

Review

A NEW APPROACH TO ELECTROACTIVE POLYMERS VIA WELL-DEFINED OLIGOMERS WITH FURTHER POLYMERIZABLE END-GROUPS

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Abstract Among the inherent drawbacks of conducting polymers are the limited processibility, uneven polydispersity in molecular weight and the existence of structure defects, which become the obstacles for many electronic, optical and biological applications that demand the materials to have well-defined structures and high chemical purity. To solve these problems, our research in the last decade or so has focused on the synthesis of electroactive oligomers of well-defined structures, controllable molecular weights, narrow or uniform polydispersity. We have developed a general strategy for the synthesis of such oligomers based on the theory of non-classical or reactivation chain polymerization. The aniline oligomers with minimum 4 nitrogen atoms and 3 phenylene rings exhibit similar characteristic redox behavior and electroactivity as polyaniline. Electronic conductivity of the oligomers of 7 or 8 aniline units approaches that of polyaniline. Solubility of the oligomers is much improved over that of conventional polyaniline. Various functional groups can be introduced into the oligomers either by proper selection of starting materials or by post-synthesis modifications via common organic reactions. The functionalized oligomers undergo further polymerizations to afford a variety of new electroactive materials, including polyamides, polyimides, polyureas, polyurethanes, polyacrylamides and epoxy polymers. Numerous potential applications, particularly as anticorrosion materials, are discussed for the oligomers and their polymeric derivatives.

Keywords Electroactive oligomers, Aniline oligomers, Re-activation chain polymerization, Amino-terminated trianilines

INTRODUCTION

Conductive polymers, such as polythiophene, polyaniline, polypyrrole, poly(*p*-phenylene vinylene), *etc.*, have been studied extensively and explored for numerous potential applications because of their high conductivity and, probably more importantly, their electroactivity and other unique properties^[1–5]. There have been many encouraging developments towards commercialization of the electroactive polymers for applications such as electroluminescent devices, corrosion resistant coatings and electrostatic dissipation coatings and fabrics^[5]. Recently, the pioneers of conducting polymer research, Alan MacDiarmid, Alan Heeger and Hideki Shirakawa, were awarded the 2000 Nobel Prize in Chemistry, which represents the highest recognition for this research field. Despite the enormous advancements in basic science and technology, one problem associated with large-scale commercial applications is the limited processibility of electroactive polymers. For instance, polyaniline solution in *N*-methyl-2-pyrrolidinone (NMP) often forms gels and unsubstituted polythiophene and polypyrrole are insoluble in common organic solvents. Many processing conditions involve the use of undesirable organic solvents that would give rise to serious environmental and regulatory concerns in many industries. More fundamentally, among the inherent drawbacks of the electroactive polymers, like most synthetic polymers, are the uneven polydispersity in molecular weight and the existence of structure defects, which become obstacles for

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many electronic and optical applications that demand the materials to have well-defined structures and high chemical purity.

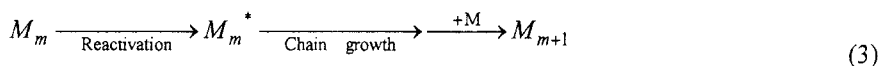
In an effort to solve these problems, our research in the last several years has focused on the synthesis of electroactive oligomers of well-defined structures. The basic idea of our approach has been that the electroactive oligomers with the same repeating unit structures as their corresponding polymers can be prepared to have well-defined structures, controllable molecular weights, very narrow or even polydispersity and designable functional end-groups. Because of the low molecular weights, these oligomers must have enhanced solubility and, therefore, could be purified, thoroughly characterized and studied for their physical and chemical properties. On the other hand, since the end-groups can be readily transformed into polymerizable functional groups, the oligomers can be functioned as the monomers for further polymerization to yield a variety of new polymers, which possess both excellent mechanical properties of typical polymers and the electroactivity of the conducting polymers. It is particularly noteworthy that electroactive oligomers often exhibit similar or even improved physicochemical properties. As an example, the aniline oligomers appear to have good or even better anticorrosion properties^[6, 7]. The electronic properties of the aniline octamer were reported to be comparable to polyaniline^[8]. Defect-free thiophene oligomers such as unsubstituted or α,ω -substituted sexithiophenes inherently possess the basic or much improved electronic and optical properties of polythiophene^[9]. The *p*-phenylenevinylene oligomers have also been synthesized and investigated for electroluminescence applications.

In this article, we demonstrate our oligomer approach to the electroactive polymeric materials with oligoanilines as specific examples. Based on a new theory, *i.e.*, re-activation chain polymerization which was established in Wei's group, a general strategy has been developed for the synthesis of aniline oligomers. More specifically, the synthesis, properties and further polymerization of amino-terminated trianilines and other higher oligomers are reviewed and discussed. Some of the potential applications of the oligomers and their polymeric derivatives are described.

REACTIVATION CHAIN POLYMERIZATION: A NEW THEORY IN POLYMER CHEMISTRY

Since the late 1980s, Wei and coworkers have been interested in the development of fundamental understanding of the polymerization mechanism and, therefore, better methodologies for the synthesis of electroactive polymers including polyaniline^[10–15], polythiophene^[16, 17] and polypyrrole^[18]. The synthesis of well-defined aniline oligomers has been designed based on a new theory termed as “non-classical chain polymerization” or “reactivation chain polymerization” as proposed by Wei^[10–19].

Since 1929, two major polymer growth processes, *i.e.*, chain and step polymerizations, have been established in the theories of synthetic polymer chemistry by Carothers^[20]. In the classical chain polymerization (Eq. 1), polymer growth is achieved by a reactive species (M_m^*) reacting with a monomer (M) to form a one-unit longer reactive species (M_{m+1}^*). Depending on the type of the reactive species, radical^[21], ionic^[22], group-transfer^[23], Ziegler-Natta^[24] and other metal-mediated/catalyzed^[25] polymerizations have been developed. In the classical step polymerization (Eq. 2), polymer growth is accomplished by reactions of functional groups between two multifunctional reactants of any length (M_m and M_n) to generate a compound of higher molecular weight (M_{m+n}). The new, reactivation chain polymerization theory integrates many synthetic and biological polymer growth processes^[26]. In this theory (Eq. 3), the polymer chain propagation is accomplished by reactivating a non-reactive or dormant chain (M_m) to a reactive species (M_m^*), which reacts with a monomer (M) (or monomers in some cases) leading to the formation of a dormant product with higher molecular weight (M_{m+1}).



This new class of polymerization process is neither a classical chain nor a classical step polymerization. Examples of this polymerization could include many synthetical and natural polymerizations, such as the oxidative polymerization of anilines and other aromatic compounds^[10-19], the recently emerged living radical polymerizations^[27, 28], in which dissociation of the capping groups can be considered as the reactivation step to allow the addition of one or more monomers before the re-capping, and biological polymerizations for the biosynthesis of nucleic acids, proteins and polysaccharides^[29]. Under proper conditions, the polymerization could be stopped at the desired stages by not reactivating the dormant chains, implying that the non-classical chain polymerization could become a living polymerization. In addition, the classical chain polymerization could be considered as a special case of the reactivation chain polymerization when the reactivation process is simultaneous or very fast^[26].

GENERAL STRATEGY FOR THE SYNTHESIS OF ANILINE OLIGOMERS

Application of this new theory has led to the development of a general, one-step synthesis of aniline oligomers of well-defined structures with controllable end-groups and molecular weights. In this method, various amounts of aromatic amine additives, such as 1,4-phenylenediamine (PDA) or *N*-phenyl-1,4-phenylenediamine (PPDA), were introduced into the aniline polymerization system in aqueous HCl solution with ammonium persulfate as oxidant at a temperature of about -5°C . The reaction conditions were very similar to the conventional aniline polymerization^[3], except for the presence of the additives. As illustrated in Fig. 1 with PPDA as an example, the aniline dimer PPDA can be considered as a chain initiator or a "dormant" chain (M_m), which could be reactivated to reactive species such as nitrenium ions, iminium ions or others (M_m^+) by oxidation, while aniline is considered as the monomer (M) because it has a higher oxidation potential than the M_m compound^[11]. The highly

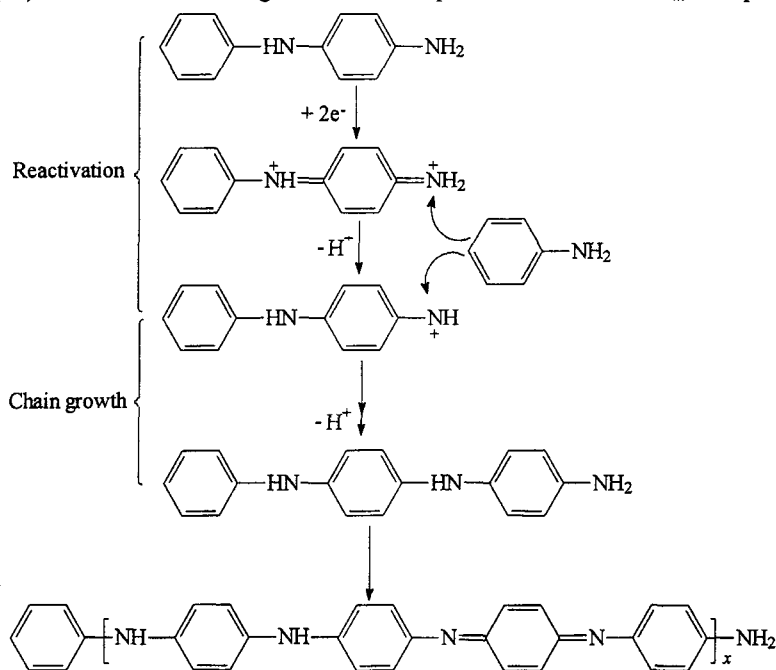


Fig. 1 Polymer growth mechanism in the oxidative polymerization of aniline

A dormant chain of aniline oligomer (PPDA shown as an example) or polymer is reactivated by oxidation to yield a reactive species such as iminium, nitrenium ions, etc., at the chain end. The chain growth is accomplished by the reactions of the reactive species with a neutral aniline monomer followed by deprotonation to afford a new dormant chain of higher molecular weight. The process repeats, leading to the formation of higher oligomers and eventually the polymers.

reactive M_m^* attacks the aniline monomer at the *para* position followed by deprotonation to afford a “dormant” aniline trimer (M_{m+1}), *i.e.*, *N*-phenyl-4,4'-diaminodiphenylamine. Since the trimer has an even lower oxidation potential, it will be oxidized to form the reactive M_{m+1}^* , which again reacts with another aniline monomer resulting in M_{m+2} . This process repeats consecutively to yield higher oligomers and polymers^[11].

The aniline dimer PPDA plays a similar role as the chain initiator in a classical chain polymerization. Therefore, the amount of PPDA added to the aniline polymerization should significantly affect the molecular weight of polymers formed. Indeed, we have found that the molecular weight decreases as the amount of PPDA is increased (Fig. 2). At 20 mol% PPDA, the number-average molecular weight (M_n) was only about 2600 as determined by gel-permeation chromatography (GPC) using standard polystyrene in calibration^[30]. The product can be best described as an oligomer. Furthermore, there is a clear trend, as shown in Fig. 2, that the molecular weight distribution (*i.e.* M_w/M_n) becomes narrower as the amount of PPDA is increased. Similarly, in the system with PDA as the initiator, both the molecular weight and molecular weight distribution also decrease with the increase in the PDA concentration. The oligomers were found to have two amino end-groups. It should be noted that with either PDA or PPDA as the initiator at 2 mol%–5 mol% or higher, the GPC curve of the product changes from a bimodal pattern to a single narrow peak.

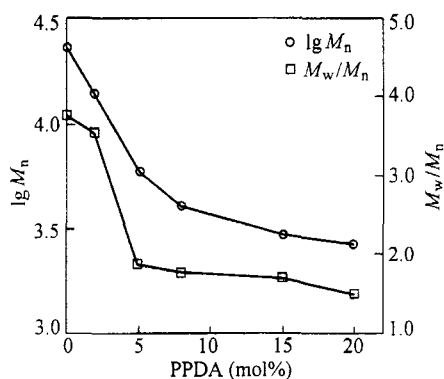


Fig. 2 Effect of the amount of *N*-phenyl-1,4-phenylenediamine (PPDA) on the molecular weight (M_n) and molecular weight distribution (M_w/M_n) of aniline polymer or oligomers

At a very high concentration of PDA (*i.e.* the molar ratio of PDA to aniline is 1:2), an amino-capped aniline trimer can be synthesized in one step as shown in Fig. 3^[31]. There are four possible structures (1–4) for the trimeric product depending on the oxidation state and the position of the quinodal diimine unit. Under the present experimental conditions, the products typically contain the isomer **1**, *i.e.*, *N,N'*-bis(4'-aminophenyl)-1,4-quinonediimine, as the major component and relatively small amount of isomer **2**. Under chemical or electrochemical reduction, a single compound **4**, *i.e.*, *N,N'*-bis(4'-aminophenyl)-1,4-phenylenediamine, was obtained, which could be recrystallized to give needle-shaped crystals. Various C- or N-substituted anilines could also be employed to yield a series of the trimeric derivatives^[31]. The trimeric products were also prepared by oxidative reactions of an amino-terminated aniline dimer, *i.e.* 4,4'-diaminodiphenylamine, with aniline monomer at 1:1 molar ratio in the presence of an oxidizing agent such as ammonium persulfate (Fig. 3)^[32, 33]. In general, the oligomers with relatively lower oxidation potentials than the monomers can be considered as the initiators to build higher oligomers. Using this general strategy with the trimer as the starting material to react with monomeric or dimeric anilines, a series of higher oligomers (*e.g.*, tetramers to heptamers, Fig. 4) with one or two amino end-groups have been successfully prepared and isolated at a number of oxidation states^[34]. The reduced form of the trimer **4** as the starting material appears to give better yields when the persulfate was used as the oxidant. By choosing appropriate starting materials and reactant stoichiometry, the oligomers containing both odd and even numbers of nitrogen atoms could be synthesized^[31, 32, 34].

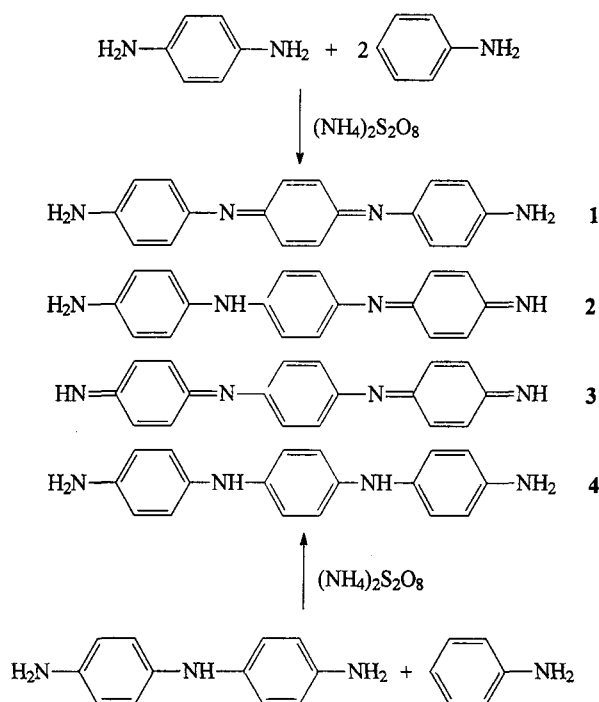


Fig. 3 The one-step synthetic routes to the amino-capped aniline trimers (with various oxidation states, 1-4)

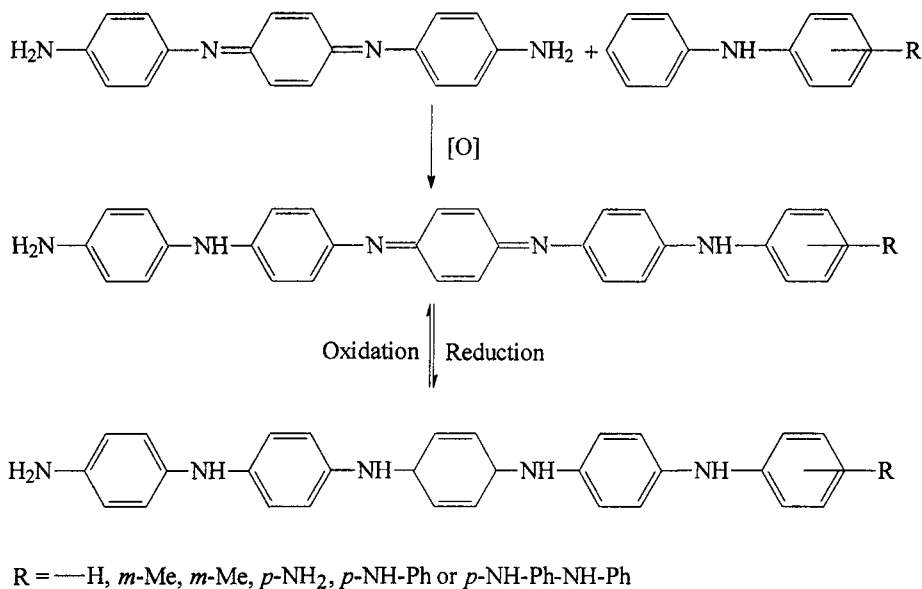


Fig. 4 Examples for the preparation of higher oligomers using the trimer as starting material

REDOX REACTIONS AND ELECTRONIC PROPERTIES OF THE OLIGOMERS

All the oligomers undergo similar redox reactions as polyaniline (Fig. 5). Their oxidation states can be changed chemically or electrochemically^[31-34]. Chemical reduction can be achieved by treatment with reducing agents

such as phenyl hydrazine, hydrazine, boron hydrides, *etc.*, or by hydrogenation in the presence of catalysts such as platinum oxide, while oxidation takes place upon exposure to air or treatment with oxidizing agents such as hydrogen peroxide, ammonium persulfate, tetraacyl lead, *etc.* The redox reaction can also be carried out electrochemically. Cyclic voltammograms (CV) of the oligomers with at least four nitrogen atoms and three phenylene rings (*e.g.*, the trimer **4** or higher oligomers) have a pattern of at least two redox pairs, which is similar to that of polyaniline although the specific values of redox potentials are different. It is noted that the electrochemical behavior (*i.e.*, CV patterns) of the lower oligomers such as 1,4-phenylenediamine and the amino-terminated dimer **5** differs significantly from that of polyaniline. Both the theoretical calculations and experimental results suggest that the minimum length of the oligomer should be four nitrogen atoms and three phenylene rings in order to maintain the essential electrochemical characteristics of polyaniline^[35–37]. Such minimum structure would allow all the typical variations of oxidation state, *e.g.*, leucoemeraldine, emeraldine and pernigraniline, as in polyaniline (Fig. 5). Electronic conductivity of the oligomers upon doping with 1.0 mol/L HCl was measured by the standard 4-probe technique. As shown in Fig. 6, the logarithm of conductivity seems to increase linearly with the length (*i.e.*, the number of aniline units) of the oligomer. The heptamer exhibited a conductivity close to 0.03 S/cm, which is lower than the value (1–10 S/cm) for polyaniline under identical doping and measurement conditions. The electronic absorption λ_{max} for the benzenoid to quinoid excitonic transition in the emeraldine base (EB) form of the heptamer was about 620 nm, again approaching that (~636 nm) for the EB of polyaniline^[38]. These observations are in line with those reported by Wudl *et al.* for the aniline octamer^[8]. It is hence reasonable to conclude that the oligomers with 7–8 aniline units should be sufficient to reach the conductivity level of HCl-doped polyaniline in a mainly amorphous state and to exhibit UV-Vis characteristics comparable to polyaniline.

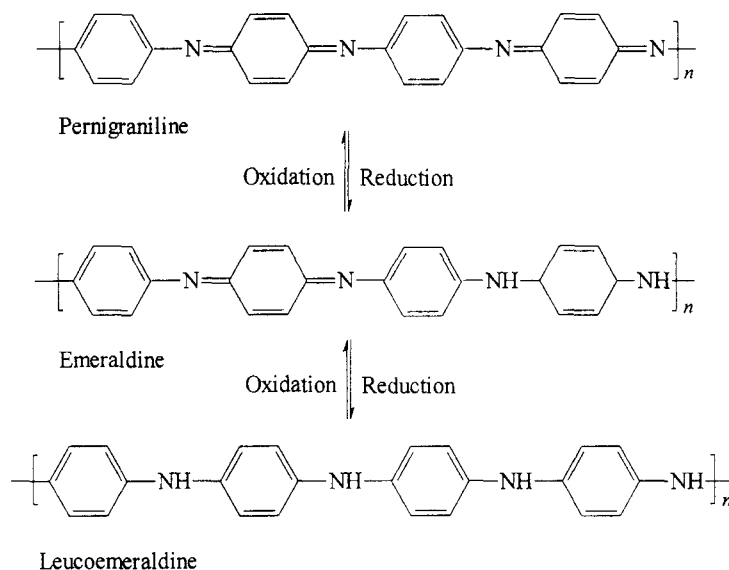


Fig. 5 Redox reactions of polyaniline

It is noteworthy that all the key redox reactions in polyaniline involve only 4 nitrogen atoms and 3 phenylene rings. Hence the amino-capped aniline trimers (as shown in Fig. 3) have all the characteristic redox reactions of polyaniline.

OTHER METHODS FOR THE SYNTHESIS OF ANILINE OLIGOMERS

There were a number of methods reported for the preparations of aniline oligomers in the literature^[8, 39–42]. Most of them involved multi-step synthetic reactions or unstable reagents. Recently, Buchwald *et al.* reported similar spectral results on the oligomers prepared via a clever synthesis in which the secondary amines (–NH–) on the

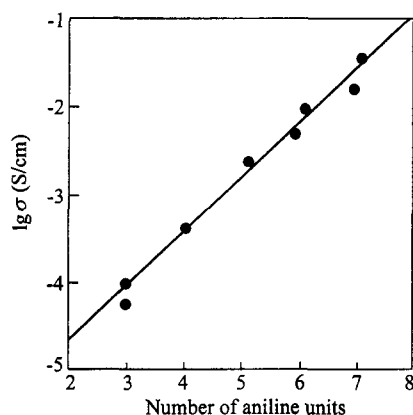
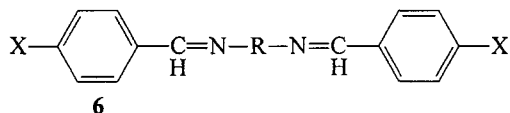
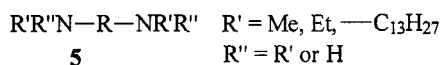
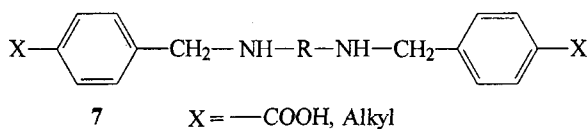


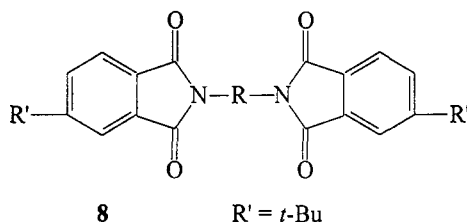
Fig. 6 Plot of $\lg\sigma$ versus number of aniline units in the aniline oligomers, doped with 1 mol/L HCl



$\text{X} = -\text{COOH}, -\text{OH}, -\text{NO}_2, \text{ Halides,}$
 Alkyl or alkoxy groups



$\text{X} = -\text{COOH}, \text{ Alkyl}$



$\text{R}' = t\text{-Bu}$

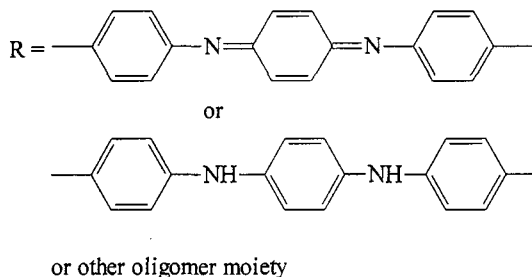


Fig. 7 Some examples (5–8) for transformation of the end-groups of electroactive aniline oligomers via conventional organic reactions

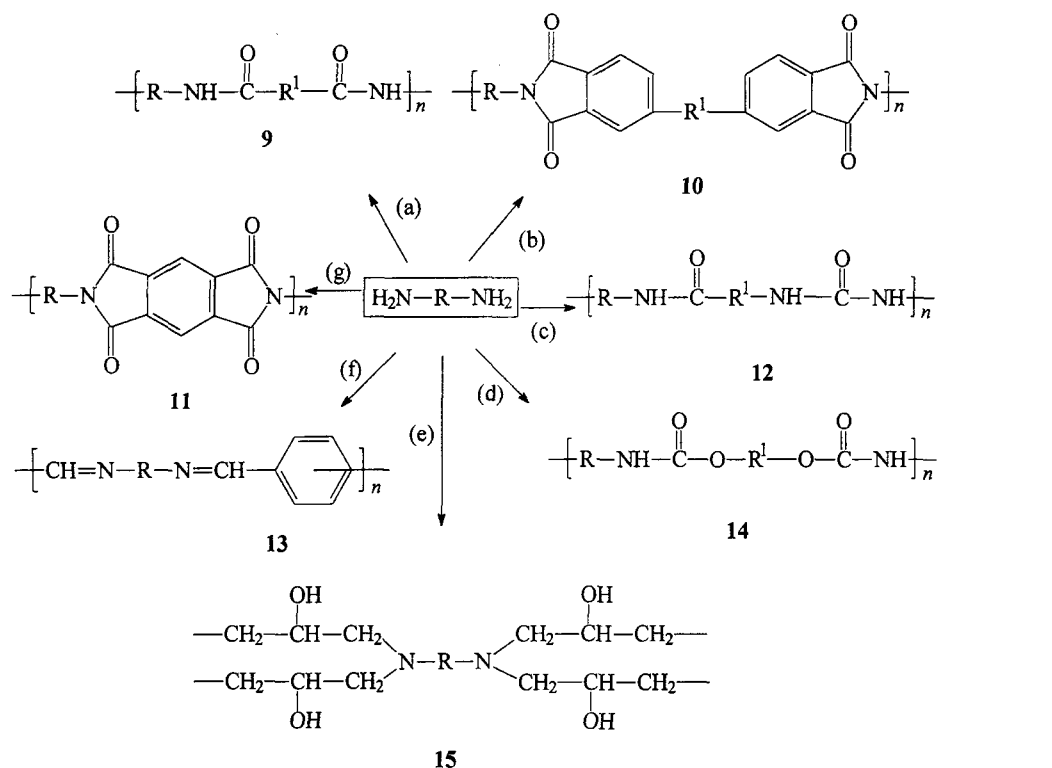
main chain are protected as a *t*-butyl carbamate (BOC) during the palladium-catalyzed coupling reactions^[43]. An Ullmann coupling reaction between acetanilides and 4-iodonitrobenzene was used in an iterative coupling/reduction sequence followed by deacetylation to afford parent trianiline and tetraaniline^[44]. In 1997, Zhang *et al.* reported a pseudo-high dilution technique by which phenyl-capped oligoanilines such as tetramer, pentamer, hexamer can be synthesized^[45]. Based on it, Wang and his coworkers have undertaken further work^[46].

FUNCTIONALIZATION OF THE ANILINE OLIGOMERS

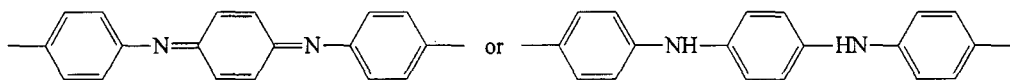
In addition to the redox chemistry, the aniline oligomers may undergo a variety of reactions on the amino, phenylene and/or quinonediimine groups of the main chain and, more importantly, on the end functional groups. As mentioned in the previous sections, one or two primary or *N*-substituted amino end-groups were obtained directly by using appropriate reactants in the oxidative reactions. The amino end-groups are very versatile and could be readily transformed into many other functional groups through conventional organic reactions of aromatic amines, such as azide and diazonium chemistry, Schiff base formation, reductive amination, *N*-alkylation or acylation, *etc.*^[33, 47]. Figure 7 shows some examples of compounds (5–8) that could be derivatized from the reactions of trimer **1** or **4**. Since numerous possible functional groups could be introduced into the aniline oligomers, we should be able to build a library of new electroactive compounds with designable end-functionality for specific applications, including electrochemically or chemically switchable surfactants, electroactive monolayer or multilayer molecular and supramolecular nanoassemblies, and further polymerizations to afford new organic or organic-inorganic hybrid polymers with electroactive oligomer building blocks. Furthermore, preliminary results of spectroscopic and electrochemical studies show that the aniline oligomers have interesting interactions with metals, metal ions and metal oxide clusters as well as with organic compounds such as tetracyanoquinodimethane (TCNQ)^[48]. There have also been reported that the aniline trimers could be employed to build electroactive dendrimers^[49].

OLIGOMERS AS BUILDING BLOCKS FOR FURTHER POLYMERIZATIONS

As compared with polyaniline, unsubstituted oligomers generally exhibit much improved solubility in organic solvents including NMP and the solutions are stable for a longer period of time (≥ 7 days) without any visible sign of gelation. The oligomers up to tetramers and some substituted pentamers show good solubility in common organic solvents such as THF, DMF, DMSO, *etc.* With appropriate C— or N— substitutions (*e.g.* —RCOOH and —RSO₃H) the oligomers could be made water-soluble. Hence, numerous new electroactive compounds and derivatives could be synthesized by conventional solution reactions. As examples, acrylamides with the aniline oligomer side groups were prepared by reacting the reduced form of the aniline tetramer, H[C₆H₄NH]₃—C₆H₄NH₂, with acryloyl chloride, which could then be polymerized via radical polymerization to afford polyacrylamides with electroactive side chains^[32]. The amino-capped aniline oligomers could be employed as difunctional monomers in conventional step polymerizations. In this capacity, the electroactive amino-terminated trimer (*e.g.*, **1**) is of particular importance because it represents the minimum structure unit of polyaniline and it can be readily synthesized in large quantity from a one-step reaction of inexpensive materials^[31–34]. Availability of the trimer allowed us to explore a variety of potentially electroactive polymers. Thus, polyamides (**9**)^[32], polyimides (**10**, **11**)^[32, 33, 50], polyureas (**12**)^[50], polyazomethines (**13**)^[47], polyurethanes (**14**)^[50] and epoxy polymers (**15**)^[6, 30] were obtained from step polymerization of the trimer (**1** or **4**) with dicarboxylic acid chlorides, dianhydrides, diisocyanates, dialdehydes, dioxyacid chlorides, and epoxy resins, respectively, as depicted in Fig. 8. Except for the crosslinked products such as epoxy polymers, the use of the reduced trimer (**4**) as the monomer appeared to result in higher molecular weight linear polymers than that of the oxidized trimer **1**. This can be attributed probably to (a) a decrease in the reactivity of the amino end-groups because of the electron-withdrawing effect of the quinonediimine group and (b) the tautomerization of **1** to **2**, which has a less reactive imino ($>C=NH$) end-group^[33].



R =



or other oligomer moiety

Reactants:

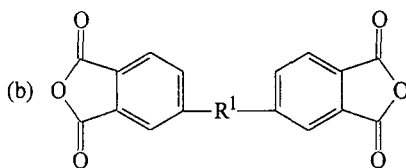
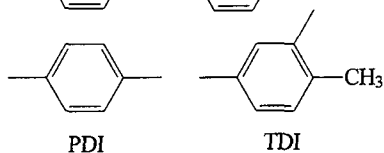
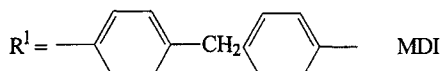
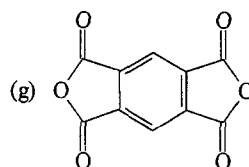
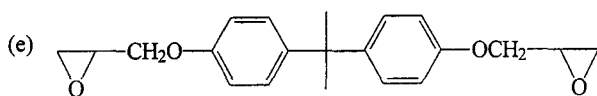
(a) $\text{Cl}-\text{CO}-\text{R}^1-\text{CO}-\text{Cl}$; $\text{R}^1 = -(\text{CH}_2)_4-$;(c) $\text{OCN}-\text{R}^1-\text{NCO}$  $\text{R}^1 = -\text{C}(\text{CF}_3)_2-$ and/or $-\text{O}-$ (d) $\text{Cl}-\text{CO}-\text{O}-\text{R}^1-\text{O}-\text{CO}-\text{Cl}$ $\text{R}^1 = p\text{-phenylene}$ (f) $\text{O}=\text{CH}-\text{Ph}-\text{CH}=\text{O}$

Fig. 8 Examples (9–15) for the synthesis of electroactive polymers of high molecular weights and good mechanical properties based on the aniline oligomers with polymerizable end-groups

As a specific example of the synthesis of polymers with the aniline oligomer building blocks, various polyureas (**12**) were prepared from the polymerization of the amino-capped aniline trimer (**1**) with 4,4'-methylenebis(phenyl isocyanate) (MDI), toluene-2,4-diisocyanate (TDI) and 1,4-phenylene diisocyanate (PDI) in good yields (90%–96%). The polymerizations were carried out at 100°C for 3 to 4 h in NMP solution in the presence of 1,4-diazabicyclo[2,2,2]octane (Dabac) catalyst. The structures of the resultant polyureas were supported by elemental analysis, ¹H-NMR, FTIR and UV-Vis spectroscopy. All the polyureas were of high molecular weights as evidenced by their large intrinsic viscosity values (≥ 1.0 dL/g), which were determined in dilute NMP solutions containing 5 wt% of LiCl at 25.0°C. The readily attainable high molecular weights in this system could be attributed to the high reactivity of the isocyanate groups. The electronic properties and characteristics of both chemical and electrochemical redox reactions of the polyureas were found to be quite similar to those of the aniline trimers.

ENGINEERING AND POTENTIAL TECHNOLOGICAL APPLICATIONS OF THE OLIGOMERS

There are many possible technological applications for the aniline oligomers and both of their small molecular and polymeric derivatives. Like polyaniline, the oligomers and their derivatives could be used, for instance, as electroactive materials in fabricating electrochromic, electroluminescent, biosensor, and electroactuator devices, chemically or electrochemically tunable gas-separation membranes, anticorrosion and antistatic coatings, rechargeable batteries, *etc.*^[1–5]. Taking advantage of their well-defined structures and designable end-groups, properly functionalized oligomers could form a variety of molecular or supramolecular assemblies for potential electronic and optical applications. By introducing silane or alkoxysilyl groups in the oligomers, one should be able to prepare electroactive organic-inorganic hybrid or nanocomposite materials via the sol-gel reactions^[51]. The oligomers or their metal complexes could find potential catalysis applications. Like many aromatic amines, the aniline oligomers in their reduced forms may serve as the antioxidants and free-radical absorbents. The oligomers may also serve as a component in conventional or conducting polymer blends to render the blends electroactive or more processible. Besides the electroactivity, the polymers containing the oligomer building blocks should have many other desirable chemical and physical properties, such as good mechanical strength and thermal stability, for applications as structural materials. Furthermore, the greatly enhanced processibility of these polymers would allow for the fabrication of electroactive nanofibers by electrospinning or other processes. Many of the above-mentioned applications have been explored or are currently under investigation in our laboratories. One of the most promising applications of our oligomer approach is in the area of corrosion prevention, which will be discussed in the next section.

ANTICORROSION MATERIALS BASED ON ANILINE OLIGOMERS

Mankind has been challenged by one of the most common scientific and technological problems, *i.e.* corrosion of metals, ever since metallic tools were invented. Based on an estimate made by NASA, corrosion costs the U.S.A alone anywhere between 70 to 120 billion dollars annually. Many ingenious prevention procedures have been introduced and many innovative corrosion-resistant materials have been invented. Currently, one of the standard industrial practices is to treat and/or coat the surface of metals with chromium-containing compounds. However, concern about the known adverse health and environmental effects of the chromium compounds is ever increasing. The use of conducting polymers such as polyaniline as corrosion inhibiting coatings for the potential replacements of chromium-containing materials has explored for many years. There have been numerous scientific papers and commercial developments in evaluating conducting polymers such as polyaniline and its derivatives for anticorrosion coating applications^[52].

However, polyanilines in their acid-doped form may not be ideal for industrial applications because of the corrosive nature of the acids and/or the difficulties in processing under environmentally friendly conditions. In 1995, Wei^[53] and Epstein's^[54] groups found that polyanilines in their base form exhibit good or better corrosion inhibition effect than the doped polyanilines. Their work suggests that the electroactivity rather than conductivity

might be more important in the polyaniline's anticorrosion effects. This represents a great leap forward both scientifically and technologically in the field of corrosion prevention. More recently, it has been demonstrated by electrochemical^[7, 30], theoretical^[55–58], salt spray^[59], UV-salt cyclic^[60], and X-ray photoelectron spectroscopic studies^[34] that the anticorrosion performance of the electroactive aniline oligomers is as good as, and oftentimes better than, that of polyanilines^[53].

SUMMARY AND REMARKS

We have described a general methodology, which has been developed based on the theory of non-classical or reactivation chain polymerization, for the synthesis of aniline oligomers with controlled molecular weight, narrow or uniform molecular weight distribution and designable end-groups. A series of oligomers were prepared by oxidative polymerization of aniline in the presence of *N*-phenyl-1,4-phenylenediamine or 1,4-phenylenediamine as initiator. The molecular weight of the oligomers is controlled by varying the amount of the initiator. As the initiator concentration is increased, the molecular weight decreases and the molecular weight distribution becomes narrower and approaches unity. Generally, lower oligomers can serve as the initiators to build higher oligomers. The oligomers with a minimum of 4 nitrogen atoms and 3 phenylene rings exhibit similar characteristic redox behavior and electroactivity to polyaniline. Electronic conductivity increases with the number of aniline units in the oligomers and approaches the value for polyaniline when the number is about 7 or 8. The solubility of the oligomers is much improved over that of conventional polyaniline. Various functional groups can be introduced into the oligomers either by proper selection of starting materials in the oxidative reactions or by post-synthesis modifications via conventional organic transformations. The functionalized oligomers can also undergo further polymerization to afford a variety of new electroactive materials, including polyamides, polyimides, polyureas, polyurethanes, polyacryl-amides, and epoxy polymers. The electroactive-conjugated oligomers of well-defined structures have many significant advantages over their corresponding polymers. There are also numerous potential applications for the oligomers and their polymeric derivatives in a variety of electronic, optical, and biological industries as well as in nanotechnology. Further research and development in this area could lead to scientifically significant and technologically important breakthroughs.

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