Molecular assembly and properties of polythiophenes

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π-Conjugated polymers are used in many industrial applications and are expected to become an integral part of future electronic and optical technologies. Molecular self-assembly is a promising method for improving the functionality and utility of π-conjugated polymers. The carrier mobility in polymer materials produced by self-assembly is influenced by the morphology and state of molecular assembly in a similar manner to the influence of crystallinity and amorphism in silicon. π-Conjugated polythiophenes with controlled molecular structures and long side chains often form π-stacked structures by self-assembly through side-chain aggregation. Such polythiophenes have higher carrier mobility, optical third-order nonlinear susceptibility and Verdet constant compared with π-conjugated polythiophenes that do not self-assemble. This review covers the development and functionalities of self-assembled π-conjugated polythiophenes with regio-regular head-to-tail, Th(R)–Ar–Th(R) and head-to-head structures with alkynyl side chains.

π-Conjugated polymers—polymers in which π-electrons on the main chain are largely delocalized, leading to useful functionalities such as electronic conductivity and non-linear optical effects—have attracted the interest of scientists in many fields [1–11]. As an electrically conducting (or carrier-transporting) material, π-conjugated polymers have already found a range of applications in industry, including use in capacitors [9], electron-beam lithography [10] and organic light-emitting diodes. Other applications have also been widely studied, including use as active materials for field-effect transistors [12,13], as optically active films and solutions of chiral polymers [14,15], as films with large Faraday rotation [16] and as light-emitting and/or carrier-transporting materials in polymer light-emitting diodes [17–20]. More recent promising applications for π-conjugated polymers include use as active materials in solar cells [21], as electrochemically active materials in batteries and electrochromic devices [1,2,8,22], as materials with large optical third-order nonlinear susceptibility ($\chi^{(3)}$) for the rapid switching of light [23] and as highly conductive and transparent materials to replace indium tin oxide [24]. Applications in sensors, anticorrosion paints and artificial muscles (or actuators) [25] have also been developed. New, effective synthetic routes for various π-conjugated polymers are therefore being actively investigated.

Examples of π-conjugated polymers include polyacetylene, poly-pyrrole, polythiophene (PTh), poly(*p*-phenylene) (PPP), poly(pyridine-2,5-diyl), poly(*p*-phenylenevinylene) and poly(aryleneethynylene), and all of these have been characterized in detail regarding their chemical and physical properties [1–11]. Polythiophene and its derivatives (Figure 1) in particular have been the subject of many recent studies [1,2,6–8,26–33]. p-Doped poly(3,4-ethylenedioxythiophene) (PEDOT) is already used industrially in capacitor electrodes and as an antistatic material amongst a range of device applications, and polythiophenes with side chains bearing sulfo groups are used as antistatic materials in electron-beam lithography [10].

Recently, PTh with long side chains (*e.g.* alkyl (R) side chains) and regio-regular structures along the PTh main chain have been attracting
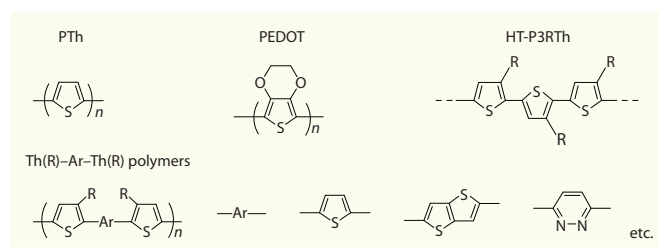

Figure 1. Examples of polythiophenes. PTh, poly(thiophene-2,5-diyl); PEDOT, poly(ethylenedioxythiophene); HT-P3RTh, regio-regular head-to-tail poly(3-alkylthiophene-2,5-diyl).

strong interest. For example, the synthesis of head-to-tail (HT) poly(3-alkylthiophene-2,5-diyl) (P3RTh) [1,2,7,26,27] initiated active studies of the molecular assembly of π-conjugated polymers [1,2,7,26–30]. Through these studies, it is now recognized that self-assembled π-conjugated polymers show superior electronic [7,12] and optical [16,23] functionalities, such as the higher electrical conductivity of HT-P3RTh compared with regio-random (rand) P3RTh. Films of HT-P3RTh also show a larger $\chi^{(3)}$ (27.2×10^{-12} esu) [23] compared with rand-P3RTh films (1.81×10^{-12} esu). π-Conjugated polymers usually respond very rapidly to light through a change in refractive index on time scales of about 10^{-12} s. Consequently, π-conjugated polymers with large $\chi^{(3)}$ are considered to be important materials for future high-speed photo-communication systems.

HT-P3TTh films show a Verdet (Faraday rotation) constant of as high as about 1×10^3 rad T^{-1} m^{-1} at 532 nm, whereas rand-P3RTh films have only a small Verdet constant [16]. Materials with a large Verdet constant are expected to serve as magnetic field sensors and be used in the construction of new opto-magnetic memory systems. HT-P3RTh, particularly HT-poly(3-hexylthiophene-2,5-diyl) (HT-P3HexTh), is now widely studied for electronic and optical applications, such as in organic transistors and solar cells.

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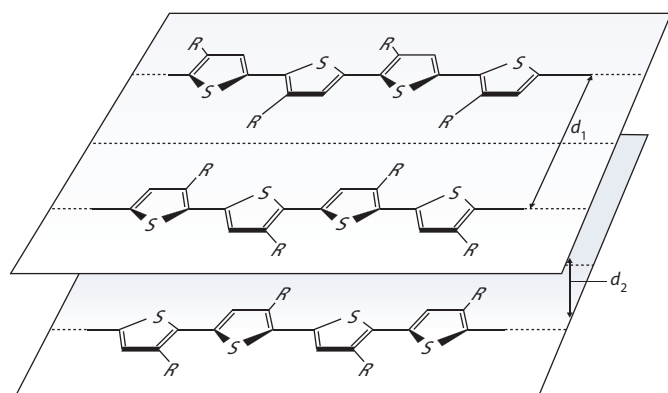Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Figure 2. Illustration of π-stacking of HT-P3RTh in the solid state

Various other types of thiophene (Th)-based polymers consisting of regularly repeating units also show a tendency to self-assemble. For example, Th(R)–Ar–Th(R) polythiophenes and head-to-head (HH) poly(thiophene-2,5-diyl) (HH-P3(C≡C–R)Th) with –C≡C–R side chains form self-assembled structures in colloidal solutions and in the solid phase. This short review reports on the molecular assembly and electronic and optical properties of these two types of polythiophenes.

Th(R)–Ar–Th(R) polythiophenes

It has been reported that π-conjugated polymers with Th(R)–Ar–Th(R) repeating units (Ar, aromatic or heteroaromatic unit) produce π-stacked molecular assemblies. McCulloch and co-workers synthesized such poly-thiophenes with fused Th units as the central –Ar– unit [31], and the resulting polymer showed a large hole mobility of about $1 \, cm^2 \, V^{-1} \, s^{-1}$ [31], comparable to that of amorphous silicon.

Many other examples of π-conjugated polymers with Th(R)–Ar–Th(R) repeating units have been reported, and various Ar units have been used in their construction, including ethene-1,2-diyl [30,32], pyridine-2,5-diyl [33], pyridazine-2,5-diyl [34], thieno(3,4-b)pyrazine [35,36], azulene [37], 2,2'-bithiophene [38,39], *p*-phenylene [30,40–42], two thiophene units and a benzothiadiazole unit [43,44], selenophene-2,5-diyl [45], and dithino[3,2-b:2',3'-d]pyrrole [46].

Th(R)–Ar–Th(R) polymers often form π-stacked molecular assemblies [47–49], and their applicability to polymer transistors [46,48,50] and solar cells [51] has been actively tested. Some Th(R)–Ar–Th(R) polymers are considered to have a coplanar structure, and the coplanar polymers in particular show a strong tendency to self-assemble. The electron-accepting units among the reported Ar units are pyridine-2,5-diyl, pyrazine-2,5-diyl, thieno(3,4-b)pyrazine and benzothiadiazole units with electron-withdrawing –C=N– imine nitrogen [2,8,52,53]. As 3-alkylthiophene (Th(R)) is an electron-donating unit, the polymer molecules are considered to have an intramolecular charge-transfer electronic structure along the polymer main chain, with negatively charged $Ar^{\delta-}$ units and positively charged $Th(R)^{\delta+}$ units. In this case, an intermolecular attractive electronic force (a kind of Madelung force related to lattice energy in ionic crystals) between the negatively charged $Ar^{\delta-}$ units and positively charged $Th(R)^{\delta+}$ units is considered to occur between face-to-face-stacked Th(R)–Ar–Th(R) polymer molecules, which promotes molecular assembly.

Various π-conjugated aromatic and heterocyclic polymers have been prepared by oxidative polymerization of the corresponding monomer (*e.g.* pyrrole and 3,4-ethylenedioxythiophene) or by organometallic polycondensation using dihalo-aromatics and dihalo-heterocycles (*e.g. p*-dibromobenzene, 2,5-dibromothiophene, 2,5-dibromopyridine) as the monomer [1–8]. Various dehalogenative (halogen-removing) C–C coupling reactions, such as nickel-promoted coupling reactions between
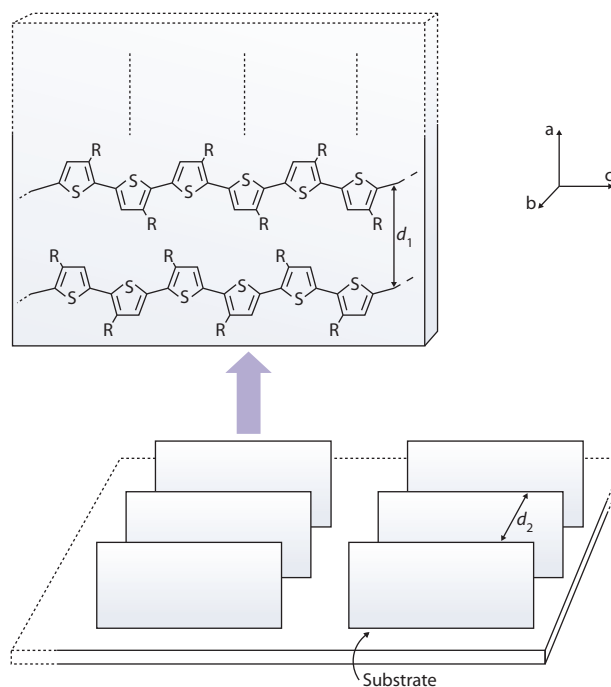

Figure 3. Alignment of HT-P3HexTh molecules on a substrate surface (*e.g.* platinum) Modified after Ref. 59 , reproduced with permission (© 2009 CSJ).

Grignard reagents (RMgX; X, halogen) and organic halides (R'X), nickel-promoted dehalogenative coupling of organic halides with zinc, and dehalogenative coupling of organic halides with zero-valent nickel complexes, have been applied to prepare π-conjugated homopolymers from dihalo-organic compounds (X–Ar–X) [8,13]:

$$n \, X–Ar–X \xrightarrow[\text{polycondensation}]{\text{Dehalogenative}} (Ar)_n \text{ polymer} \quad (1)$$
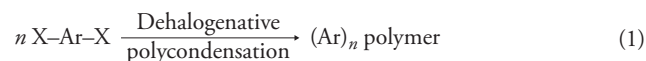
The preparation of copolymers $(Ar–Ar')_n$ consisting of different Ar and Ar' groups can be carried out via palladium-catalyzed organometallic C–C coupling reactions using X–Ar–X and m–Ar'–m monomers (m–, metallic group such as stannyl $R_3Sn–$ or boronic $(RO)_2B–$):

$$n \, X–Ar–X + n \, m–Ar'–m \xrightarrow[\text{C–C coupling}]{\text{Pd-catalyzed}} (Ar–Ar')_n \quad (2)$$
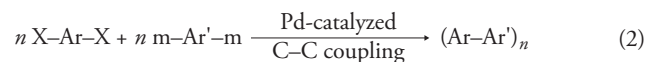
π-Conjugated polymers composed of an Ar group and an acetylenic group (–C≡C–) can also be prepared by palladium- and copper-catalyzed organometallic polycondensation:

$$n \, X–Ar–X + n \, H–C≡C–Ar'–C≡C–H$$
$$\xrightarrow[\text{C–C coupling}]{\text{Pd- and Cu-catalyzed}} (Ar–C≡C–Ar'–C≡C)_n \quad (3)$$
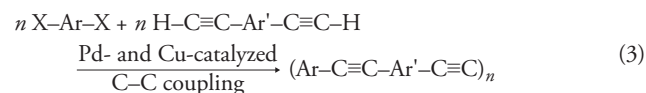
Polypyrrole [1,2] and PEDOT [1,2,11,54] are typical π-conjugated polymers consisting of electron-excessive (or electron-donating) repeating units and are usually prepared by chemical oxidation of the corresponding electron-excessive monomers (*i.e.* pyrrole and 3,4-eth-ylenedioxythiophene, H–Ar–H) with oxidizing reagents such as $FeCl_3$ and $(NH_4)_2S_2O_8$, or by electrochemical oxidation of the monomer (n H–Ar–H (oxidation) → $(Ar)_n$ polymer). Because of the electron-excessive nature of pyrrole and 3,4-dioxyethylenethiophene, chemical and electrochemical oxidation of the monomers proceeds smoothly to produce the corresponding π-conjugated polymers.
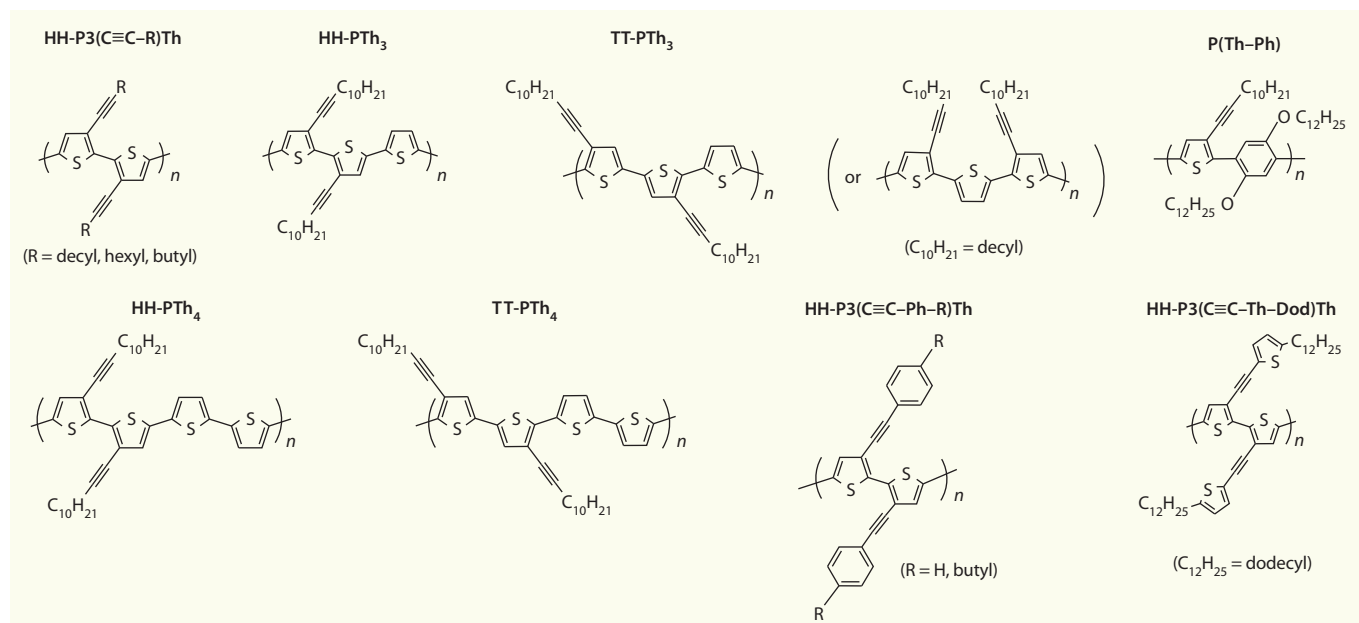
Figure 4. New polythiophenes with –C≡C–R side chains

In oxidative polymerization, π-conjugated polymers consisting of electron-excessive units are usually obtained in an oxidized (or p-doped) state, and neutral π-conjugated polymers are obtained by chemical (*e.g.* with N_2H_4) and electrochemical dedoping of the as-obtained polymer. In π-conjugated polymers, p-doping and n-doping occur by oxidation and reduction of the polymer, respectively. On oxidation, some of the π-electrons are removed from the main chain, which generates positive carriers, making the polymer electrically conductive [1–8]. On reduction, negative carriers are generated in the polymer main chain. The ease of oxidation and reduction of the polymer essentially depends on the ease of oxidation and reduction of the repeating unit (*e.g.* Th, pyrrole, benzene or pyridine) [8].

Dedoped neutral π-conjugated polymers consisting of electron-excessive units are easily oxidized (or p-doped) by chemical (*e.g.* with I_2 or Fe(III) salts) and electrochemical (or p-type doping) methods, allowing the p-doped state to be readily recovered. The oxidized polymers behave as p-type electrically conducting materials with positively charged $Ar^{\delta+}$ units in the polymer main chain. The maximum doping level of p-type conducting polymers, corresponding to the δ value of $Ar^{\delta+}$ in the polymer main chain, is usually in the range of 0.3–0.5. $Ar^{\delta+}$ has counter anions such as BF_4^- and sulfonates RSO_3^- (*e.g.* alkylnaphthalene sulfonate and polystyrene sulfonate). Oxidative polymerization is therefore an efficient and convenient route for the preparation of π-conjugated polymers. However, there are limitations regarding the range of suitable monomers, and the π-conjugated polymers obtained by oxidative polymerization often seem to include some irregular bonding units (*e.g.* thiophene-2,4-diyl in addition to the normal thiophene-2,5-diyl unit in PTh).

Pyridine and 1,10-phenanthroline with electron-withdrawing imine –C=N– nitrogen are typical π-electron-deficient compounds. Oxidative polymerization of these electron-deficient (or electron-accepting) monomers is usually not possible. π-Conjugated polymers consisting of electron-deficient units are usually prepared by dehalogenative organometallic polycondensation of X–Ar–X, and the π-conjugated polymers thus obtained are usually in a non-doped neutral state. Such neutral polymers $(Ar)_n$ can be chemically (*e.g.* with sodium naphthalenide, $Na^+C_{10}H_8^-$) or electrochemically reduced (or n-doped) to give n-type conducting materials with negatively charged $–Ar^{\delta+}–$ units in the polymer main chain.

Thiophene, benzene and their derivatives have moderate electron-excessive and electron-deficient character, and non-substituted PTh,

P3RTh, PPP and PPP derivatives can also be prepared by organometallic polycondensation. Polythiophene and PPP are active for both p-type doping and n-type doping. Of the two polymers, Th has a more electron-excessive character, allowing PTh to accept p-doping more readily than PPP [52]. These polymers can also be obtained by chemical and electrochemical oxidative polymerization of Th, P3RTh, benzene and benzene derivatives, respectively, and the as-prepared polymers obtained by oxidative polymerization are usually in the p-doped state.

Organometallic polycondensation is suited to the preparation of π-conjugated polymers in a neutral state with well-defined bonding between the repeating monomeric units, and many Th(R)–Ar–Th(R) polymers have been prepared by this method. Regio-controlled HT-P3RTh can also be prepared by organometallic polycondensation, which often results in π-stacked molecular assemblies accompanied by side-chain crystallization. These characteristics can be confirmed by X-ray diffraction (XRD) analysis. HT-P3RTh molecules are considered to form a π-stacked assembly (Figure 2) in colloidal solutions and in the solid state [1,2,7,8,12,29]. Although certain details of the packing structure (*e.g.* the slip of adjacent HT-P3RTh chains) remain to be elucidated, π-stacking seems to be possible between polymers with regio-controlled structures due to the ordered packing of side-chain alkyl groups. In contrast, such an ordered packing of side-chain alkyl groups is not possible for rand-P3RTh, which prevents π-stacking of poly(3-alkylthiophene-2,5-diyl) molecules.

Owing to the formation of a π-stacked molecular assembly, HT-P3HexTh (R = hexyl) films show a much higher hole mobility ($\mu = 0.1\ cm^2\,V^{-1}\,s^{-1}$) compared with rand-P3HexTh films, which do not form self-assembled π-stacked structures [12,55,56]. The difference between HT-P3HexTh and rand-P3HexTh films is comparable to the difference between crystalline silicon and amorphous silicon, although the crystallinity of HT-P3HexTh is much lower than that of crystalline silicon. Some Th(R)–Ar–Th(R) polymers with controlled molecular structures form similar π-stacked molecular assemblies and show high carrier mobility ($\mu = 1\ cm^2\,V^{-1}\,s^{-1}$) [31].

In the π-stacked molecular assembly of HT-P3RTh with long R side chains, the R chains are considered to be well packed in an assumed pseudo-hexagonal form (see Figure 6), and the formation of the π-stacked molecular assembly is considered to be assisted by crystallization of the R side chains. When the R side chain is shorter, as in HT-P3HexTh (R = hexyl), the side chains may be liquid-like at room temperature.
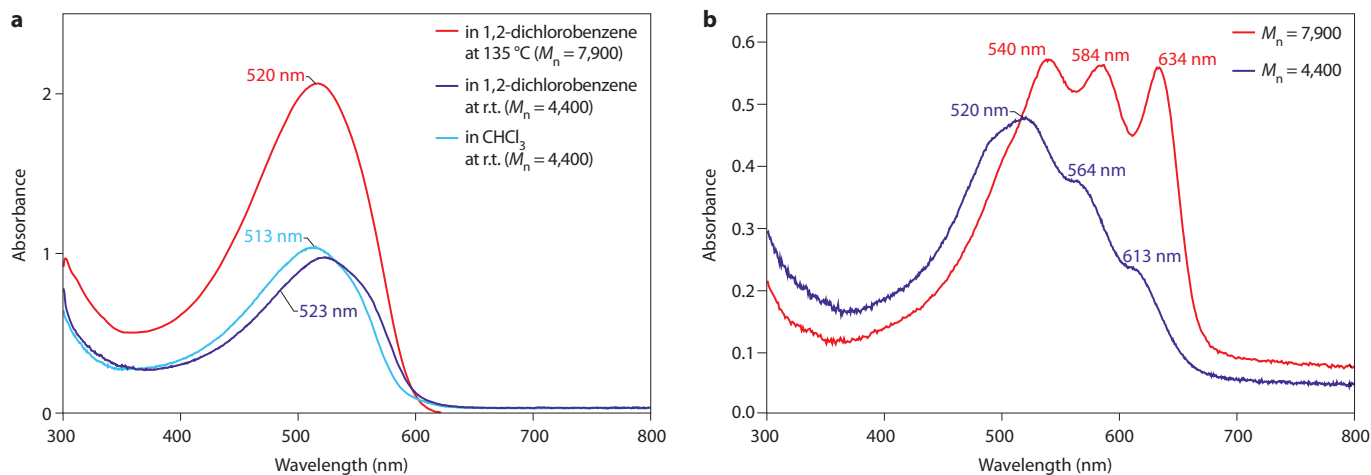
Figure 5. UV–vis spectra for HH-P3(C≡C–Dec)Th in (a) 1,2-dichlorobenzene and chloroform and (b) cast film. Data for polymers with number-average molecular weight of 7,900 (original polymer) and 4,400 (chloroform-soluble part) are shown. Modified after Ref. 59, reproduced with permission (© 2009 CSJ).

The Th(R)–Ar–Th(R) polymers are considered to form a similar π-stacked molecular assembly assisted by side-chain crystallization. Of course, π–π electronic interactions between the face-to-face-stacked π-conjugated PTh main chains are also considered to have an important role in the formation of a stable π-stacked molecular assembly.

Various molecules containing π-conjugated units, such as graphite and DNA, are known to form π-stacked structures. The graphene sheets in graphite and the base pairs in DNA have π-stacking distances of 3.25 and 3.4 Å [57,58], respectively, and the structural stability of DNA is considered to be maintained by the π-stacking force between base units (*e.g.* cytosine, adenine and thymine). In contrast, HT-P3RTh and other thiophene-based polymers have a longer π-stacking distance of about 3.8 Å, presumably due to the presence of the large sulfur atom in the Th unit. Elucidation of the π-stacking behavior of HT-P3RTh and other Th-based polymers is expected to contribute to the determination of π-stacking forces among molecules, including in graphite and DNA.

Strong π-stacking of Th-based polymers generally brings about a large shift in ultraviolet–visible (UV–vis) absorption peaks to longer wavelengths. For example, HT-P3RTh in chloroform (good solvent) solution undergoes a large (greater than 100 nm) [2,7,8,26,27,29] shift in the UV–vis absorption peak to longer wavelengths when the solution becomes colloidal by the addition of methanol (poor solvent), or when the polymer is cast as a film (Figure 3). When cast, as with other strongly π-stacked Th-based polymers, HT-P3RTh tends to align such that the long side chains (*e.g.* alkyl side chains) are oriented toward the substrate surface (Figure 3).

p-Doped (or oxidized) HT-P3RTh molecules are also arranged in a similar manner on the surfaces of various substrates. In this system, the d_1 distance (Figures 2 and 3) becomes longer compared with that of non-doped neutral HT-P3RTh, whereas the d_2 distance becomes shorter. These data suggest that the p-dopant, such as BF_4^-, is located near the end of the alkyl side chain (not between the face-to-face-stacked PTh main chains), and that the π–π stacking force between the PTh main chains becomes stronger in the p-doped state, which shortens d_2. Similar results have been obtained for non-doped neutral HH-P3(C≡C–R)Th and p-doped HH-P3(C≡C–R)Th [59].

The Th(R)–Ar–Th(R) polymers also form a similar aligned structure when cast, particularly when the shift in the UV–vis peak due to formation of the π-stacked structure is larger than about 50 nm [30]. Many other types of Th-based π-conjugated polymers with long side chains, such as a copolymer between 4-alkylthiazole and Th, also form π-stacked structures, and these also assume similar aligned structures on substrate surfaces when the UV–vis shift due to formation of the π-stacked structure is large (greater than about 50 nm) [30].

In contrast to HT-P3RTh and the Th(R)–Ar–Th(R) polymers, non-substituted PTh molecules are aligned such that the PTh main chain is perpendicular to the substrate surface in vacuum-deposited films [8]. Other non-substituted π-conjugated polymers such as PPP [8] and π-conjugated oligomers such as oligo-thiophenes and co-oligomers of Th and pyridine are aligned such that the π-conjugated main chain is perpendicular to the substrate. Even long *n*-alkanes, such as *n*-C$_{30}$H$_{62}$, are aligned in this way.

Head-to-head poly(thiophene-2,5-diyl) with alkynyl side chains

Recently, the Chemical Resources Laboratory reported the preparation of new π-conjugated polythiophenes with alkynyl –C≡C–R side chains [59]. Examples of the synthesized polymers are shown in Figure 4. Because no significant steric repulsion occurs between the main PTh chain and the –C≡C–R side chain, the polymers, except for P(Th-Ph), are considered to have a coplanar linear structure.

The –CH$_2$–CH$_2$–R' group in HT-P3RTh seems to be sterically repulsed by the PTh main chain, and the UV–vis absorption shift to longer wavelengths as a result of the formation of the π-stacked structure may arise from two factors: π–π electronic interactions among PTh main chains, and higher coplanarity of the PTh main chain in the π-stacked molecular assembly than in a single HT-P3RTh molecule. The formation of a π-stacked molecular assembly may force the PTh main chain to form in a coplanar fashion, even if the original HT-P3RTh main chain is somewhat twisted by the steric repulsion between the PTh main chain and the –CH$_2$–CH$_2$–R' group.

In contrast, there seems to be no steric repulsion between the –C≡C–R side group and the PTh main chain even in the single polymer molecule, as judged from CPK molecular models, calculations and single-crystal X-ray molecular structures of the corresponding dimeric compounds [59]. In addition, the regio-regularity of HH-P3(C≡C–R)Th polymers is 100% controlled by the synthetic route. Consequently, the analysis of HH-P3(C≡C–R)Th polymers is expected to provide fundamental information about the π-stacking forces between π-conjugated polymers and the effects of π-stacking on the electronic states of polythiophenes with long side chains. HH-PTh$_3$, TT-PTh$_3$, HH-PTh$_4$ and TT-PTh$_4$ have molecular structures similar to those of the Th(R)–Ar–Th(R) polymers, with the –Ar– units between the two Th(–C≡C–R) units.

Comparison of the UV–vis spectra of HH-P3(C≡C–Dec)Th in 1,2-dichlorobenzene solution and in cast films (Figure 5) reveals a large shift in the UV–vis peak, suggesting the formation of π-stacked
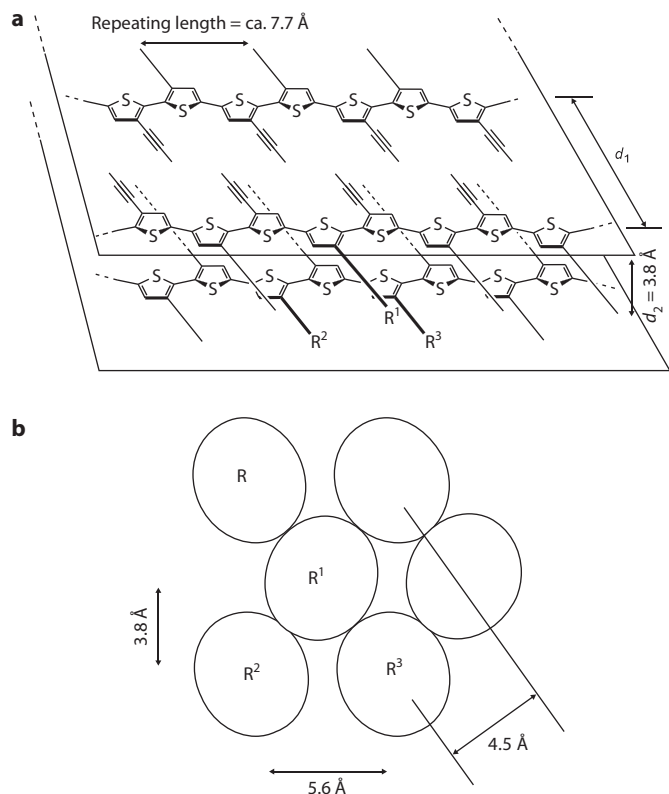
Figure 6. (a) Illustration of packing model for HH-P3(C≡C–alkyl)Th in the sold state and side view of the packed –C≡C–alkyl side chains. (b) Side view of packed –C≡C–alkyl side chains, seen from the direction of the side chain. Adapted from Ref. 59, reproduced with permission (© 2009 CSJ).

structures in the solid. The UV–vis shift is larger for polymers with higher molecular weight. It is considered that a longer polymer molecular chain provides a larger number of interacting sites between HH-P3(C≡C–R)Th polymer molecules, which intensifies the interactive forces between the polymer molecules.

The UV–vis absorption shift of the HH-P3(C≡C–R)Th polymer as a result of the formation of the cast film is considered to mainly originate from electronic interactions among polymer molecules, not from higher coplanarization of the PTh main chains in the solid, as even the original single HH-P3(C≡C–R)Th molecule has a coplanar structure. However, the lack of clear vibrational structures in the UV–vis spectrum of the HH-P3(C≡C–R)Th polymer in solution suggests that the polymer molecule has some rotational freedom in solution that is frozen in the solid.

Figure 6 shows the model packing of HH-P3(C≡C–alkyl)Th in the solid, similar to that of HT-P3RTh shown in Figure 2, based on interpretation of the XRD patterns of solid-state HH-P3(C≡C–alkyl)Th assuming a π-stacked structure similar to that for HT-P3RTh. It is reasonable that d_1 becomes longer as the alkyl chain in the –C≡C–R side chain lengthens. The increase in d_1 with the number of carbon atoms in the –C≡C–alkyl side chain, $\Delta d_1/\Delta$(number of carbon atoms in the alkyl group), is about 2.0 Å/C, which is longer than the repeating length of the –CH$_2$– group (1.25 Å/CH$_2$). These data exclude the possibility of an interdigitation packing mode and support the end-to-end packing mode shown in Figure 6, similar to the case of HT-P3RTh shown in Figure 2.

The well-packed –C≡C–alkyl side chains assist the π-stacking of HH-P3(C≡C–alkyl)Th. HT-P3RTh molecules on a substrate are usually aligned only in the edge-on mode as shown in Figures 3 and 7. However, because of the strong π-stacking of HH-P3(C≡C–alkyl)Th, this polymer can align in two ways on a substrate. When the polymer is cast from a solution, the polymer molecules become aligned in an

edge-on fashion (Figure 7), similar to the case for HT-P3RTh (Figure 3). When the cast film or polymer powder is rubbed with a spatula, on the other hand, the polymer molecules become aligned in a side-on fashion [59], similar to the orientation in graphite or mica. The plane (or sheet) formed by HH-P3(C≡C–alkyl)Th molecules by end-to-end packing of the polymer molecules (Figure 6(a)) is considered to have high stability, which is also similar to the structures of graphite and mica. In contrast, the plane (or sheet) formed by HT-P3RTh molecules does not seem to have such high stability, and the formation of a side-on alignment of HT-3RTh on the surface of a substrate is not easy.

The edge-on alignment seems to be more stable than the side-on alignment, and the side-on form returns to edge-on during repeated electrochemical p-doping and dedoping. The electrochemical p-doping potentials (peak current anodic potential, E_{pa}) of HH-P3(C≡C–Dec)Th in the edge-on state ($E_{pa} = 0.94$ V vs. Ag$^+$/Ag) and the side-on state ($E_{pa} = 0.63$ V vs. Ag$^+$/Ag) are different, and cyclic voltammetry indicates that the p-doping potential of HH-P3(C≡C–alkyl)Th film in the side-on state changes to that of the edge-on state during repeated voltage scanning [59]. The lower E_{pa} of the side-on state compared with the edge-on state indicates that electrochemical oxidation of HH-P3(C≡C–Dec)Th takes place more easily in the side-on state, presumably because of enhanced electron transfer from HH-P3(C≡C–Dec)Th to the substrate (platinum plate).

The –C≡C–R group is an electron-withdrawing group, and due to its electron-withdrawing effect, electrochemical p-doping (or oxidation) of HH-P3(C≡C–alkyl)Th requires a potential about 0.3 V higher than that needed for non-substituted PTh. After electrochemical p-doping of the HH-P3(C≡C–alkyl)Th cast film, d_1 becomes longer, while d_2 becomes shorter. These data suggest that the dopant (e.g. BF$_4^-$) is located at the end of the –C≡C–alkyl side chain (not between the π-stacked PTh layers) in the p-doped HH-P3(C≡C–alkyl)Th film, similar to the case described above for the p-doped HT-P3RTh cast film. Similar results have been reported for the location (at the end of the side chain) of the p-dopant in p-doped PEDOT [60] and in a p-doped copolymer of isothianaphthene and dialkoxy-p-phenylene [61].

Because HH-P3(C≡C–alkyl)Th has a longer effective π-conjugation length, it shows a larger $\chi^{(3)}$ than HT-P3RTh: $\chi^{(3)}$ for HH-P3(C≡C–Dec)Th is 3.6×10^{-11} esu, compared with 1.8–2.7×10^{-11} esu for poly(3-hexylthiophene)s such as HT-P3HexTh and rand-P3RHexTh (Hex = hexyl). Processable π-conjugated polymers with large $\chi^{(3)}$ are important materials for the rapid switching of light in applications such as photocommunication systems [62].

The packing structure of polythiophenes with –C≡C–alkyl side chains changes with the number density of –C≡C–alkyl side chains. Thus, TT-PTh$_3$ (Figure 4) packs according to an interdigitation packing mode (Figure 8), whereas HH-P3(C≡C–alkyl)Th adopts an end-to-end packing structure (Figure 6). The interdigitation packing mode for TT-PTh$_3$ has been proposed on the basis of XRD data [59]. TT-PTh$_3$ has a molecular structure similar to that of Th(R)–Ar–Th(R) polymers, with the thiophene-2,5-diyl unit as the central –Ar– unit, and some of the Th(R)–Ar–Th(R) polymers are considered to have packing structures similar to that shown in Figure 8.

π-Stacked molecular assembly of π-conjugated polymers often occurs in five-membered-ring π-conjugated polymers, such as HT-P3RTh, Th(R)–Ar–Th(R) polymers, HH-P3(C≡C–R)Th, poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl) [29] and copolymers of Th and 4-alkylthiazole [63]. Similar molecular assembly is also possible in six-membered-ring π-conjugated polymers, such as HT poly(6-alkylpyridine-2,5-diyl) (HT-P6RPy) [64] and poly(pyrimido[5,4-d]pyrimidopyrimidine-2,6-diyl) [65]. However, the electronic interactions between π-stacked HT-P6RPy molecules are not as strong as those observed for the five-membered-ring π-conjugated polymers. π-Conjugated polymers consisting of 2,5-dialkoxy-*p*-phenylene units with long alkoxy side chains also tend to self-assemble into π-stacked structures.

π-Stacked π-conjugated polymers formed by self-assembly offer superior carrier mobility, optical rotation or circular dichroism (with a
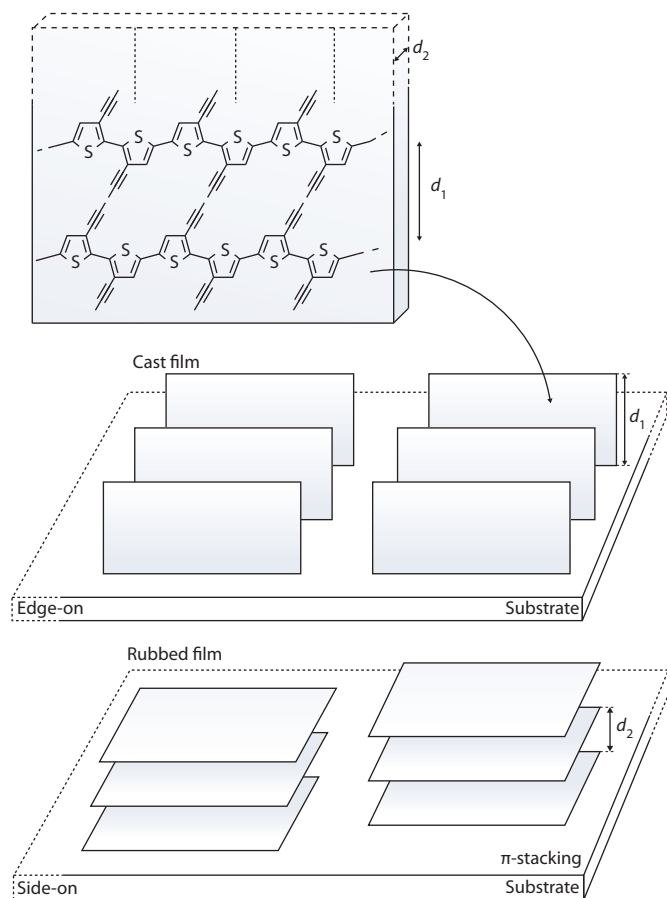
Figure 7. Two types of alignment of HH-P3(C≡C–alkyl)Th on a substrate surface. Modified after Ref. 59, reproduced with permission (© 2009 CSJ).

Figure 8. Interdigitation packing model for TT-PTh₃. Adapted from Ref. 59, reproduced with permission (© 2009 CSJ).

couplet) [66], Faraday effect, electrical conductivity and $\chi^{(3)}$, and many efforts have been made to capitalize on the merits of such systems. In polymer light-emitting diode applications, however, π-stacked polymers have degraded light emission properties due to the formation of an excimer or excimer-like adduct in the solid.

Summary and perspectives

The π-stacking behavior of thiophene-based π-conjugated polymers with long side chains was reviewed, focusing on Th(R)–Ar–Th(R) polymers and HH polythiophenes with –C≡C–R side chains. π-Stacking of π-conjugated polymers brings about important electronic and optical functionalities for the polymers, and many studies have been carried out on π-stacking of HT-P3RTh. New information about the π-stacking behavior of these polymers will provide a basis for a better understanding of the π-stacking forces between π-conjugated polymers, the structures of π-stacked polymers and the electronic and optical effects of π-stacking on π-conjugated polymers.

π-Conjugated polymers are used industrially as capacitor electrodes, in electron-beam lithography and in organic light-emitting diodes. Polymer-based solar cells [21,51,67–80], field-effect transistors and electroluminescent diodes are also targets for π-conjugated polymers. For practical applications, the stability of the polymer against oxidation [69] and control of the band gap [68,69] are particularly important and have been investigated in detail. Solar cells are attracting particular interest as an application for π-conjugated polymers. The production of large, flexible polymer solar cells by printing and roll-to-roll processes [70] has been proposed, and bulk-heterojunction solar cells using π-conjugated polymers (*e.g.* HT-P3RTh [77] and a copolymer consisting of electron-accepting aromatic units and electron-donating aromatic units [74,76])
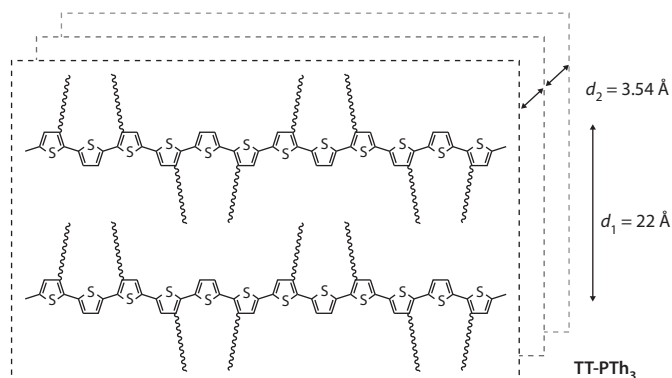
or oligomers (*e.g.* oligo(*p*-phenylenevinylene) [79,80]) and fullerene derivatives have been reported. Recently, polymer solar cells capable of 6% power conversion [74,76] with an internal quantum efficiency approaching 100% have been reported [74], and power conversion higher than 7% is anticipated. The molecular assembly of π-conjugated polymers will be important for achieving even better performance for polymer-based solar cells.

Acknowledgments

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