# Polymeric Energy Materials: Development and Challenges

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The discovery of conjugated, conducting polymers (CPs) polyacetylene (PA) in 1977 opened up a new frontier in the field of polymer science for both academia and industries. CPs possess characteristics such as excellent tunability, ease of synthesis, eco-friendliness, processability etc. These features have enabled the exploration of its applicability in energy and electronics devices. It has also paved way for extensive research world over to develop novel methods for synthesizing CPs with required properties. An important area in the field of synthesis of CPs is to produce conducting nanocomposites with the combination of conducting polymers and inorganic materials in order to achieve high magnitude of electrical conductivity. Several polymeric materials such as, as poly(3,4ethylenedioxythiophene) (PEDOT), polypyrrole (PPy), and polyaniline (PANI) have exhibited potential in various applications such as, "energy harvesting", "energy storage", "light emitting", and "sensing". The objective of this review is to develop better understanding on conducting polymers used for energy and electronics application. The review presents the state of research in the development of CPs with a focus on general synthesis method, morphology and dependent properties along with the discussion on challenges with possible solutions.

## Introduction

With ever increasing population, the demand for electrical energy is growing exponentially. Lot of efforts is being made to fulfill the growing demand. The major challenge that is needed to be addressed is the storage of electrical energy. Current storage mechanisms have inherent limitations such as large volume and weight, low efficiency, lesser charge density, hazardous nature and high cost. Hence, novel energy storage devices are the need of the hour. The solution to the limitations of existing storage technologies is the use of CPs. CPs at Nano- size generates interesting physicochemical properties which make them promising candidate for potential storage applications.

At present, supercapacitor and lithium ion battery are the candidates which help to meet the next generation energy requirement. CPs are the fundamental material for the fabrication of the energy storage devices [1]. They play exceptional characters in both physical and practical requirements of these devices [2]. Extensive work have been reported in exploring CPs such as, PEOT, PPy, and PANI for the energy storage capacitance [3]. This polymer possesses low electrical conductivities therefore require morphological insertion of the foreign materials to guarantee satisfactory rate performance [4]. CPs materials are smart materials used for the fabrication of electrodes, separators membrane between electrodes and may be used as effective electrolytes in Li-ion batteries [5]. Compare to many CPs, the most commonly employed polymers includes PA [6], polyphenylene (PPh) [7], PANI [8], PPy [9], and polythiophene (PTh) [10]. Besides light weight and flexibility, CPs are outstanding in number of applications such as light emitting diodes, transistors, electrochromic devices, capacitors, photovoltaic cells and sensors [11-23].

There are many challenges in the development of these materials with desired morphology and therefore thorough research is required for using these materials in energy storage devices. This review discusses various aspects of polymeric energy materials that are characterized primarily by their inherent conductivity and distinct morphology.

## Characteristics of conducting polymers

Numerous exciting features of using CPs materials to engineered electronic and energy devices have been reported by many researchers along with their limitations [24]. Life time of the electronic and energy devices depend on the stability of each component used to engineer them [25]. Majority of the polymer-based photovoltaic cells have short life when they are operated in air which is much shorter compared with silicon- based solar cells [26-27]. Unavoidable degradation of polymeric materials when they are in contact with various environmental, working parameters and chemical atmosphere has been reported by few researchers [28-29]. During charge and discharge processes some CPs undergo capacitance loses [30]. In contrast, low electrical conductivities of the CPs also limit their applications and device performances [31-32].

## General Synthesis method for conducting polymers

Since last decade, researchers have made enormous progress in polymerization methods to synthesize reliable,

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stable, flexible and safe CPs which make them economically viable. The main aim in the synthesis of CPs is to introduce carbon-carbon double bond (C=C) in the polymeric backbone. After the discovery of polyacetylene, efforts were made to synthesize it effectively. First attempt included use of "Ziegler–Natta" catalysts [33]. A novel method for synthesizing long polyacetylene chains is the use of thermal energy in conversion of precursor polymers [34]. Ring opening metathesis polymerization is a facile method to introduce C=C in linear and branched alkyl chains [35].

Synthesis of commercial and reliable CPs requires effective carbon–carbon single bond [36]. Effective C-C single can be achieved by chemical and electrochemical polymerizations [37,38]. PANI, PPy, PTh, etc. and their doped forms are the result of chemically or electro-chemically oxidative polymerization [39,40]. A flexible integrated device was subsequently fabricated based on ultrathin Si substrates. The thickness of the ultrathin Si could be controlled by the etching time and the substrate became flexible when the thickness went down to dozens of micrometers [41]. Due to small surface area of the working electrode in electrochemical polymerization, bulk production is not possible and therefore their applicability is limited. In chemical polymerization, the powdered form of the raw materials has solubility issues, which limits its usage [42]. Random couplings for asymmetric monomers are also observed by both electrochemical and chemical type of polymerizations [43]. To overcome this problem, transition metals and their compounds were used as catalyst and these metal-catalyzed cross-coupling reactions have turned out to be a powerful tool for the synthesis of CPs [44-49]. Direct arylation polycondensation (DArP) is the emerging process for the production of CPs [50-52]. However, DArP does not result in excellent morphology [53]. In CPs band gap plays a vital role to make it prolific for application in electronics. Conducting polymer hydrogels emerge as a novel class of polymeric materials that show great potential in many energy, environmental, and biomedical devices [54]. To attain specific band gap value and to adjust the electronic energy levels of the CPs, introduction of Lewis acid and Lewis base into polymeric backbone is required [55]. In recent years, researchers have focused on the side chain and addition of substituents in CPs to increase their "solubility", "process ability", "energy level", "band-gap", "molecular interaction" and "morphology" [56-57].

**Properties and their morphological relation**

Deeper understanding of material morphology and relation between the chemical components, molecular structure and their electronic properties is to be developed. At present, morphologies such as "nanoparticles", "nanofibers", "continuous films", "porous films" and "polymer gels" have caught the attention of several researchers due the size of the particle, their physicochemical characteristics and excellent morphology. It has led to wide applications in almost every field of technology [58-61].

The electronic properties of CPs hang on the shape and structure of the polymer chains and the alignment of these chains with respect to each other [62-66]. In amorphous polymers, the charge transport behavior is non-uniform which limit their use as CPs. This limitation is resolved by charge–phonon couplings [67-68]. In crystalline polymers, charge mobility is found to be lower compared to polymer having a single backbone [69-70]. Various synthetic approaches have been employed to synthesize zero-dimensional stable nanoparticles by controlling their morphology [71]. Core-shell and hollow nanoparticles structures exhibit superior conductivity [72]. Nanofibers have also gained attention to engineer various devices for practical applications due to their large aspect ratios and curvatures. Their morphology depends upon the concentration of the reactant [73]. Organic polymeric films are extensively being used for electronic applications compared with their inorganic counterparts due to mechanical properties such as elasticity and plasticity, ease of processing, ability to tune, and lesser weight [74]. Poly (3-hexylthiophene) (P3HT) has been widely used in polymer-based electronics devices. These devices are transistors, light-emitting diodes (LEDs) and solar cells [75]. Excellent crystalline structure, increased mechanical flexibility and accelerated charge transport compared to the solid thin film is achieved when morphology change occurs in one Dimensional (1D) nanostructures [76].
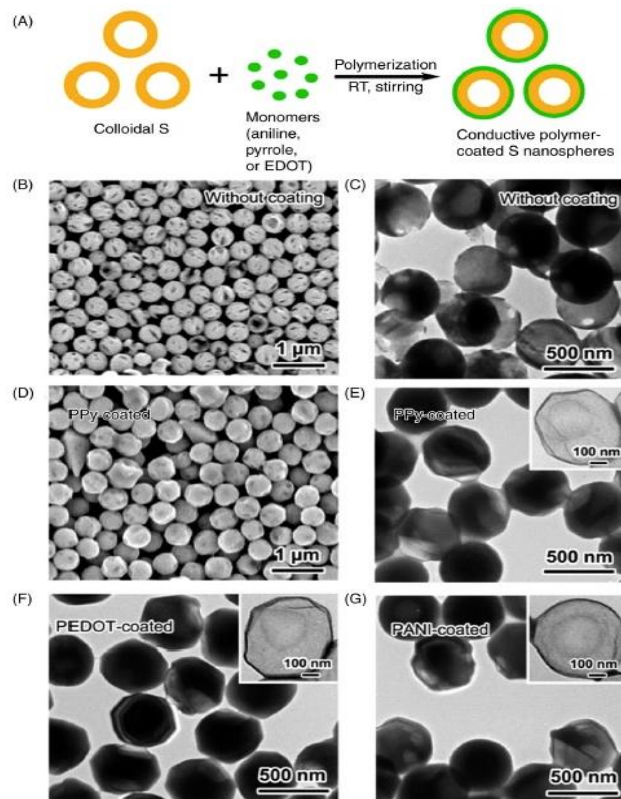


**Fig. 1.** (A) CP's Nanosphere (B) and (D) Scanning electron microscopy (SEM) and (C) and (E) transmission electron microscopy (TEM) of PPy. (F) & (G) TEM images of the PEDOT and PANI.

Low energy due to presence of twists in the structure can be reduced using suitable orientation and hence increase the conductivity [77]. If the polymeric chains are lengthier than the crystalline spheres then the chains get twisted and offer resistance conductive pathway [78]. It is also observed that flow of charge is more along the polymeric backbone than the other crystallographic sphere [79]. Doping with primary or secondary dopants also helps to increase the charge flow [80].

Polymers with electrochemical properties have extensively being used over past few decades [81]. The electrochemical characteristics of the CPs mainly depend upon the combination of two different materials in which one is electron donor while other is acceptor [82]. Radical polymers have emerged as new materials with a non-conjugated backbone and stable radical groups. These radical polymers have shown advantages such as easy synthesis on large scale with excellent electronic properties, tunability to p-type and n-type and device stability by functional groups' change [83]. Electroluminescent properties of CPs also used extensively in number of applications such as light-emitting devices, photovoltaic devices, molecular electronics and luminous nanoparticles [84].
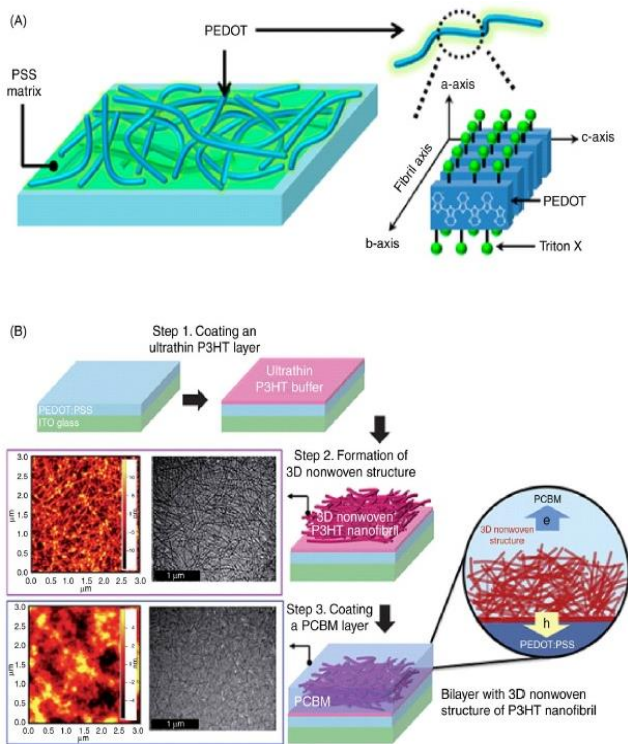


**Fig. 2.** (A) polymer solar cell (B) Fabrication of a three-dimensional (3D) nanofiber [84].

Along with the conducting characteristics of the CPs, their mechanical properties also play a vital role to make them reliable for practical use. The mechanical properties of the polymer are greatly affected by its elasticity (See **Fig. 3**). Elasticity of any polymer depends upon its density, arrangements of particles and morphology,

especially the degree of crystallinity [85]. Alternate double bonds present in backbone of a conjugated polymer are accountable for their toughness and frangibility [86]. In the polymeric backbone, the presence of connected or isolated rings, dimension and composition of branched substituents, molecular weight microstructure order and inclination to form crystallites are few of the characteristics of the polymer which decides its mechanical behavior [87,88].
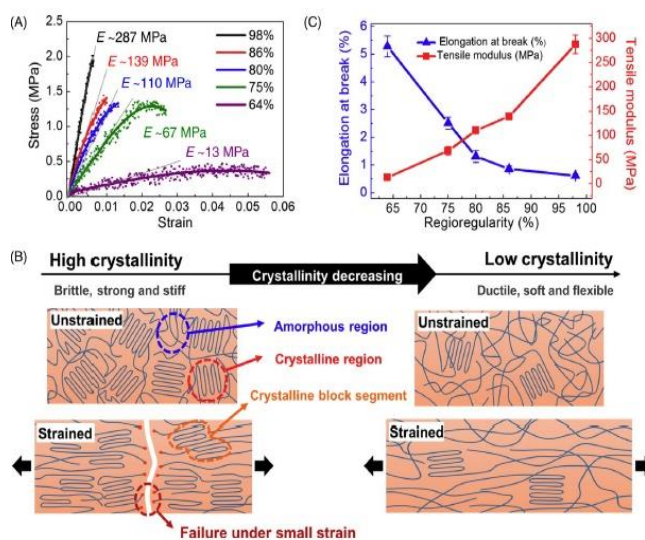


**Fig. 3.** Mechanical properties and deformation mechanism of P3HT thin films [87].

## Challenges and their possible remedy

The challenges in use of CPs are stability, electrical conductivity, temperature tolerance, large scale production, etc. Life time of electronic and energy devices are governed by the degradation time of the polymeric materials. The life-span of photovoltaics cell fabricated by polymers ranges between minutes to a few days which is much lower compared to solar cell made up of silicon. By controlling the morphology and chemical modification in polymeric materials, stability and life enhancement can be achieved. Capacitance loss is another challenge in some of the CPs which is the result of irreversible redox reactions. Improvement in the electrical conductivities of CPs decreases the internal resistance; accelerate the response speed and performance of the fabricated devices. Polymeric materials also have poor temperature tolerance and hamper their candidature for fabricating energy and electronic devices. At present this challenge is sorted out by conducting a transfer process in which the devices and polymer substrate are cast separately and cladded at low temperatures. This process results in mismatching of the fabricated devices on the basis of appearance, performance and has fabrication complexity and high cost. Large scale production of polymer materials for electronic and energy devices applications is still challenging. Few of these challenges can be overcome using low-temperature processing methods.

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Organic polymeric materials, whenever exposed in various environmental conditions get degraded. By controlling the morphology and chemical modification in polymeric materials, stability and life enhancement can be achieved. For example, insertion of fullerene (C60) in between the active film of aluminium acts as protective layer and hamper the deteriorating reaction thereby increasing its life [**89**]. Capacitance loss is another challenge in some of the CPs which is the result of irreversible redox reactions [**90**]. The application and device performance of electronic and energy devices is based on the electrical conductivity of the material from which they are fabricated. Low electrical conductivities limits their applications and performance. In this context, supercapacitors fabricated from naked polyaniline films have low electrical conductivity of 0.05 S cm−1 and demonstrated low specific capacitance of ~26 F g−1 at 0.5 A g−1. It was enhanced upto the level of 570 S cm−1 having specific capacitance of ~110 F g−1 by incorporating carbon nanotubes [**91**]. Improvement in the electrical conductivities of CPs decreases the internal resistance, accelerate the response speed and performance of the fabricated devices. In this regard numerous work is carried out throughout the globe to synthesize promising polymers with required morphologies [**92**].

Temperature tolerance is another significant challenge in this field. Majority of the polymeric materials have poor temperature tolerance and hampers there candidature for fabricating energy and electronic devices. High temperature fabrication methods, such as chemical vapor deposition and thermal annealing require polymeric material with outstanding temperature tolerance compare to conventional polymers such as polyethylene and polyethylene terephthalate having temperature tolerance ability of 80 and 150°C, respectively. At present this challenge is sorted out by conducting a transfer process in which the devices and polymer substrate are cast separately and cladded at low temperatures. This process results in mismatching of the fabricated devices on the basis of appearance, performance and many more. Besides this, the process has fabrication complexity and high cost which limits their industrial usage. To overcome the above-mentioned challenges, advancement in low-temperature processing methods is require along with enhancing their thermal stability [**93**].

Numerous polymeric materials are successfully used in various industrial production, however, large scale production of polymer materials for electronic and energy devices applications is still challenging. For aiming high device performance, stability, temperature tolerance, etc.in fabricated electronic and energy devices on large scale requires polymeric material with excellent morphology. Large scale production of the electronic and energy devices is not achieved by conventional synthesis methods. To scale-up the production, new synthetic approaches with novel methodologies are to be used.

## Conclusion

Conducting polymers have been extensively used for the fabrication of numerous electronic devices. Remarkable advancement in the field have been observed over the recent years as the researchers around the globe are trying to design and synthesize novel conducting polymers. Still various challenges exist in the large- scale applicability of the CPs. This has limited their usage at commercial level. These challenges are, control over the morphology, mechanical and electrical properties, stability and environmental degradation, low resistance to high temperature and Scaling up the production quantity.

The primary solution to most of these challenges is to develop an economically viable synthesis technique or methodology. The key to the success of this development would be the level of predictability achieved in the molecular design of conducting polymers as it would lead to commercialized production and usage of these polymers.

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**Abbreviation**

(a) Conducting polymers (CP's)
(b) Polyacetylene (PA)
(c) Poly(3,4ethylenedioxythiophene) (PEDOT)
(d) Polypyrrole (PPy)
(e) Polyaniline (PANI)
(f) Polyphenylene (PPh)
(g) Polythiophene (PTh)
(h) Direct arylation polycondensation (DArP)
(i) Poly(3-hexylthiophene) (P3HT)
(j) Scanning electron microscopy (SEM)
(k) Transmission electron microscopy (TEM)