphology

All the polymer samples of powder 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 or amorphous conditions.

Results and Discussion

The classification of amorphous, partially crystalline, and crystalline forms belonging to conducting polymers employed in the present study is given in Fig. 1 in the form of typical X-ray diffraction patterns and their corresponding molecular arrangements. 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 and based on the key shown in Fig. 1.

The X-ray diffraction patterns of chemically synthesized emeraldin base (EB-) and emeraldine salt (ES-) forms of PANis and the respective SEM morphology are depicted in Fig. 2(a)-(b) and (c)-(d). The EB- and ES-PANis show partially crystalline structure, the volume of crystalline domains being 60 and 65% (X_{cr} = 60 and 65%) respectively. The crystal structures of the crystalline components of EB- and ES-PANis have been determined by earlier workers[15,16] and also from our work[17] to belong to orthorhombic crystal lattice. The unit cell dimensions are (i) for EB-PANi: a = 0.763, b = 0.577 and c =
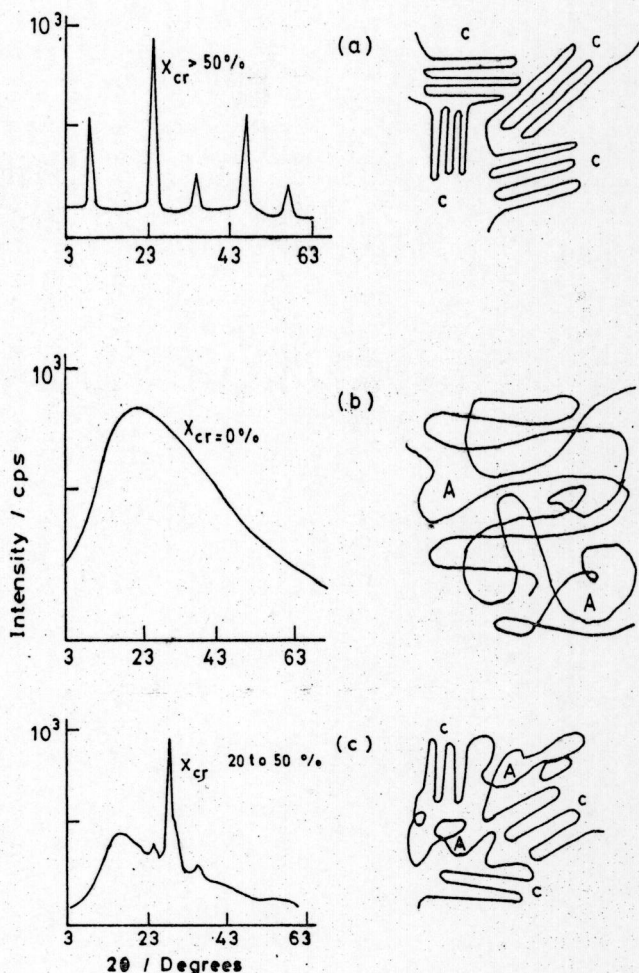

Fig. 1—Typical X-ray diffraction patterns depicting the (a) crystalline (random orientation), (b) amorphous (disordered) and (c) partially crystalline (less ordered) polymers; also schematically shown are the corresponding molecular arrangements (on the right). A—amorphous; C—crystalline.

1.051 nm; V_o = 0.463nm^3, and (ii) for ES-PANi: a = 0.762, b = 0.847 and c = 1.051 nm; V_o = 0.626 nm^3. For chemically synthesized Pth (with too less or no surfactant), the structure is found to be completely amorphous (X_{cr}=0%) as is evident from [Fig. 3(a) and (e)]. In these chemically synthesized conducting polymers, the different crystalline order characteristics are due to:

(a) Formation of only flexible polymer chains in case of completely amorphous phase.
(b) Also its co-existence along with rigid polymer molecules in crystalline domains of the partially crystalline polymers.
(c) Presence of sufficiently ordered organization of the polymer molecules in case of crystalline polymers during chemical synthesis process.

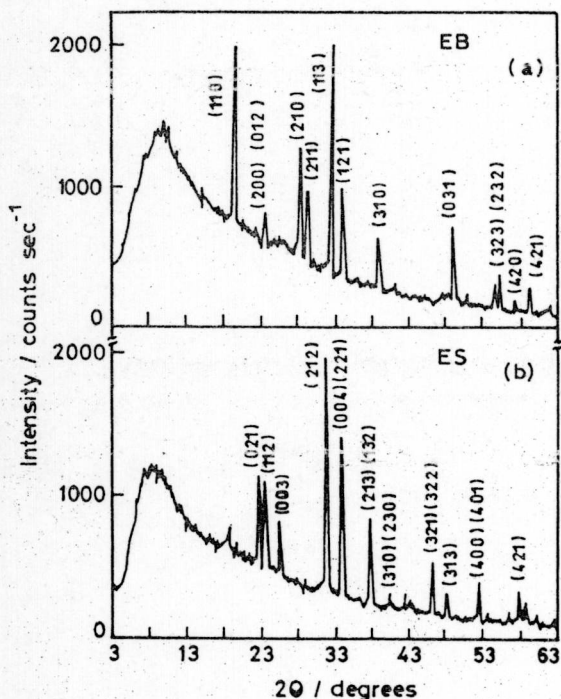However, with these initial structures of PANis, and Pth, the chemically synthesized polymers have

Fig. 2—X-ray diffraction patterns and the observed SEM morphology for: (a) PANi-EB and (b) PANi-ES. [ES and EB have the same orthorhombic lattice but different unit cell parameters]; (c) and (d) correspond to the EB and ES morphological structures respectively.

been considered for high temperature annealing possibly to induce or improve crystalline order. *Ex-situ* high temperature X-ray diffraction studies in case of amorphous-Pth samples have also been carried out. The results cited in Figs 3 and 4 may be summarized as follows:

The *ex-situ* high-temperature X-ray diffraction results of chemically synthesized amorphous-Pth show a dissociative phase transition on high-temperature annealing. The amorphous-Pth dissociates to crystalline-6T (hexithiophene) oligomer as depicted in a sequence shown in [Fig. 3(a)-(d)]. The transition starts around 500°C and completes at 600°C with 75% crystalline-6T in the amorphous-Pth matrix as clearly seen from [Fig. 3(b)-(d) and (f)]. The morphology of blunt-clusters of amorphous-Pth and the tiny-needle clusters of crystalline-6T powders are shown respectively in [Fig. 3(e) and (f)]. They are distinctly different. These morphological observations support the enhancement of the structural order of the Pth-dissociated less crystalline hexithiophene on annealing at two different temperatures 502 and 608°C. An increase in crystalline order from $X_{cr} = 48$ to 75% is observed. However, both the results of X-ray diffraction and morphology of Pth indicate that
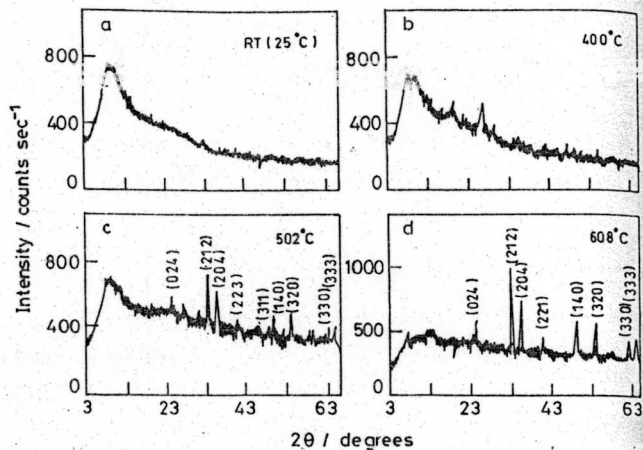

Fig. 3—X-ray diffraction patterns and the observed morphology during amorphous-Pth to crystalline-6T (hexathiophene) oligomer (dissociation) phase transition; the *ex-situ* X-ray diffraction patterns at (a) ambient (~25°C), (b) 400, (c) 502 & (d) 608°C; and (e) & (f) are morphological structures of Pth before (amorphous-Pth) and after the transition (crystalline-6T).
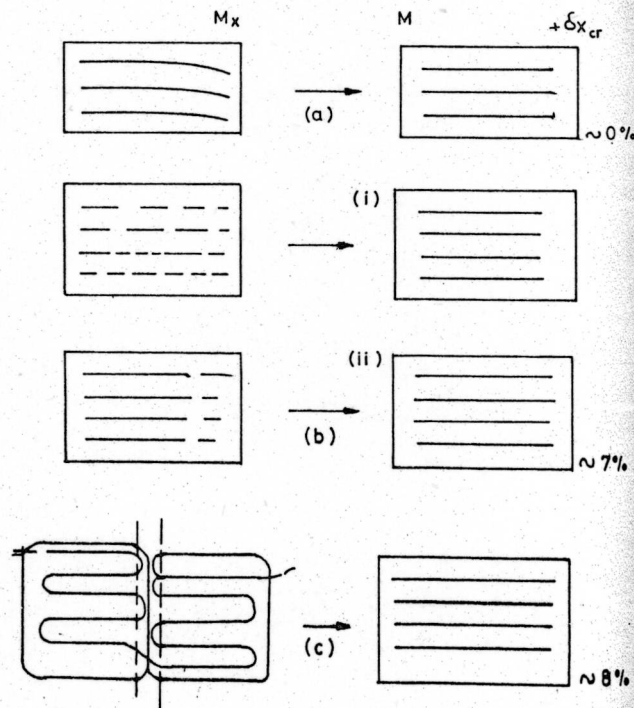

Fig. 4—A schematic illustration of molecular changes during (a) recovery, (b) re-crystallization and (c) crystallite growth phenomena on annealing partially crystalline conjugated conducting polymers. Mx & M represent molecules before and after annealing; increase in degree of crystalline order (δX_{cr}) is typically given.

there seems to be no inducement of crystalline-polymer (or polymer crystalline order) on high temperature annealing of amorphous-Pth polymer matrix. But there is a dissociative transformation to crystalline-hexithiophene (6T) oligomer since the observed crystallographic data of 6T match very well

with the standard values reported by Garnier *et al*[19]. Although crystalline-6T is an interesting and useful conjugated oligomer material like crystalline polythiophene polymer, it is not the desired and appropriate structural result required in the present context.

Mechanism of enhancement of structural order in partially crystalline polymers

A secondary means of improving crystalline order in partially crystalline polymers is to increase volume of the crystalline domains in the matrix by high temperature annealing. It is obtained by means of (i) increase in number of crystallites, (ii) reducing the non-crystalline (disordered) regions, and (iii) increase in size of crystallites (or ordered domains). The increase in crystalline order of the polymers can be estimated in terms of the (i) extent of sharpening (lower value of "half width" or FWHM) and (ii) increase in intensity, and (iii) symmetry or shape of the X-ray diffraction peak profiles.

During recovery annealing, the minor defects like small kinks or folds of otherwise linear polymer molecules already present in the ordered domains are relieved. This kind of internal ordering does not give any visible change in the X-ray diffraction response but can be regarded as self-recovery of crystalline domains from minor defects of the polymer macromolecules. Hence recovery annealing does not practically improve the degree of crystalline order, while recrystallization and crystallite growth annealing give rise to appreciable enhancement of crystalline order in the partially crystalline conducing polymers. During the annealing recrystallization, fusion of ordered oligomers in otherwise non-crystalline polymer region takes place to increase the number of crystalline polymer domains. When there is sufficient time/energy available during annealing, new (additional) ordered polymer domains are formed in the non-crystalline (partially ordered due to less-conjugation) regions of the matrix. Also, annihilation of minor chain-defects in already existing crystalline domains do occur, giving rise to linear and appreciable extension of molecular conjugation length. This method of recrystallization can have enhancement of crystalline order up to 10%. Whereas the crystallite growth by annealing enhances slightly higher crystalline order than that occurs for recrystallization, by the following two means:

(i) Fusion of short oligomers to the ordered polymer molecules by appreciably extending the polymer conjugation and hence increasing the crystallite size.

(ii) Fusion of at least two small crystallites by elimination of narrow crystallite boundaries and thereby becoming bigger crystallites.

This mechanism of molecular aspects of the secondary phenomena of recovery, recrystallization and crystallite growth is depicted schematically in Fig. 4.

An enhancement of crystalline order from $X_{cr} = 35$ to 56% due to high temperature annealing (380°C for 30 minutes) is assessed to correlate degree of crystalline order and molecular conjugation. Considering the polythiophene (pth) X-ray diffraction data[18] by Mo *et al.*, the following salient features can be compared:

(i) The sharpening of X-ray diffraction peaks or less values of FWHM indicates the gradual increase in conjugation length of 1200 thiophene rings or molar mass equivalent to $\sim 10^5$ amu for an increase of crystalline order from $X_{cr} = 35$ to 56%.

The enhancement of crystalline order during annealing re-crystallization regime obtained mainly due to increase in coherence length is mostly due to:

(ii) Increase in the molecular conformational order leading to increase in crystallite size and newly formed (additional) crystalline domains. It is basically the enhancement of conjugation and orderly organizations of conjugated molecules contribute to a higher density value of higher crystalline polymers. Hence, density of partially amorphous material becomes less than that of the fully crystalline polymer as found out experimentally.

(iii) Although exposure of the polymers to slightly higher temperature is to further improve structural order, the onset of polymer degradation occurs and hence sets a practical limit for the heat-treatment/annealing temperature/time under specified atmosphere like vacuum or Ar.

(iv) One of the most effective concerns of the conjugated polymer structural order is the extent of homogeneity and compact packing of the conjugated molecules. It may be quantitatively regarded that the degree of conjugation is along the linear polymer main chain that determines the molecular and crystalline orders of the polymers. Higher the molecular order, higher is the

crystalline order and so higher are the charge transport behaviors including electrical/electronic conductivity of the polymers.

It is now intriguing to ask: how do such useful recovery, re-crystallization and crystallite growth phenomena can be measured and manifested in partially crystalline conjugated polymers? Initially, as there is not much change in either conjugation length or volume of the crystalline domains during the recovery regime, no measurable change occurs either in d-values, intensity or in shape of the diffraction peaks. In the re-crystallization regime, an appreciable increase in intensity and a "little" narrowing of the peaks are found. During the crystallite growth period, there is an appreciable increase in both intensity and sharpening (less FWHM) of the peaks does occur. The general background of the X-ray diffraction pattern of the crystalline/partially crystalline conductive conjugated polymers after annealing is found to be relatively less, while distinctively sharp X-ray diffraction peaks show slightly less d-values. This indicates the compactness of the polymer macromolecules and their ordered organization forming inter-molecular layers during the annealing. (This reduction in intermolecular layer distance in higher or highly crystalline conjugated polymer thin film is more effective although small but appreciable changes in d-values and FWHM (and orientation) are observed. In case of partially crystalline or amorphous polymers of intrinsic Xcr < 20%, not only the intensities are very low, the peak(s) are broad at higher-d-values corresponding to the same crystal lattice in the form of turbostatic structure. It reflects the insufficient structural ordering and organization of the polymer molecules). This situation may now be compared to the molecular mechanism of recovery, re-crystallization and crystallite growth shown in Fig. 4 and in the schematic illustration given in Fig. 1. At this juncture, it is to be noted that electrochemical synthesis of conjugated polymer thin films in microemulsion media by Levi et al.[20], Phani et al.[21], and Mani et al.[22] give rise to highly crystalline and molecular orders. This approach remains also as the best way to overcome the problems of chemical processibility, less structural order, thin film inhomogenity, thermal instability and less operating (active) life of the conducting polymer films obtained by multiple-step processes[18,22,23].

The difference in the structural characteristics including orientation effect depend on temperature, substrate and vacuum condition of the deposition with always a possibility of some loss of polymer material and the oxide impurity effect. It is for these reasons that chemical and electrochemical means are preferable for obtaining highly ordered conjugated polymer structures, and particularly the electrochemical approach for it has an excellent control at the electronic, atomic or ionic, molecular and lattice levels of the polymer thin films. This part of the experimental analysis will be discussed in our next communication.

Conclusion

Systematic analysis of X-ray diffraction and scanning electron microscopy data of partially crystalline conjugated polymers indicate (i) an altogether high crystalline order PANis up to 65%, (ii) Pth-dissociated hexithiophene and its increase in crystalline order due to high temperature annealing up to about 30%, (iii) no initiation of crystalline polymer phase in the amorphous matrix (Pth), and (iv) the mechanism of observed increase in crystalline order due to high temperature annealing is explained in terms of molecular phenomena taking part in the re-crystallization and crystallite growth processes.

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