

Chapter 6

Cardanol-Derived-Amphiphiles-Based Soft Templates for Conducting Polymer Nanoarchitectures

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Abstract In recent times, there is a growing trend among researchers in utilizing plant based starting materials to synthesize functional nanomaterials. Toward this goal, cashew nut shell oil-derived cardanol caught great attention due to its wide availability, low cost, easy isolation and unique molecular architecture. In this chapter, we summarize the literature based on soft template approach of cardanyl amphiphiles for fabricating conducting polymer (polyaniline and polypyrrole) nanostructures. The amphiphiles synthesized from cardanol has typical surfactant structure with sulfonic acid polar head and hydrophobic aliphatic tail, often referred as dopants due to its post-polymerization doping effect on polymer chain. The soft- templates were generated by selectively mixing monomer and dopants for different polymerization conditions such as emulsion, dilute, interfacial, dispersion and gel phase. The templates upon treatment with polymerization initiator produce conducting polymer morphology such as nanofibers, nanorods, nanotubes, nanospheres, hollow nanospheres and nanotapes. The cardanyl amphiphilic dopants electrostatically complex with conducting polymer nanomaterials and significantly improve the solubility, solid-state ordering, conductivity and optical properties.

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6.1 Conducting Polymers and Its Nanostructures

Conducting polymers are class of π -conjugated materials that can conduct electricity via the π -electron delocalization through alternative single and double bonds present in the polymer backbone [1–5]. Conducting nature was intrinsic to the π -conjugated electrons present in the conducting polymer backbone. Some important members of conducting polymer family are polyacetylene (PA), polypyrrole (PPy), polythiophene (PT), poly (p-phenylene) (PPP), poly (p-phenylenevinylene) (PPV) and polyaniline (PANI), etc. [5–9]. Among various types of conducting polymers, polyaniline and polypyrrole receive a special attention owing to its easy synthesis, low cost of production, acid-base and redox control on structures and conductivity, etc. [6–9]. Polyaniline and polypyrrole are generally synthesized by chemical or electrochemical oxidative polymerization of monomers in acidic aqueous solution [10–15]. Usually acid-base treatment (often referred as doping–dedoping process) brings about changes in charge and electronic states of the polyaniline and polypyrrole, while retaining the same the structural backbone. The three commonly known forms of polyaniline are (i) fully reduced colorless leucoemeraldine, (ii) fully oxidized brown-colored pernigraniline and (iii) half-oxidized blue-colored emeraldine base (see Fig. 6.1). All these three forms are found to be insulators of electricity in normal conditions. Green-colored conducting emeraldine salt form of polyaniline is obtained by *in situ* or post-doping using mineral/organic acid [16–20]. Similar to polyaniline, neutral polypyrrole upon doping produces charged polypyrrole (with quinoid like structures) which remarkably changes the conductivity from insulating states to metallic with the formation of polaron and bipolaron charge carriers [6, 7, 21–23]. The optical, electrical, thermal, electrochemical and solid-state properties of these interesting polymers were extensively studied and well documented

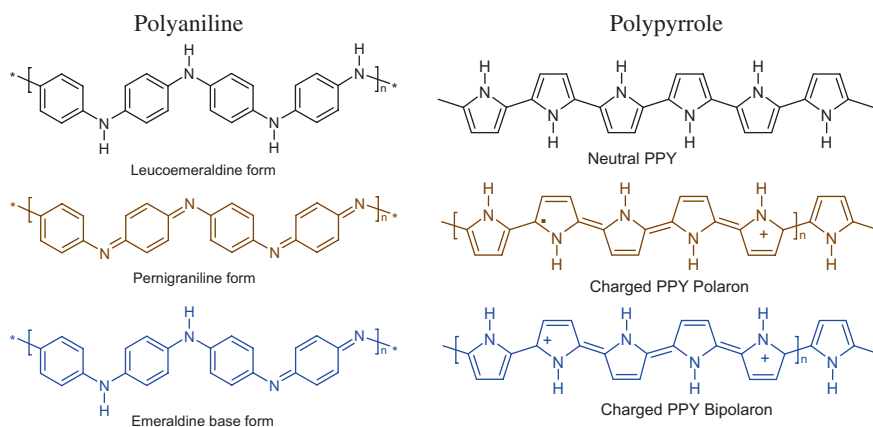


Fig. 6.1 Various forms of polyaniline and polypyrrole

by various groups around the world [23–27]. Polyaniline and polypyrrole found to have promising applications in different fields such as sensors, actuators, catalysis, memory devices, modified electrodes, DNA sensing, metallic corrosion protection, electromagnetic interference shielding, super capacitors and many other applications [27–40].

Ever since the emergence of the nanotechnology, there are tremendous efforts directed toward restricting the morphology of conducting polymers into nanometric scale for the expected supreme performance over bulk conducting polymer materials [41, 42]. The miniaturization of conducting polymeric materials yields profound changes in physical properties such as optical, electrical, mechanical and dimensional properties (such as surface area, volume). [41–52]. Different physical or chemical methods such as electrospinning, templating, emulsion and interfacial polymerization methods were utilized for the development of conducting polymer nanostructures [53–56]. Templating method utilizing hard or soft templates was extensively used for fine tuning the size, shape and other physiochemical properties of the resulting conducting polymer nanomaterials [56–60]. The use of hard templates such as porous silica or alumina often encounters difficulty in post-polymerization removal of template and purification [41, 60]. On the other hand, the use of soft templates such as micelles, gels and liquid crystals is easily applied for nanomaterial synthesis without any tedious post-polymerization steps [58–66]. This chapter summarizes the utilization of soft templates derived from cashew nut shell liquid (CNSL) as amphiphilic dopants for constraining the morphology of polyaniline and polypyrrole in nano/micro-dimensions.

6.2 Design and Synthesis of Cardanyl Amphiphiles

The synthesis of nanomaterials utilizing renewable resource feed stocks is highly attractive in both academic and industrial point of view because of its ability to replenish non-renewable petroleum-based starting materials [67, 68]. CNSL is a natural organic plant-based renewable resource and a by-product from cashew industry, often considered as an industrial waste and pollutant. Technical CNSL contains a variety of phenolic derivatives with anacardic acid as the major chemical constituent [67, 68]. Preheating and subsequent vacuum distillation (230 °C at 5 mm of Hg) of CNSL result in the decarboxylation of anacardic acid to yield cardanol. Cardanol is a unique amphiphilic phenolic molecule with *meta*-pentadecenyl chain with one or two or three unsaturated bonds [67, 68]. Recently, there is a renewed interest in utilizing the unique chemical features of cardanol to synthesize cardanyl-based amphiphiles for developing various self-assembled nanostructures. For example, G. John et al. synthesized glycolipids by tethering glucopyranose to cardanol, and the sugar moiety acts as a nonionic polar head group and bestows chirality to the molecule [69, 70]. Soft materials, such as twisted fibers, helical coils and high axial ratio nanotubes, were formed through the self-assembly of amphiphilic glycolipids. Pillai and co-workers synthesized amphiphilic sulfonic

and phosphonic acids as dopants from cardanol derivatives and utilized for bulk polyaniline synthesis [71–73]. They observed that cardanol upon treatment with conc. H_2SO_4 produces a resin rather than ring sulfonation due to the presence of unsaturated bond in pentadecyl side chain. Hence, in the first step hydrogenation of cardanol was carried out to saturate the side chain and the saturated cardanol (3-pentadecylphenol) was sulfonated to give the sulfonic acids. These saturated aromatic cardanyl sulfonic acids were found to be good dopants for bulk polyaniline and their blends. But these saturated cardanol-based dopants have limited solubility in water at room temperatures, and it does not act as suitable soft templates for conducting polymer nanomaterials. To address this issue Jayakannan and co-workers came up with new chemical approaches for the direct utilization of cardanol to synthesize water-soluble dopants which can act as soft templates for the growth of polyaniline nanomaterials and related polymeric systems [74–89].

The design of cardanyl amphiphiles is very simple; the in-built long *meta*-pentadecenyl side chain attached to the cardanol acts as the flexible hydrophobic tail component, and sulfonic acid group introduced either through diazotization reaction or by direct ring opening reaction serves as a polar head. The molecular design is optimum for imparting dopant functionality and amphiphilic surfactant properties. The chemistry employed for the synthesis of the amphiphilic molecules is direct single-step reaction, which gives fairly good yield. In the first synthetic approach, cardanol under basic conditions reacted with diazotized sulphanilic acid to yield 4-[4-hydroxy-2(*Z*)-pentadec-8-enyl]phenylazo]-benzenesulfonic acid (dopant-1) (see Fig. 6.2). Dopant-1 is an amphiphilic anionic surfactant molecule having a flexible tail and polar azobenzenesulfonic acid head group [76, 77]. Orange red-colored dopant-1 shows molecular dye properties such as molecular light absorption and emission properties which were valuable tools for tracing the molecular self-assembly. In the second approach of cardanol derivatization, direct coupling reaction of butane sultone with cardanol and saturated pentadecyl phenol using potassium tert-butoxide as base produced two amphiphilic molecules (*Z*)-4-(3-(pentadec-8-enyl)phenoxy)butane-1-sulfonic acid (dopant-2) and 4-(3-pentadecylphenoxy)butane-1-sulfonic acid (dopant-3), respectively [78, 79] (see Fig. 6.2). Dopant-2 is having optimum

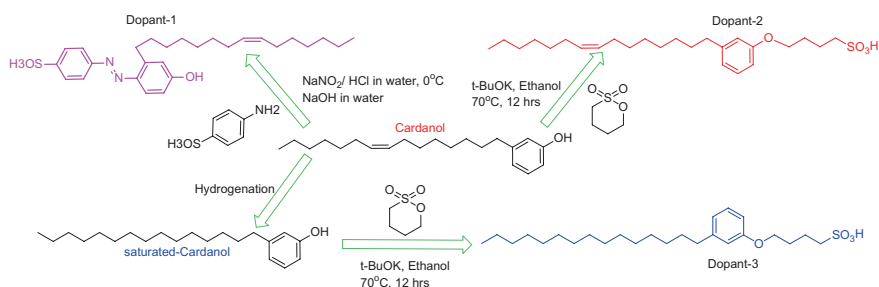


Fig. 6.2 Synthetic strategies for cardanol-based amphiphiles (dopant-1, dopant-2 and dopant-3). Reprinted with permission from ref [74] (2009, <http://ir.niist.res.in:8080/xmlui/handle/123456789/878>), [78] (2009, American Chemical Society), 81 (2008, American Chemical Society)

polar head to tail balance and capable of showing typical micellar characteristics and emulsification behavior with different aromatic monomers. The dopant-3 derived from 3-pentadecyl phenol is partially soluble in water, but it has the advantage of forming organogel in ethanol and other polar solvents.

6.3 Self-Assembly Properties of Amphiphilic Dopants

The two cardanol-based sulfonic acid amphiphiles dopant-1 and dopant-2 were soluble in water, whereas the saturated cardanol derivative dopant-3 was only sparingly soluble in water. The dopant-1 and dopant-2 have typical surfactant structure and forms micelles in aqueous solution. The critical micellar concentration values of the dopants determined by multiple techniques such as UV-visible absorbance spectroscopy, fluorescence studies, ionic conductance and surface tension techniques were shown good agreement, and the values were obtained in millimolar range [74, 77, 81].

The dopant-1 upon dissolution in water resulted in pale yellow-to-brown-colored clear solutions [77] (see Fig. 6.3). Dynamic light scattering (DLS) studies of dopant-1 showed that the cardanyl azobenzenesulfonic acid molecule exists in the form of the micelles (at 1×10^{-3} M) in water with an average diameter of

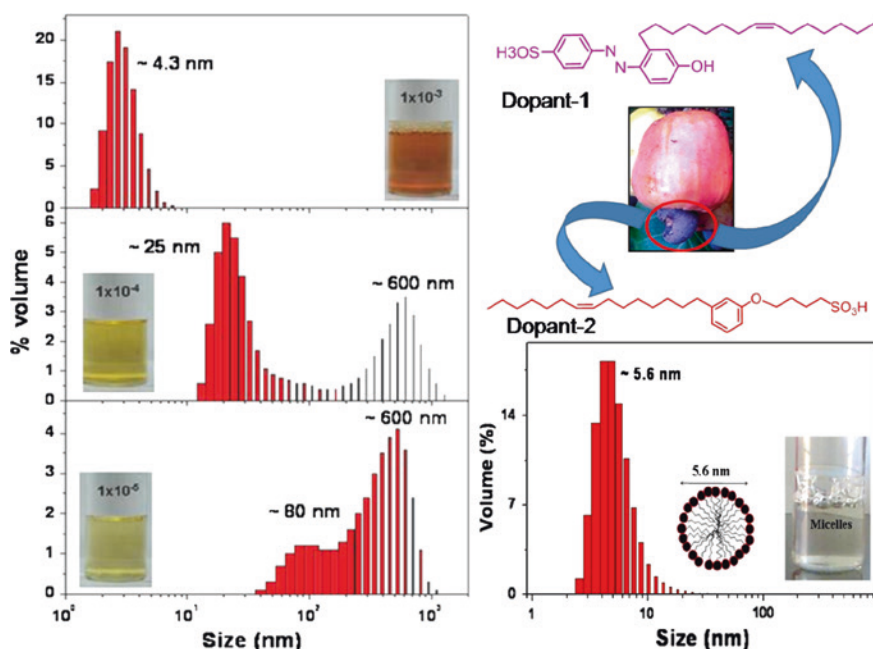
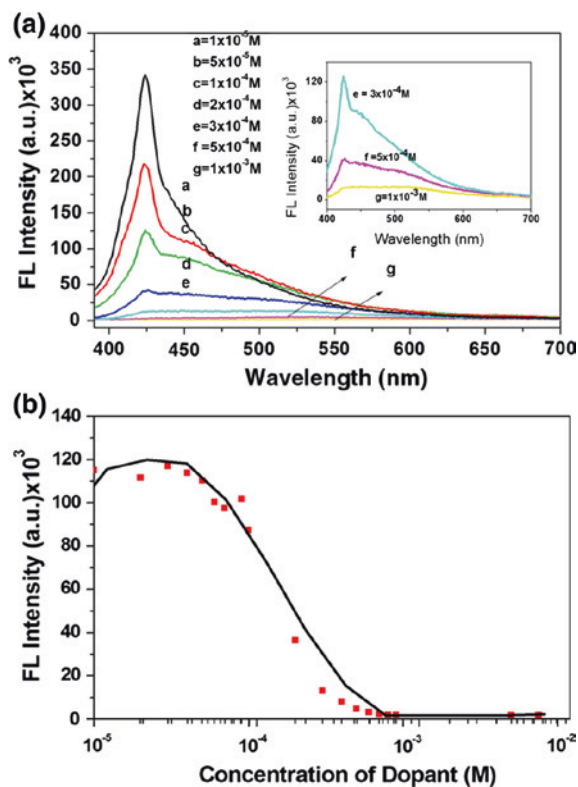


Fig. 6.3 DLS histograms of dopant-1 and dopant-2 in water. Reprinted with permission from Ref. [74] (2009, <http://ir.niist.res.in:8080/xmlui/handle/123456789/878>), [78] (2009, American Chemical Society), [81] (2008, American Chemical Society)

4.29 nm. DLS profile of 1×10^{-4} M dopant solution showed a bimodal distribution with maxima centered at 25 and 600 nm. A further decrease in dopant concentration (1×10^{-5} M) increases the aggregate size to 600 nm. DLS study indicated that at lower concentrations the dopant molecules were existing as open aggregates (like layers) in water and completely transformed to micelles as the concentration of dopant becomes 1×10^{-3} M [74, 81]. The dopant-2 upon dissolution in water forms a colorless clear solution at lower concentration and become clear soapy solution at higher concentration above CMC. DLS study of the dopant-2 in water for the concentration of 1.1×10^{-2} M shows that the amphiphilic cardanyl butane-sulfonic acid molecule existed as 5.6-nm-size micelles in water [78] (see Fig. 6.3).

Dopant-1 possesses fluorescence property which is peculiar and rarely seen in amphiphilic dopants. Fluorescence property of the dopant-1 provides great deal of information regarding the self-assembly behavior in aqueous solution [77]. The fluorescence spectra of the dopant-1 at different concentrations in water were obtained by exciting molecule at 360 nm wavelength. The fluorescent intensity of the dopant-1 is highly dependent on its concentration in water, and the emission maximum is centered at 450 nm. The emission intensity of the dopant increases with the increase in the dopant concentration (1×10^{-6} to 1×10^{-5} M) and

Fig. 6.4 Concentration depended fluorescence studies of dopant-1: (a) fluorescence emission spectra, (b) intensity change. Reprinted with permission from Ref. [74] (2009, <http://ir.niist.res.in:8080/xmlui/handle/123456789/878>), [77] (2007, American Chemical Society)



attained maxima at 1×10^{-5} to 7×10^{-5} M (see Fig. 6.4). Further increase in the dopant concentration (6×10^{-5} to 6×10^{-4} M) decreases the emission intensity, and the fluorescence nature is completely lost above 1×10^{-3} M. This nonlinear trend is due to the existence of dopant-1 aggregates in more than one form depending on its concentration in water. At low concentration, the dopant-1 molecules existed as isolated molecules, and with an increase in concentration, they form fluorescent layer structures. At higher concentration, the dopant-1 molecules forms well-defined spherical micelles and the fluorescence property is quenched [74, 77]. Concentration-dependent DLS and fluorescence studies of dopant-1 pointed out the involvement self-assembly which eventually leads to spherical micelles at higher concentration.

The dopant-3 molecule showed organogel formation in various organic solvents such as ethanol, methanol, chloroform, DMSO. [79]. Among different solvents, ethanol produced stable opaque white gel for wider concentration range. Differential scanning calorimetric (DSC) analysis of the gel in ethanol showed a broad melting peak at 65 °C with respect to gel-to-sol transitions, and upon cooling the sol-to-gel transition phase occurred at 53 °C [79]. SEM analysis of the xerogels showed the presence of long self-assembled fibrous tape-like morphology characteristic of the typical organogel texture, which is further supported by AFM analysis (see Fig. 6.5) [79]. TEM analysis revealed that the inner parts of the fibrils possess hollow space similar to nanotubes. The average inner and outer diameters of the nanotubes were 60 and 175 nm, respectively. The morphological studies of nanotubes conducted support the logical conclusion that nanotubes are formed by a multilayer packing of self-assembled dopant-3 molecules [79].

6.4 Soft-Template Formation with Monomers

Synthesis of conducting polymer nanostructures with various types (like nanofibers, nanorods, nanotubes and vesicles) has been achieved through polymerisation of soft template produced by aggregating monomers (aniline or pyrrole) into the self-assembly of dopants (dopant-1, dopant-2 and dopant-3). These dopant plus monomer soft templates produced in solution phase or gel phase upon treatment with suitable initiators induce polymerization of the monomers trapped inside the molecular templates and thereby translate the template morphology into the resultant polymer morphology. The polymerization method utilized were emulsion, interfacial, dispersion, gel-assisted routes and copolymerization employing ammonium persulfate or ferric chloride as the initiator [74–88].

The soft-template formation very much depends on factors such as concentration, types of monomer with which it combines, polymerization routes, pH. In the emulsion route, the dopant-1 plus aniline template mostly existed in more than one form of assembly such as layered membranes and cylindrical micelles depending on the concentration of the dopant-1 in solution. SEM and TEM studies of the dopant-1 plus aniline template confirm the formations of cylindrical micellar

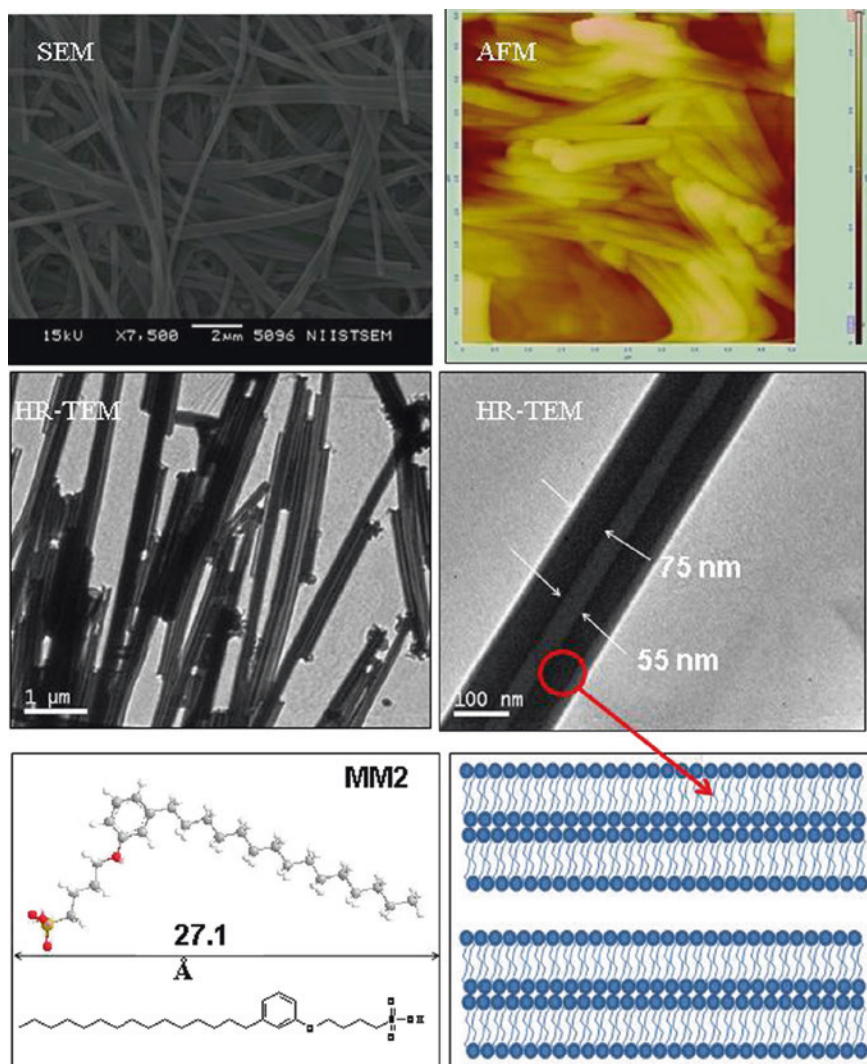


Fig. 6.5 SEM, AFM and TEM images of xerogel of dopant-1 in ethanol (*top and middle rows*) and theoretical structure and packing of dopant-1 in gel (*bottom row*). Reprinted with permission from Ref. [79] (2009, American Chemical Society)

templates exclusively at higher dopant concentrations [76, 77]. Interestingly, the emulsion of pyrrole showed a completely different aggregation pattern with dopant-1, and spherical aggregates of 650 nm were formed at higher concentration of dopant-1. The sizes of the dopant-1 + pyrrole micelle aggregates were reduced to 150–200 nm and even less at dilute concentration of dopant-1 [84, 85]. Soft templates of aniline and pyrrole together with dopant-1 exhibited short flaky rods at higher concentration and hollow spheres and nanotubes at lower concentration

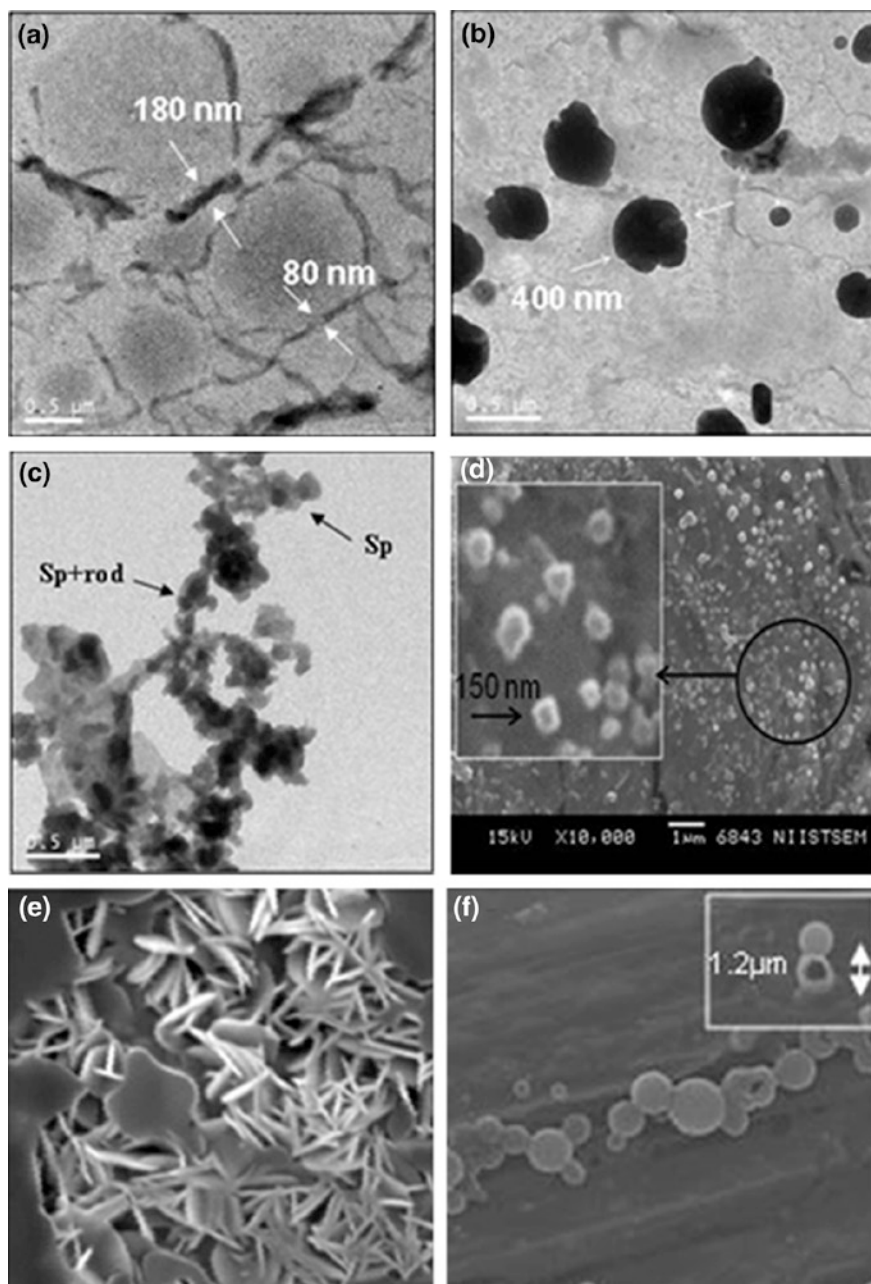


Fig. 6.6 Self-assembled molecular templates of dopant-1 with monomers: (a) aniline + dopant-1 in emulsion route, (b) aniline + dopant-1 in interfacial route, (c) aniline + dopant-1 in dilute route, (d) pyrrole + dopant-1 in emulsion route, (e) aniline + pyrrole + dopant-1 in emulsion route, (f) aniline + pyrrole + dopant-1 in dilute route. Reproduced with permission from Refs. [81] (2008, American Chemical Society), [85] (2009, John Wiley and Sons) and [86] (2010, American Chemical Society)

[86] (see Fig. 6.6a–f). In Interfacial route, the templates were assembled by introducing ammonium peroxydisulfate (APS) into dopant-1 micelles. DLS showed that the 4.3-nm-size micelles undergo aggregation in the presence of APS to produce larger micrometer size. The TEM images of the dopant-1 plus APS templates exclusively consist of spheres of 0.5 μm to 200 nm.

The dopant-2 molecule is structurally analogous to commercially available surfactant dodecylbenzenesulfonic acid (DBSA), which is widely used dopant for polyaniline and polypyrrole. In emulsion polymerization conditions, dopant-2 exhibits typical micellar behavior and forms cylindrical micellar templates of ~ 150 nm diameter with length up to 1–3 μm with aniline monomer [78] (see Fig. 6.7). In the case of biphasic (organic/water) dispersion polymerization conditions, the template formed is mostly spherical vesicles with size in the range of $\sim 450 \pm 200$ nm in diameter and wall thickness of 20 ± 10 nm (see Fig. 6.7). In dispersion templating, during the first step, aniline complexes with sulfonic acid part of the micelles in water to produce cylindrical aggregates, and in the second stage, the organic solvent (toluene) molecules get stacked in the hydrophobic core of the micelles which transforms the templates into vesicular shape [78]. Saturated cardanol-based dopant-3 retained the gel structure upon cooling a solution of aniline and dopant-3 in ethanol from 60 $^{\circ}\text{C}$ to room temperature. The aniline plus dopant-3 gel template is in the form of self-assembled cylindrical nanostructures with average diameters 200 nm and length up to 4–5 μm (see Fig. 6.7). TEM

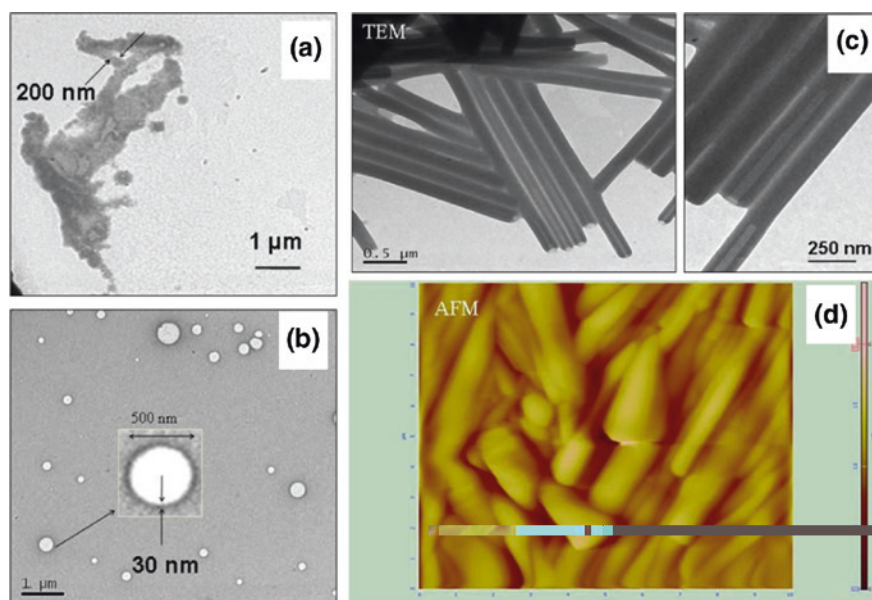


Fig. 6.7 Self-assembled molecular templates of dopant-2 and dopant-3 with aniline monomer: (a) dopant-2 \downarrow ← aniline in emulsion route, (b) dopant-2 \downarrow ← aniline dispersion route, (c, d) TEM and AFM of dopant-3 \downarrow ← aniline in gel route. Reproduced with permission from Refs. [78] (2009, American Chemical Society) and [79] (2010, American Chemical Society)

images indicated that during the gel formation the aniline monomers selectively occupied inside the cavity of the nanotubes formed by dopant molecules.

6.5 Template-Produced Conducting Polymer Nanostructures

The morphology of the dopant-1-templated polyaniline nanomaterials by emulsion polymerization route depended on the type of micellar structure (see Fig. 6.8). At very high dopant-1 concentrations (1×10^{-1} M) in the emulsion, the template formed exhibited less colloidal stability and mostly produced micron-sized polyaniline aggregates and hollow spheres. With further decrease in concentration, but still well above CMC, the cylindrical micelles templates were stable and yielded very uniform nanofibers (see Fig. 6.8). At a concentration above the CMC, a mixture of both nanotubes and nanofibers was produced [76, 77, 81]. The bilayered template formed at a dopant-1 concentration below CMC exclusively yielded nanotubes. Interestingly, thick emulsion of cylindrical micellar template (dopant-1 + aniline) formed above CMC value when diluted by adding water and oxidized using APS yielded nanorods rather than fibers. In the interfacial (biphasic) route, during the course of polymerization aniline monomers slowly diffuse

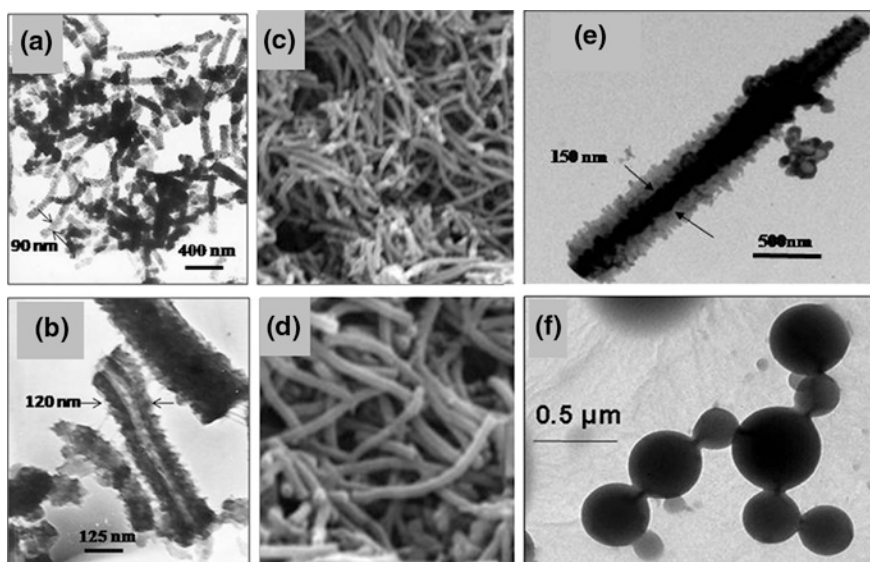


Fig. 6.8 TEM and SEM images of nanofibers by emulsion route (a, c), TEM and SEM image of nanotubes by emulsion route (b, d), TEM image of polyaniline nanorod by dilute route (e) and TEM image of nanospheres by interfacial route (f). Reprinted with permission from Refs. [77] (2007, American Chemical Society) and [80] (2007, American Chemical Society)

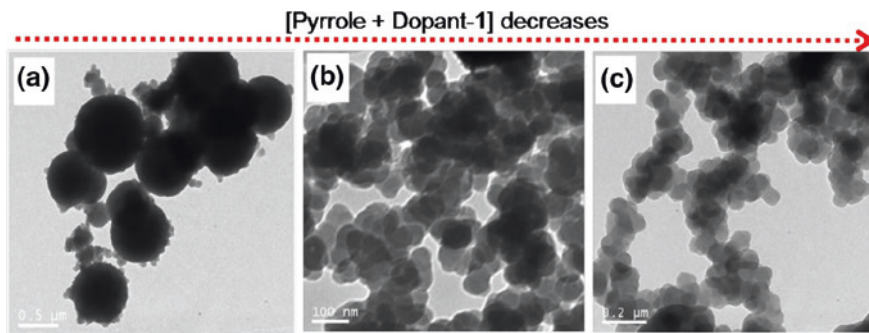


Fig. 6.9 TEM images of polypyrrole nanospheres under emulsion (a) and dilute route (b, c). Reprinted with permission from Ref. [85] (2009, John Wiley and Sons)

from organic layer and move toward the aqueous phase containing dopant-1 plus APS template through interface and get adsorbed on it. The subsequent polymerization results in the formation of nano/microspheres as evident from SEM and TEM images of the polyaniline formed [80]. The dopant-1 is unique in the sense that it self-assembles to more than one type of template by small variations in the concentration, combination of the constituents and types of polymerization employed and leads to the production of different kinds of nanostructures.

In the case of polypyrrole, the concentration of dopant-1 and stability of template formed with pyrrole mainly play a major role in the formation of different morphologies [84–86]. Emulsion template of pyrrole with very higher concentrations (far above CMC) of dopant-1 resulted in emulsion plus the precipitate, which upon polymerization produced mostly coral-like aggregated structures. Reducing concentration of pyrrole plus dopant-1 (still above CMC) produced submicron-sized polypyrrole spheres (500–600 nm), and a further decrease in concentration (close to CMC) yielded uniform polypyrrole nanospheres of diameter in the range of 150–250 nm (see Fig. 6.9) [84, 85].

The emulsion templates formed from dopant-1 with aniline-pyrrole mole composition (95:5) produced short nanorods upon copolymerization. The stability and competitive interplay of monomers (aniline and pyrrole) helps to produce molecular templates with intermediate structure, which is responsible for the fiber-to-rod-to-sphere transitions in copolymers [86]. The nanorod composition when further diluted with water produced hollow spheres and nanotubes under copolymerization route (Fig. 6.10).

The emulsion polymerization of cylindrical emulsion template of dopant-2 transforms the polyaniline morphology into a uniform mat of nanofibers of diameter ~ 80 nm with an average length of few microns (see Fig. 6.11) [78]. Interestingly, vesicular templates produced from dopant-2 + aniline in toluene-water dispersion yielded planar polyaniline nanotapes rather than vesicles upon adding APS and subsequent polymerization (see Fig. 6.11). During dispersion polymerization, the vesicular templates get ripped out from vesicular surface

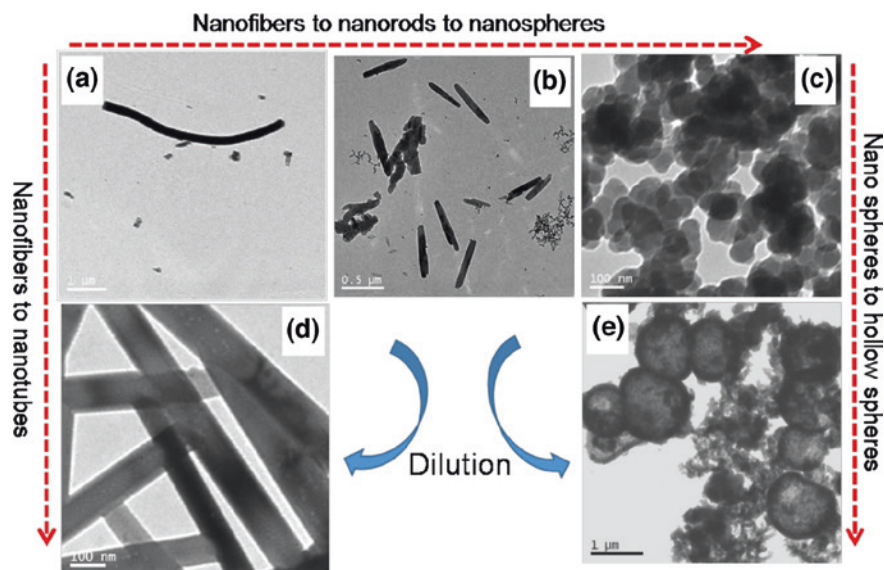


Fig. 6.10 (a) TEM image of polyaniline nanofibers, (b) polyaniline–polyppyrrrole copolymer nanorods, (c) polypyrrrole nanospheres, (d) polyaniline–polyppyrrrole copolymer nanotubes and (e) polyaniline–polyppyrrrole copolymer hollow spheres. Reprinted with permission Ref. [86] (2010, American Chemical Society)

which produces nanotapes [78]. Optimum surfactant geometry of dopant-2 enables to form stable templates which upon emulsion and dispersion polymerization process produce nanofibers and nanotapes, respectively. The gel template formed by dopant-3 plus aniline in ethanol upon polymerization yielded very uniform nanofibers with an average fiber diameter of ~ 135 nm and length up to $5 \mu\text{m}$ long (see Fig. 6.11). On the other hand, when the polymerization was carried at sol state (at 65°C), it has not yielded good nanostructures; instead agglomerated particles were formed. The physical state of the organogel helped to transcribe the morphology of the resulting polymer nanostructures.

6.6 Properties of Conducting Polymer Nanomaterials

Post-polymerized nanomaterials contain sulfonic acid head of amphiphilic dopants which complexes with nanomaterials (polyaniline/polypyrrrole) electrostatically and makes these structures easily dispersible in solvents such as water, chloroform, methanol, DMF and DMSO [74, 75, 79]. This increased solubility/dispersibility enables the complete structural characterization by spectroscopic techniques such as NMR, UV–Vis and FT-IR [74–87]. Generally, in the literature the NMR spectra of polyaniline/polypyrrrole are seldom reported due the insoluble nature of these materials. The cardanol dopant-based polymer nanostructures are

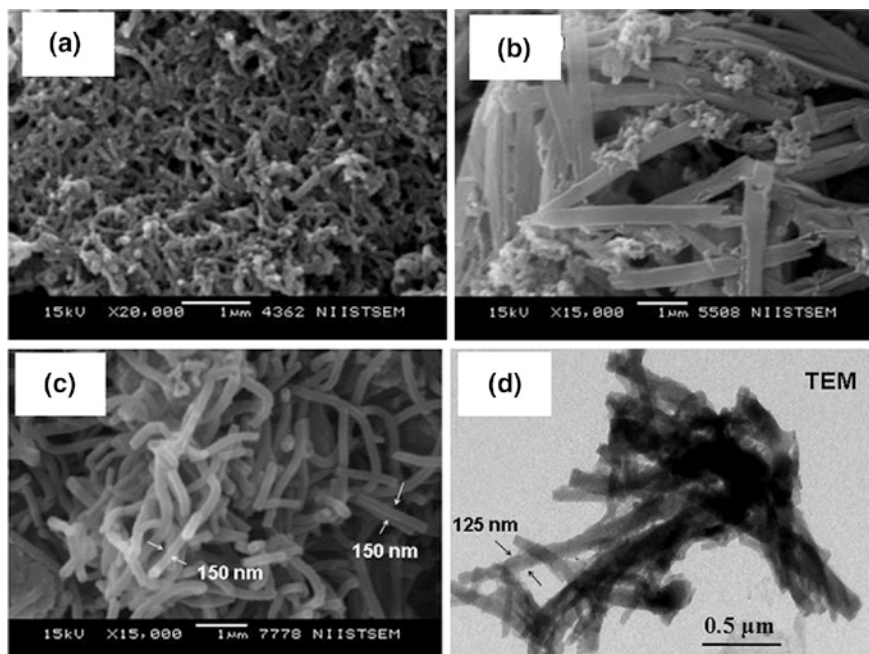


Fig. 6.11 (a) SEM images of polyaniline nanofibers synthesized using dopant-2 by emulsion route, (b) polyaniline nanotapes by dispersion route, and (c, d) SEM and TEM images of polyaniline nanofibers synthesized using gel dopant-3. Reproduced with permission from Refs. [78], (2009, American Chemical Society) and [79] (2010, American Chemical Society)

highly soluble in NMR solvents like d_6 -DMSO. For example, $^1\text{H-NMR}$ spectra of the polyaniline nanomaterials show the peaks corresponding to the dopant molecule in addition to the peaks for the polymer structures indicating post-polymerization doping. The aromatic peaks of polyaniline backbone appeared at 7.65 and 7.52 ppm, and additionally the three equally intense peaks (triplet) at 7.1, 7.2 and 7.3 ppm corresponding to the free radical NH proton resonance due to the ^{14}N with unit spin were also observed. $^1\text{H-NMR}$ study confirms the doping associated with strong complexation of cardanyl sulfonic acid dopant to the polymer nanostructure.

Polyaniline/polypyrrole polymers are highly rigid due to their linear aromatic backbone, and lack of flexibility to chain folding prevents them acquiring crystalline nature. Therefore, generally emeraldine base forms as well as mineral acid-doped emeraldine salt forms of these polymers are highly amorphous [41]. In the presence of amphiphilic cardanyl sulfonic acid dopants, the dopant-polymer complex undergoes various interactions, which improves the solid-state packing of the polymer chains inside the nanostructures. The powder X-ray diffraction patterns of nanostructures showed lower angle peaks characteristics of the interdigitations

of dopant molecules between polymer chains [74–87]. This improved solid-state packing also reflected in reasonable high electrical conductivity observed in nanostructures.

Fluorescence emission studies of polyaniline nanospheres synthesized from interfacial method and polyaniline nanofibers synthesized by emulsion route revealed that nanospheres have much more fluorescence quantum yield than fibers [74, 77]. The better fluorescence properties of nanospheres were correlated with the more expanded chain conformation and more effective layered packing of azochromophore group of dopant-1 in the polymer chain. The polyaniline nanorods obtained by dilute condition route with dopant-1 were found to be very weakly luminescent since the dilute reaction conditions will make the dopant well dispersed in polymer matrix and prevent close packing of chromophores in the resulting sample.

6.7 Conclusion

Simple chemical approaches were developed to synthesize amphiphilic dopants from the renewable resource cardanol. The cardanyl dopants were self-assembled and utilized as soft templates for the formation of polyaniline and polypyrrole nanostructures. Cardanyl dopant-1 and dopant-2 have a typical surfactant structure having a sulfonic acid polar head and pentadecenyl chain as hydrophobic tail. The concentration-dependent micellation behavior and its size in aqueous solution were characterized by various techniques like fluorescence measurements and DLS studies. Different types of stable soft templates formed by these dopants with monomers (aniline and pyrrole) under different types of polymerization route (emulsion, dilute, interfacial and dispersion) yielded various polymeric nanostructures such as nanofibers, nanotubes, nanorods and nanotapes. The gel-forming dopant-3 derived from saturated cardanol has limited solubility in water; however, it forms gel in polar solvents like ethanol. The nanotubular gel template of dopant-3 filled with aniline upon polymerization produced nanofibers. The copolymer nanorods were produced from soft emulsion templates of dopant-1 with co-monomers (aniline 95 % and pyrrole 5 %) through copolymerization. Dilute copolymerization produced hollow spheres and nanotubes from the same diluted emulsion templates. The cardanyl amphiphilic dopants acted as dopant-cum soft template and greatly improved the properties of nanomaterials such as solubility, solid-state ordering, conductivity and optical properties. In short, cardanyl amphiphilic soft-template-assisted polymerization is easy, facile and efficient for the creating the architectural library of conducting polymer nanomaterials.

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