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Review

Vapour phase polymerisation of conducting and non-conducting polymers: A review

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ABSTRACT

Vapour phase polymerisation (VPP) is a well established technique in which the monomer is introduced to an oxidant-coated substrate in vapour form. Polymerisation then takes place at the oxidant vapour interface. VPP is a technique that could be used to immobilise materials to the modified electrode surface. This review article concentrates on the VPP of conducting polymers such as Polypyrrole (PPy) polythiophen (PT) and polyaniline (PANi). VPP of conducting polymers and other non-conducting polymers have extensively been investigated. This review article is divided into three main parts as given in Table of contents related to the VPP process of some important conducting polymers such as PPy, PT, PANi and Poly(3,4-ethylenedioxythiophene). A total of 181 references are cited in this review article and it attempts to look into VPP from inception of the method till present day.

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1. Introduction

Polypyrrole (PPy), polyaniline (PANi), polythiophene (PT) are all π conjugated conducting polymers and are known as intrinsically conducting polymers (ICP). The usefulness of these conjugated polymers is a result of their ability to be deposited as thin films on to donor substrates. They are usually polymerised and simultaneously doped

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using electrochemical techniques in solution. They have attracted the attention of researchers in textile field due to their potential application in composite with natural, artificial or synthetic fibres. They have good conductivity, high stability and a good film forming property.

The conductivity of conducting polymers is attributed to the delocalisation of π-bonded electrons over the polymeric backbone, shows electronic properties, such as low ionisation potentials and high electron affinities [1,2]. They have attracted a great deal of attention in scientific activity in recent years as electronic conductors. Other applications include antistatic coatings, transparent conductors for display, organic thin film transistors, printed circuit, photovoltaic cells, smarts windows, capacitors and sensors. Conducting polymers have been widely used in the areas of bioanalytical science due to their inherent charge transport properties and biocompatibility [3,4]. Recently, conducting polymer nanomaterials have offered a great possibility for novel applications in synthesis and characterisation techniques [5–8]. Conducting polymers have been reviewed by many scientists especially in biosensor evaluations [9]. Some conducting polymers are doped and/or covalently or physically modified by nanomaterials [10] such as carbon nanotubes [11] graphene [12] metal nanoparticles [4,5,13]. They are also modified by bionano-materials [9,14], especially proteins [15], neurotransmitters [16], nucleic acids [17] and DNA [18] which exhibit unique catalytic properties that can be easily employed in the design of biosensors [19]. Conducting polymers have been used as impedance type gas sensors at low cost, highly sensitive and selective room temperature [6,7]. Serra et al. showed that conducting polymer sensors obtained by vapour phase polymerisation (VPP) are suitable for odour recognition [20]. Doping and undoping play key roles in the sensing mechanism of conducting polymer based sensors. Among these conducting polymers, PPy has superiority for commercial applications because of its unique properties [21].

Three polymerisation methods exist for conducting polymers. They are wet chemical oxidation, electrochemical polymerisation and VPP. VPP is a technique in which the monomer is introduced to an oxidant-coated substrate in vapour form. Polymerisation then takes place at the oxidant vapour interface as shown in Fig. 1. VPP can be either chemical vapour phase polymerisation (CVPP) or electrochemical vapour phase polymerisation (EVPP). CVPP is a solvent free process used to get uniform, thin and highly conductive polymer layer on different substrates. Stussi et al. described VPP as an innovative technological method that allows formation of layers of conducting polymers of any desired form and thickness in a uniform way on an insulating substrate [22]. The vapour phase deposition process has several advantages over other methods for depositing conducting polymers since the monomers are applied as vapour rather than a solution and there is no liquid to act as transport medium for particle agglomeration. However, most conducting polymers suffer from insufficient conductivity which limits their use as current path in electronic devices. Intensive research has been conducted on VPP to overcome these drawbacks. ICP layers formed on the substrates via VPP have high electrical conductivity, and they are nearly agglomeration free because there is no liquid involved to act as transport medium. VPP also makes smooth homogeneous layer and VPP method is one way to achieve a clear thin film and a very smooth surface [23].

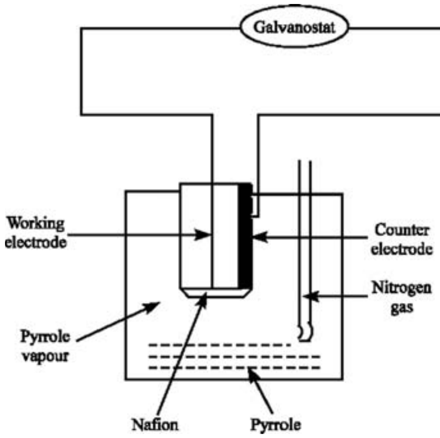

Fig. 1. Schematic diagram of vapour phase polymerisation cell [31].

Spin coating, solvent casting or printing are other common techniques available for depositing thin and even polymer coatings. Most conducting polymers are difficult to process in this way because they have the major disadvantage of being insoluble in most solvents. Shin et al. have reported that dopants with long chains such as alkylbenzenesulfonic acids could overcome insolubility in most solvents with aniline, although polyaniline is produced by chemical polymerisation [24]. They also found out that the solubility and electrical conductivity of doped PANi increased with longer alkyl chain length of dopants. When PANi was doped with bulky alkylbenzenesulfonic acid, the solubilities were more than 80 wt% because the bulky dopants decreased interactions between polymer chains. The solubility of PANi increased with longer alkyl chain length of dopants because the longer alkyl chain acted as a better surfactant and increased free volume between polymer chains.

Mohammadi et al. conducted the first studies of VPP of conducting PPy using iron (111) chloride and H_2O_2 as oxidants at low pressure and several other researchers used normal pressure for their VPP [25–30]. Other researchers that have reported VPP technique for PPy include: Dallacqua, Lawal and Wallace, Subramaian, Winter Jean, Fu, Ueno and Uezu [26,27,31–35].

Fe(III) chloride and Fe(Tosylate)$_3$ are most common oxidants used in VPP [36,37], Fe(III) sulphonate [38], CuCl2 [39] and $HAuCl_3$ [40] have also been used as oxidants. Dopants (counter ion) that have been incorporated into conducting polymers (CPs) during electrochemical polymerisation and VPP include 2,4,6 trimethylbenzen, paratoluensulfonate, tiron, polyvinyl alcohol, methanesulfonate, octanesulfonate, butanesulfonate and polystyrenesulfonate [13,41–45]. Surfactants in solution and sulfonated dyes have been incorporated into conducting polymers as counter ion to induce interaction with particular proteins [46]. Complex and more delicate entities like antibodies or, enzyme [47–51] or carbon nanotubes [11,52–54] can also be directly incorporated as counter ions.

The use of ferric *p*-toluenesulfonate as an oxidant was initially reported by Ali et al. for the chemical polymerisation of 3, 4-ethylenedioxythiophene [55]. Subsequently, Fu et al. reported the use of Fe (III) *p*-toluenesulfonate as an oxidant for VPP on polyurethane foams [33]. Winther-Jean et al. used this same salt extensively as an oxidant for growing PPy and poly (3,4-ethylenedioxythiophene) (PEDOT) films by VPP [30,38,56]. Subramaian et al. used Fe(III) alkyl benzene sulphonate. In contrast to $FeCl_3$, Fe(III) *p*-toluenesulfonate does not crystallise as the solvent evaporates and this represents a significant advantage as it is necessary to suppress crystallite formation in the dried oxidant in order to obtain smooth PPy films [26]. VPP method can be used to deposit both PPy and PEODT even on non-conductive substrates, such as glass, PET and PES film surfaces. VPP have great advantages especially in PEODT processing, because there is no need to use poly(styrenesulfonate) (PSS) [57,58].

Functional polyelectrolyte such as dextrant sulphate, chondroitin and heparin act as dopants. They have been incorporated into polymer structure and they still retain their inherent bioactivity [59]. Nafion (perflorinated sulphonate), another polyelectrolyte also acts as dopant in solution and in vapour polymerisation [31,32,47,60]. Dopants

Table 1
Some of the dopants commonly used for vapour phase and wet oxidation polymerisation of conducting polymers.

S/N	Dopant	Reference
1	Fe(III) tosylate is also used as an oxidant.	[168]
2	Pyridine	[169]
3	p-toluene sulphonic acid (p-TSA)	[170]
4	Diethylene glycol (DEG).	[171]
5	12-molybdophosphoric acid	[30]
6	10-molybdo-2-vanadophosphoric acid	[30]
7	Fe(III) chloride	[30,93,171]
8	Fe(III) p-toluenesulfonate	[30,33,38,172]
9	poly(styrenesulfonate) (PSS)	[128]
10	Fe(III) alkylbenzenesulfonates	[26,41]
11	Iodine	[173]
12	Pyrocatechovoilet	[174]
13	Poly(styrenesulfonate)(PSS)	[58]
14	Benzenesulfonic acid (BSA)	[24]
15	p-toluenesulfonic acid (TSA),	[24]
16	Dodecylbenzenesulfonic acid (DBSA)	[24]
17	Butylbenzenesulfonic acid (BBSA)	[24]

commonly used in VPP and solution polymerisation of conducting polymers are as shown in Table 1. In the course of this review, we would like to report a systematic study of VPP of conducting polymers. VPP process of some important conducting polymers such as PPy, PT, PANi and PEODT were investigated. Non conducting polymers, styrene, polyvinyl, ethylene, butadiene and propylene were also investigated.

2. Vapour phase polymerisation of conducting polymers

2.1. Polpyrrole

PPy has extensively been investigated by researchers for commercial applications because of its excellent properties, such as good electrical conductivity, excellent environmental stability and ease of preparation [26,42]. Because of PPy's high electrical conductivity, long term environmental stability and ease of synthesis by chemical or electrochemical means, it has been used to construct chemical sensors [61,62]. It has also been used in production of photovoltaic cells, actuators and electrochemical cells [63,64]. PPy can be modified by covalently attached redox groups [65], proteins [66,67], low [68] and high [69] molecular weight molecular imprints. PPy is often applied in the design of biosensors based on immobilised enzymes [70,71], antibodies or single stranded DNA [72]. Conducting polymers such as polypyrrole, and polyaniline [73] are usually polymerised and simultaneously doped using electrochemical techniques. They can also be synthesised by chemical oxidative means, which can occur in the vapour phase. Among the conducting polymers of heterocyclic system (polypyrrole, polyanialine and polythiophene), polypyrrole attracted the most attention [74–78]. PPy has been extensively investigated owing to its good environmental stability, high conductivity and ease of polymerisation. The properties of PPy, such as, conductivity, strength and morphology are very dependent on the dopants, conditions and mode of polymerisation employed. Some polyelectrolytes (PE) are readily incorporated into a PPy during polymerisation as counter ion as shown in Fig. 2 and polymerisation process follows the path way in Fig. 3.

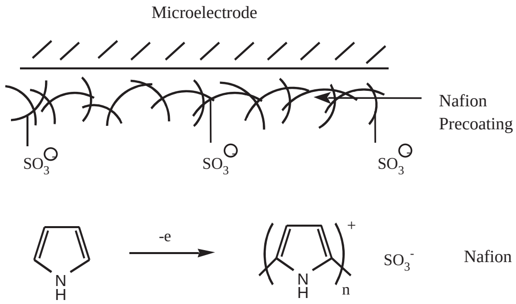

Fig. 2. Polyelectrolytes incorporation into PPy during VPP.

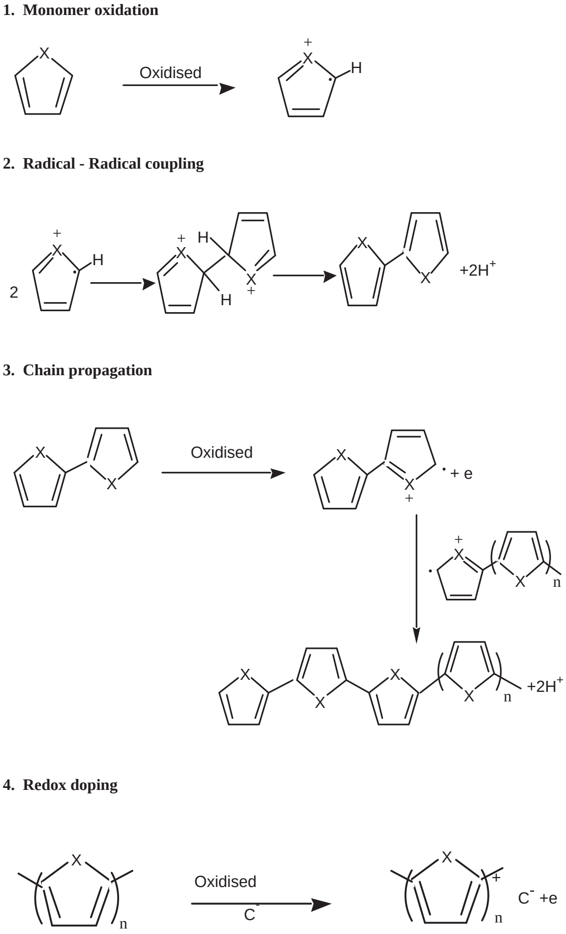

Fig. 3. Nucleation/growth mechanism for heterocyclic conducting polymers. [175].

In vapour phase chemical polymerisation of PPy, Sachin et al. used polyethylene oxide (PEO) [79], Miyata et al. and Kise et al. used poly (vinyl) alcohol and polyurethane foam as supporting substrate [29,80–84], Qian et al. used paper [85], Shang et al. deposited PPy on a flexibble substrate [86], Wallace et al. and Chen et al. deposited PPy on carbon nanotubes (CNT) [42,87], Wang et al. deposited PPy on a fibrous material [88], Dall-Acqua et al. deposited PPy on cellulose textile substrate [27] and Perruchot et al. deposited PPy on glass coated with organosilane [89]. Cho et al. deposited PPy on aramide to form a highly conductive composite [90], while Babu et al., Bashir et al., Najar et al., Tan and Ge used cotton thread, varied oxidants and monomer concentration, temperature polymerisation time and solvent effects [91–94]. During VPP, continuous vapour phase at a speed of 1.5m/min was used by Wang et al. and Najar et al. used 1 m/min [93,95–97]. The disadvantage of Wang et al.'s method is that more gas was used up during VPP. Chen et al. studied the manufacturing of PPy conductive paper. The effects of oxidant concentration, pretreatment time, drying time, and reaction time on the properties of the polypyrrole conductive paper were investigated [98]. Wang et al. prepared patternable, electrically conductive coatings having a super hydrophobic and superoleophobic surface using one-step VPP of PPy in the presence of a fluorinated alkyl silane directly on fibrous substrates [88].

Kim et al. obtained conductive thin films of ferric chloride doped PPy by in situ VPP method under ambient conditions [99]. Homogeneous and thin conductive PPy films were uniformly fabricated at nano-level thickness on the plastic film substrates by continuous roll process. The conductivity of the films rapidly increased with the increasing deposition time of the pyrrole monomer. Subramaian et al. carried out VPP of pyrrole monomer using Fe(III) benzenesulfonate, p-ethylbenzenesulfonate, dodecylbenzenesulfonate and p-toluenesulfonate [26]. As the chain length of the Fe (III) alkylbenzenesulfonate increased it was found that the film forming ability of the polypyrrole was enhanced, probably as a result of a decrease in polymer chain interaction resulting from increased free volume between polymer chains. Ueno et al. developed transparent, electrically conductive composite derived from PPy and polyvinyl-chloride by VPP and they studied the effect of environment on polymerisation and reaction mechanism [34].

2.2. Polypyrrole composite

VPP can be used to deposit composite on conducting surfaces [80]. Han et al. fabricated porous PPy/polymethylmethacrylate composite film prepared by vapour deposition of pyrrole and used it for ammonia detection [100]. Han et al. also studied the electrical and optical properties of micro-pattern of PPy by using VPP [101]. The PPy thin film prepared by VPP showed superior surface resistance characteristics and the surface of PPy thin film prepared was smoother than that prepared by liquid phase polymerisation. Lee et al. recently directly synthesised PPy-carbon nanotube composite by VPP [102]. The conductive PPy was filled as a matrix material between the CNT networks by self-organization of the pyrrole monomer. This process increased the carrier mobility for electrical conductivity because it acts as conducting bridge connecting PPy. The process also increased the conductivity up to five times and simultaneously improved the thermal stability. The characterisation of the composite film was established by TEM, XRD, TGA, and IR/Raman spectroscopic analysis. Kim et al. reported the In-situ blends of PPy/PEODT synthesised as thin-films on glass substrates using the vapour-phase polymerisation (VPP) technique [28]. The blend ratios of PPy to PEDOT were controlled by adjusting the amount of liquid-phase monomers placed in the VPP chamber. There have been reports on PPy/PEDOT blend systems prepared by the electrochemical/VPP method on the surface of conductors [103,104]. Egami et al. used CVPP to prepare and characterise conductive fabrics coated uniformly with PPy nanoparticles. They successfully fabricated a conductive fabric coated densely and uniformly with polypyrrole nanoparticles that were less than 50 nm in size by exposing a fabric immersed in a solution containing an oxidising agent and a dopant to pyrrole vapour [105]. Lawal and Wallace introduced nafioion into PPy matrix by electrochemical VPP [31,32]. This produced a uniform, homogeneous and conductive thin film of PPy composite. The composite films (PPy/Nafion) also show surface features of highly ordered structural regularity.

2.3. Polyaniline (PANi)

(PANi) has been shown to be the most promising material to fulfil such applications as photovoltaic cell being air stable, good conductivity, cheap to produce in large scale and most importantly processible to some degree [2]. Ray et al. show that the oxidation state of the “emeraldine” base form of PANi can vary depending on whether its synthesis is performed in the presence or absence of air [106]. Chemical doping of leucoemeraldine, the completely reduced form of PANi, to selected oxidation states can be accomplished by a variety of oxidising agents such as $FeCl_3$, $SnCl_4$ and TCNQ. The nominal main chain architecture which best describes PANi is given by

$$[(C6H4{-}NH{-}C6H4{-}NH{-})1-x(C6H4{-}N{=}C6H4{=}N{-})x]n$$

PANi can be formed under mild oxidative conditions, although formation of the most highly conducting form requires the presence of acid as shown in Fig. 3. Processing routes were first described by Cao et al. using two specific functional acids, camphor–sulphonic acid (CSA) and dodecyl benzene sulphonic acid (DBSA) in various organic solvents. Fig. 4 shows illustration of the acid doping of PANi [107].

PANi processability can be improved if PANi is protonated with specific bulky protonic acids. Well-known examples of such acids are p-dodecyl benzenesulphonic acid (DBSA), camphor-10-sulphonic acid (CSA) and methyl benzene sulphonic acid (MBSA) [108–110]. PANi Emaraldine salts (PANi-Cl, PANiBr, and PANi-ClO_4) were synthesised by the electrochemical method using different acids (HCl, HBr, $HClO_4$) and they can also be synthesised using electrochemical/VPP method. The sensor properties of PANi have been changed depending on the nature of dopant anion. PANi was found to be a better choice for detection of gases, such as ammonia, due to its higher sensitivity, reversible response and shorter response time. The effect of ammonia and water on the conductivity of polyaniline has been investigated along with the polymer adsorption capacity.

Bandar et al. synthesised higher soluble nanostructure PANi by VPP and determined its crystal structure [111]. Chen et al. synthesised chiral PANi films via chemical VPP and Gao et al. synthesised crystalline PANi with dendritic morphology using slow vapour phase chemical oxidative polymerisation, which opens up possibility for further understanding PANi's chain elaborately arranged, crystal structure model, and essence of the molecular interaction [112,113].

Kim et al. fabricated and studied the properties of PANi nanofilms prepared through VPP while Norris et al., fabricated ultrafine conducting fibres: PANi /polyethylene oxide blends [114,115]. Wallace et al. fabricated transparent and flexible carbon nanotube/PPy and carbon nanotube/PANi pH sensors [42].

2.4. Polythiophens

Polythiophens (PTs) are an important class of conjugated polymers that form some of the most environmentally and thermally stable materials. PTs have been used in many areas, such as electrical conductors, non-linear optical devices, LEDs, transistors, electrochromic or smart windows, photo-resistance antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, microwave absorbing

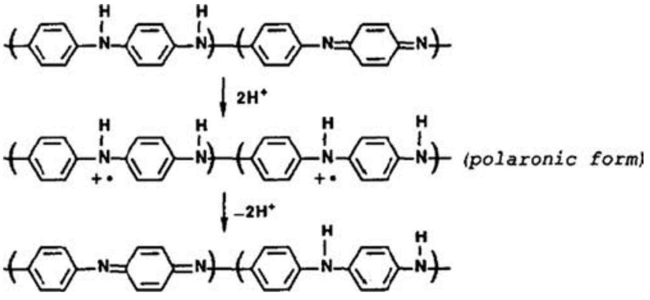

Fig. 4. Illustration of protonic acid doping of polyaniline [176].

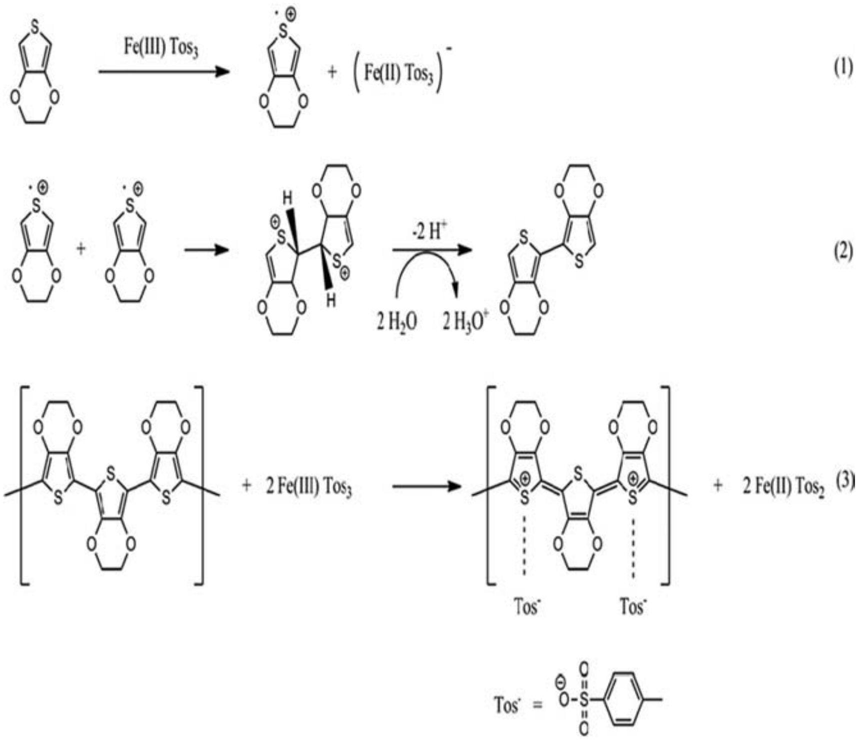

Fig. 5. Proposed polymerisation mechanism for VPP PEDOT: (1) EDOT is oxidised by Fe (III) to a cation radical; (2) EDOT cation radicals form dimers that subsequently get deprotonated; (3) PEDOT polymer is doped and a tosylate ion resides in the film to act as a counter ion [168].

materials, new types of memory devices, nano-switches, imaging materials and polymer electronics.

EVPP of PTs requires a more extreme oxidation potential and attachment of simple functional groups, e.g., alkyl sulphonates, to the monomer can reduce the oxidation potential and significantly improved the electrical conductivity. Bahattchanyya et al. used the COOH functional groups in the copolymer of thiophene-3-acetic acid (TAA) and 3, 4-ethylenedioxythiophene (EDOT) for immobilisation of a biomolecule [116,117]. The PEDOT thin films were directly grown on the polymeric roll film substrates by polymerising EDOT monomer in vapour phase.

Otero et al. electrodeposited PTs films using EVPP: and studied its temperature influence and electrical properties [78]. Wei et al. used infrared and photoelectron spectroscopy study of vapour phase of poly (3-hexylthiophene) [118]. Choi et al. also produced PEDOT effectively via VPP with the addition of imidazole (Im) based derivatives [119,120]. The addition of Im that has one and/or two alkyl substituents significantly improved the electrical conductivity of PEDOT thin films. They micro patterned PEDOT using ink-jet printing/soft lithography while Kim et al., explored direct photo patterning of a vapour polymerisable and photo-cross-linkable EDOT to make it suitable for use in electronics applications [121]. Ali et al. studied the effects of solvents on PEDOT thin films deposited on a 3-aminopropyltrimethoxysilane (APS) monolayer by VPP while Chelawat et al., obtained PEDOT thin films through oxidative CVPP by using bromine [122,123]. The use of bromine eliminates any post processing rinsing step required with other oxidants like iron chloride and hence makes the process completely dry. Film properties are further compared with the PEDOT films deposited using iron chloride as the oxidant. Fabritto et al. used vacuum vapour phase polymerised PEDOT thin films for use in large-scale electrochromic devices [124–129]. Han et al. used simultaneous vapour-phase polymerisation of PEDOT and a siloxane into organic/inorganic hybrid thin films [130]. Im et al. systematically controlled the electrical conductivity of PEDOT via oxidative CPPV [131–133]. Jang et al. fabricated PEDOT thin films by VPP for optoelectronic device applications [134,135]. Jones Jr et al. polymerised PEDOT on flexible substrates for enhanced transparent electrodes using VPP [136]. Joyner et al. studied the effect of pre-sulfiding of catalysts for the vapour phase catalytic synthesis of thiophenes [137]. Winther- Jensen et al. fabricated PPy and PTs using Fe(III) sulfonates as oxidising agents during VPP [38,36,138], while Kim et al. produced the blend of PPy and PT using VPP [28]. They found that increasing the PEDOT monomer ratio changed the electrical conductivity, colour and light transmission from 4 S/cm for the pristine PPy to 58 S/cm in the case of a PEDOT ratio of 1.0. Zuber et al. reported improved PEDOT conductivity via suppression of crystallite formation in Fe(III) tosylate during VPP [139]. Fig. 5 shows schematic equivalence of mechanism of reaction during polymerisation of PTs. Bashir et al. used CVPP to coat flexible textile fibre (viscose) with highly conductive polymer, poly (3,4-ethylenedioxythiophene) (PEDOT) in the presence of ferric(III) chloride ($FeCl_3$) oxidant [92].

3. Vapour phase polymerisation of non conducting polymers

Monomers of non-conducting polymers such as styrene in vapour phase polymerise readily at room temperature in the presence of catalyst [140].

3.1. Styrene

Polystyrene has some attractive physical characteristics including high melting point (270 °C), low specific gravity (1.045), excellent hydrocarbon resistance, a high degree of dimensional stability, enhanced mechanical performance at elevated temperature and very good electrical properties. This combination of properties opens a wide variety of applications including automotive, appliance, medical, electrical/electronic, fibbers, and films.

Collis et al. studied the polymerisation and oxidation of styrene vapour both in the absence and presence of the liquid monomer.

When liquid styrene is absent, no appreciable polymerisation takes place in the gas phase below 500 °C, at which temperature paralysis starts to occur; but styrene reacts with oxygen above 300 °C, undergoing some polymerisation simultaneously with oxidation [140].

Anjou et al. designed polystyrene-based nanocomposite by vapour-phase assisted surface polymerisation [141,142]. Recently, Alsheareaeh and El-Shall studied ion mobility and the mechanism of the gas phase thermal polymerisation of styrene and the structures of the early oligomers [143]. The mobility measurements provide structural information on the ionised oligomers based on their collision cross sections (Ω) which depend on the geometric shapes of the ions.

3.2. Polyvinyls

Polymers derived from simple alkenyl monomers containing carbon–carbon double bonds are often referred to as vinyl polymers. Andou et al. used photo-induced vapour-phase assisted surface polymerisation of vinyl monomers using immobilised free radical initiators [141,142,144,145].

3.3. Ethylene

Polymers derived from alkenes such as ethylene and propylene are often called polyolefines.

Beigzadeh et al. studied ethylene polymerisation under single liquid phase and vapour-liquid phase conditions in a continuous-flow tubular reactor [146]. Bruk et al. studied properties of thin poly(tetrafluoroethylene) films deposited on solid substrates by electron beam polymerisation from vapour phase [147,148]. Chung et al. examined kinetic analysis of VPP of ethylene over polymer supported (CH3)$_2$Si[Ind]2ZrCl$_2$ catalyst [149]. Cullis et al. studied kinetic analysis on the VPP of ethylene over polymer supported (CH$_3$)2Si[Ind]2ZrCl$_2$ catalyst [140]. Dubinikova et al. looked into the effect of oxygen on the activity of a supported vanadium catalyst during VPP of ethylene while Giardini–Guidoni et al., looked into chain carrier ions participating in the VPP of ethylene oxide. Oxygen was introduced into the reaction zone at the stage of formation of the active centres in the course of polymerisation [150,151]. It is shown that the formed catalytic system is most exposed to the inhibiting effect of oxygen. Gorbach et al. studied the dynamics and stability analysis of solid catalysed gas-phase polymerisation of olefins in continuous stirred bed reactors. The stability and dynamic behaviour of two types of continuous stirred bed reactors (CSBR) have been analysed. Both the vertical CSBR of BASF and the horizontal CSBR of Amoco were examined [152].

3.4. Butadiene

Butadiene-styrene copolymer serves as both rubber and paint of emulsion or latex. Berndit et al. used in-situ-drifts investigations of the VPP of 1, 3-butadiene on supported Nd and La allyl complexes. DRIFT spectroscopy was successfully used to investigate interactions of lanthanide complexes with aluminium organic co catalysts and for in situ studies of the insertion/polymerisation of gaseous 1, 3-butadiene on the 'adducts' of both catalyst components as well as on silica-supported allyl complexes/cocatalysts [153].

Ebastine et al. and Zoeliner polymerise butadiene using VPP. The gas phase polymerisation of butadiene with a heterogeneous Ziegler catalyst based on neodymium was studied by using video microscopy and a stirred tank reactor of laboratory scale. Using video microscopy, the start up of polymerisation and the particle growth of individual catalyst particles were measured at different reaction conditions [152–154].

3.5. Propylene

VPP of propylene is a rapidly growing industrial process which is usually carried out in a fluidised bed reactor. Propylene from VPP is reported to have some properties distinct from those formed in slurry or fluidised process [155].

Grunze et al. and Hungenberg et al. studied progress in VPP of propylene with supported TiCl$_4$ and metallocene catalysts. They discovered that, the application of process parameters and catalyst (TiCl$_4$ and metallocenes) are tools for tailoring product properties [156,157]. These are demonstrated in terms of molecular mass, molecular mass distribution, melting behaviour and mechanical and optical properties of photopolymers, random copolymers and bi-phasic impact polymers. Hwang et al. looked into UV-induced graft polymerisation of polypropylene-g-glycidyl methacrylate membrane in the vapour phase and Ibraheem et al. also looked into UV-induced graft polymerisation of polypropylene-g-glycidyl methacrylate membrane in the vapour phase. They studied the developments in modelling gas-phase catalysed olefin polymerisation fluidized-bed reactors (FBR) using Ziegler-Natta catalyst [158–160]. Choi and Ray also used Ziegler-Natta catalyst to polymerised propylene in gas phase over a TiC1$_4$, 5 AlCl$_3$, and (Stauffer Type AA) catalyst with A1Et2C1 cocatalyst both with and without H$_2$ present. The effects of polymerisation temperature, monomer concentration, catalyst composition, and hydrogen were investigated [161,162].

3.6. Others

Algaier et al. investigated the effect of temperature on the rate of poly(ethyl cyanoacrylate) (PECA) growth and its molecular weight during its VPP [163]. They observed that the surface bound initiators provide insight into the important mechanistic aspects that impact the polymerisation's success. Babkin et al. and Bayley et al. reported gas-phase graft polymerisation of acrylonitrile on ultrafine chlorinated polyvinyl chloride fibre while Jardke et al. polymerised poly(phenylquinoxalines) by VPP [164–166]. They described VPP as a new method that can be used to fabricate electron transport layers based on poly (phenylquinoxalines) (PPQs) for organic light emitting diodes (OLEDs). Chen et al. produced polymethyl methacrylate using VPP [167]. Preheated monomer (methyl methacrylate) and initiator (t-butyl peroxide) vapours were metered into a pressure-controlled reaction chamber. Inside the chamber, gases pass through a high-temperature hot-zone where primary free radicals are formed. The gas mixture then condenses and polymerises on a back-cooled target substrate.

4. Applications/structure

VPP methods have been used to deposit thin films on flexible substrate such as wood, cotton and conducting surfaces.VPP methods have also been used in fabrication of electronic nose and DNA sensors [177,178]. VPP methods provide highly ordered polymer network structure and the polymer thin films remain stable in ambient condition. The growth of thin films at nano-level thickness, high conductivity and surface structure of high integrity provided by VPP can be applied in production of organic optoelectronic devices, antistatic transparent films, plymeric electroluminescent diode and metalisation of insulators.

Several atomic force microscopy (AFM) studies of surface morphology of materials produced by VPP show very smooth and uniformed structure as shown in Fig. 6 [28,99,179]. Polymer films produced by

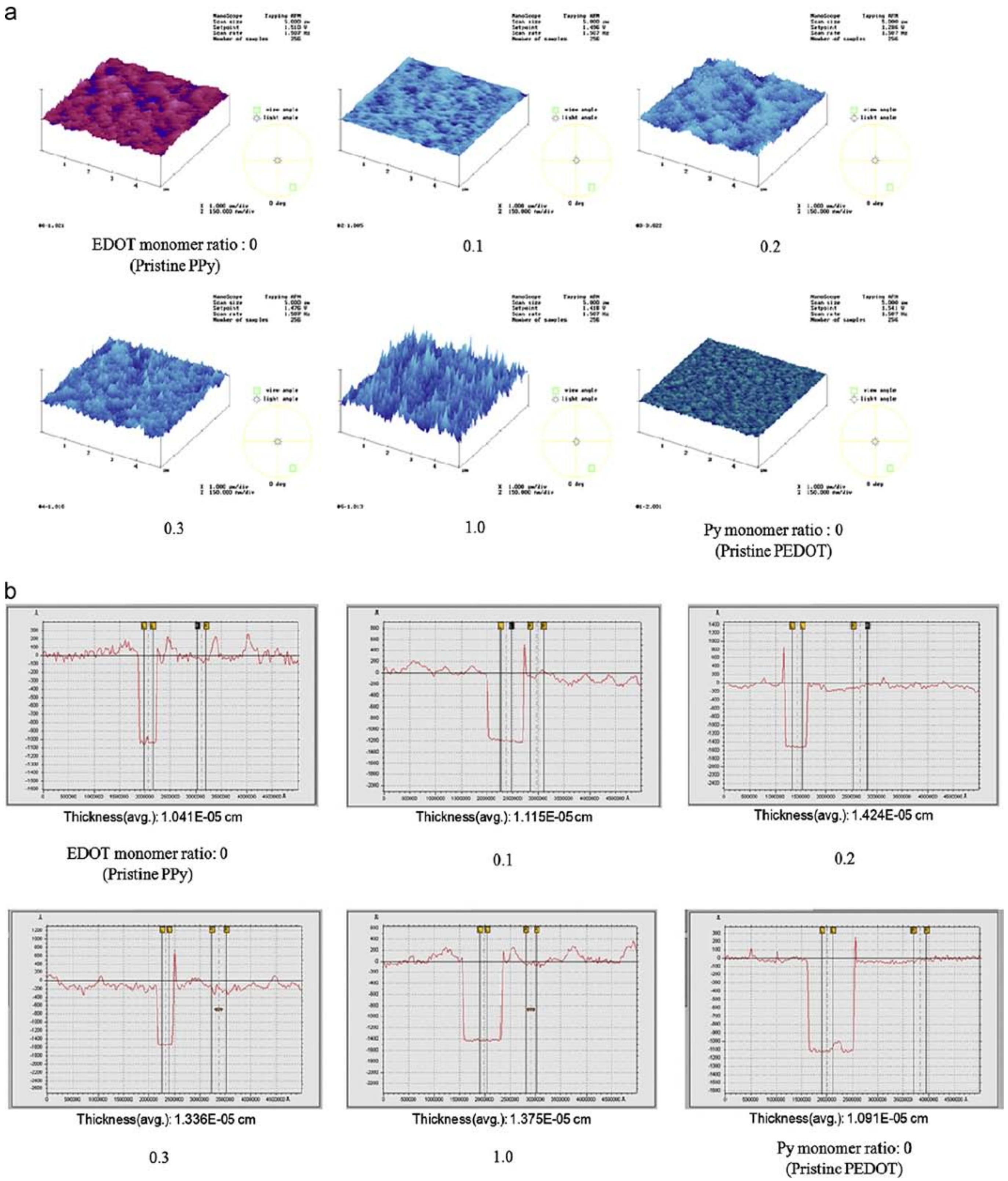

Fig. 6. (a) AFM images and (b) Surface profiles by alpha-step of PPy/PEDOT blends film surfaces at various Py/EDOT monomer ratios. [28].

VPP methods have very smooth homgenious structure, when compared to solution oxidative and electrochemical methods which are significantly rougher. Scanning electron microscopy (SEM) studies show VPP methods produce very smooth and uniform thin films that are non porous when compared to solution deposition which yield less uniform and more porous surfaces as shown in Fig. 7 [178,180].

5. Conclusions

VPP's of some important conducting polymers, such as PPy, PTs and PANi have been extensively reviewed; they have many advantages due to their charge transport properties that enhanced their conductivities. Some non-conducting polymers which were

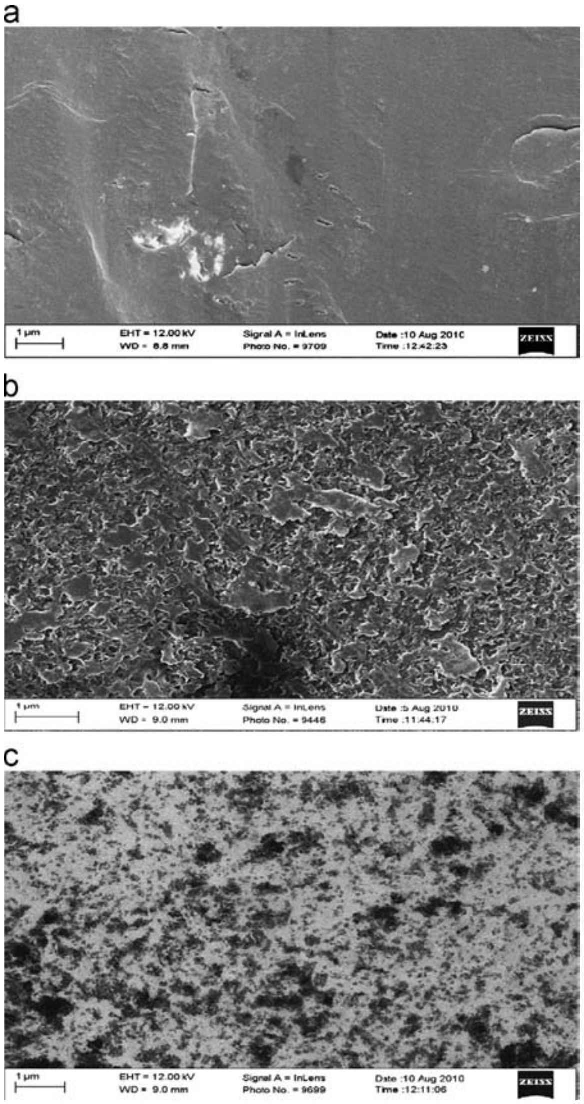

Fig. 7. SEM images of (a) VPP PEDOT (b) in situ PEODT and (c) PEODT: PSS [180].

polymerised using VPP were also reviewed. While VPP is novel, it produces shorter polymer chains and there are partial penetrations into the substrate. Future work will focus on the use of VPP for mass industrial production of conducting polymer electrodes, production of longer chain and conjugation length polymers.

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