# Novel Electrically Conducting Polyurethanes With Oligoanilines: Synthesis, Conductivity, and Electrochemical Properties

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**ABSTRACT:** New class of conducting polyurethanes (CPUs) containing oligoanilines, namely tetraaniline (TAni) or trianiline (TriAni), in the backbone have been synthesized and characterized by formal spectral techniques. The unique properties of these CPUs, viz., electronic conductivity and electrochemical activity arising from the presence of oligoaniline units have been evaluated. The basic polyurethane backbone is derived from toluene diisocyanate, isophorone diisocyanate or hexamethylene diisocyanate, and polypropylene glycols of molecular weight 425 and 2000. In the first category of polyurethanes, the prepolymers obtained from the above reactants were chain terminated by TAni in emeraldine base oxidation state. The conductivity of these CPUs films ranged from $1.2 \times 10^{-5}$ to $1.77 \times 10^{-3}$ S cm$^{-1}$. These polymers showed lower conductivity due to the presence of nonconjugated polyurethane segments. These CPUs exhibited slightly different electrochemical activity than that of TAni. The second category of CPUs is obtained from prepolymers by chain extension with TriAni. The conductivity of these polymers is similar to the TAni analogues but are electrochemically inactive. The anticorrosion properties of two of these polymers have also been evaluated in this study. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40794.

## INTRODUCTION

Despite possessing the major drawback of being insoluble, intractable and infusible, the conducting polymer, polyaniline still enjoys the attention of scientists worldwide culminating in major breakthroughs in their processability and applications. The two general strategies that address these hurdles are (i) addition of branched flexible groups onto the conjugated main chain and (ii) plasticizing by introducing bulky organic counter ions. Apart from this the third method is use of nanotechnology, i.e., use of nanoscaled poly or oligoanilines for desired applications. The interesting property of the oligoanilines is their ability to get processed in much more facile fashion due to their increased solubility in common organic solvents, compared to full-fledged polymers. The important oligoanilines which have been synthesized are trimer, tetramer, pentamer, octomer, and others.[1–7] Structurally, these can be classified as phenyl/NH$_2$, phenyl/phenyl, and NH$_2$/NH$_2$ end capped oligomers.[3,8] The amino group at the end of the oligomer unit gives an opportunity for further functionalization. The conjugation length and formation of polaron/bipolarons is greatly reduced in oligomers and hence the conductivity is also lower in these oligomers. This is typically found in the range $10^{-2}$ to $10^{-4}$ S

cm$^{-1}$ which is sufficient for applications such as sensors, electrostatic discharge (ESD), electromagnetic interference (EMI) shielders, and more importantly corrosion protection coatings.

Polyurethanes are versatile organic polymers with potential applications such as adhesives, elastomers, coatings for textiles/paper, foot wear, furniture/foams, packaging material, and for automotive finishes.[9–11] They also cater the human health needs as a promising biomaterial[10] where the biocompatible products range from nasogastric catheters, peritoneal dialysis, infusion pumps to implanted pacemaker parts.

There have been attempts to incorporate the "oligoanilines" into variety of conventional polymers so as to get electrochemical activity or conductivity to the whole polymer.[12–23] Wei and coworkers[12] prepared an electroactive and biodegradable polylactide-b-(ANI)$_5$-bpolyactide(PLA-b-(ANI)$_5$-b-PLA) film useful for tissue engineering. The same group synthesized water-soluble and biocompatible triblock copolymers of PEO1500-b-(ANI)$_5$-b-PEO1500[13] and PEO750-b-(ANI)$_5$-b-PEO750.[14] It is found that these copolymers form large aggregates, and their sizes decrease with increasing pH values or changing the redox state of aniline blocks from emeraldine base (EB) to leucoemeraldine base (LEB). Wang et al.[15] synthesized a diblock oligomer

of poly(L-lactide)-b-(ANI)$_4$ ((PLLA)$_{24}$-b-(ANI)$_4$) by ring-opening polymerization of L-lactide. By changing the aniline block from LEB to EB state, the morphologies of the self assemblies vary from spherical micelles to ring-like aggregates composed of much smaller spherical micelles. Later, they synthesized oligostyrene-b-(ANI)$_3$-b-oligostyrene with tert-butylcarbamate-protected trianiline (TriAni).[16] The block oligomer self-assembled into spherical micelles and vesicles in tetrahydrofuran before and after removing the protecting group, respectively.[16] Wang et al.[17] have reported polyimides from diamino capped TriAni which are electroactive with good thermal stability. Similar electroactive polyimides have been synthesized and studied for their electrochemical activity.[18] The polymer on GC electrode showed three oxidations and three corresponding reductions. The conductivity of the polymer is $1.04 \times 10^{-4}$ S cm$^{-1}$. Polystyrene based, tetraaniline (TAni) terminated "star"-shaped polymer has been studied[19] for the electrochemical activity which exhibited similar two electrochemical oxidations and reductions. A diblock copolymer based on TAni and poly(ethylenglycol)methylether was synthesized for possible biomedical applications.[20] Electrochromic properties have been studied[21] for poly(arylene ether sulfone) containing TAni. The polymer is soluble in common organic solvents and exhibited good electrochromic behavior with other possible applications such as antistatic coating and wave-absorbing material. Electrochemical[22] and conductivity studies[23] on poly(methacrylamide) containing four and five aniline u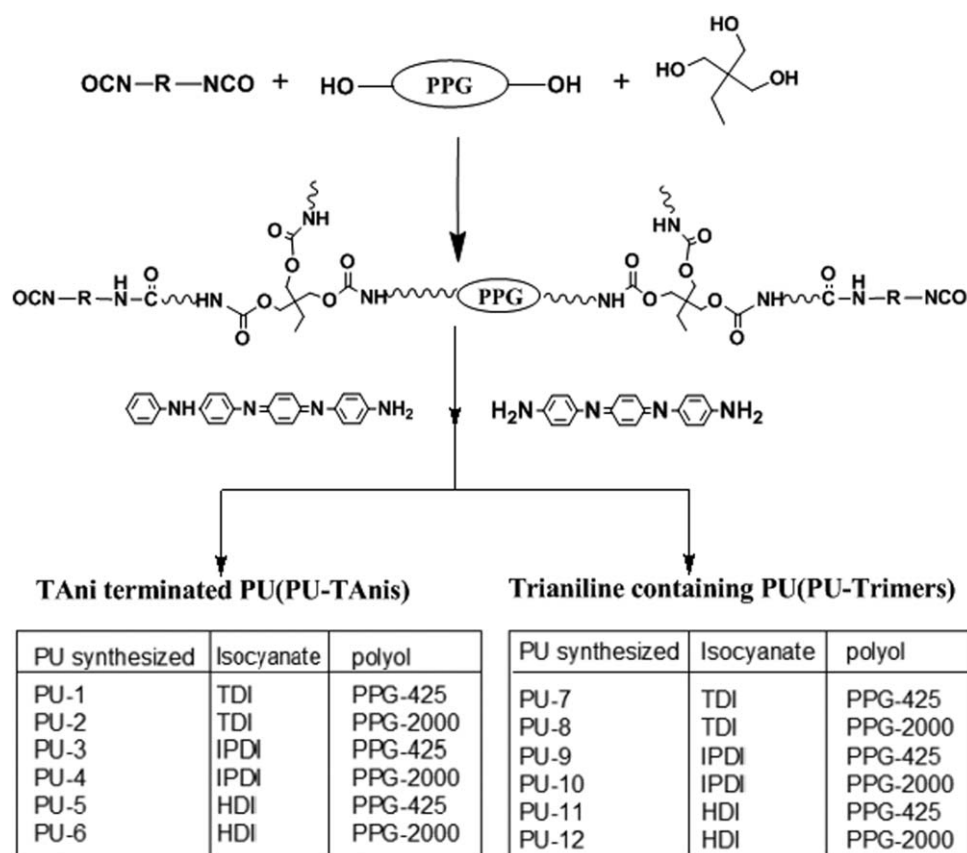nits have been reported in the literature. Apart from being electrochemical active, the polymer containing pentaniline as pendant group is electronically conducting to the tune of $10^{-4}$ S cm$^{-1}$ after doping with mineral acid. Some reports[24,25] of hexaaniline and hexadecaanilines grafted on fullerene (C$_{60}$) and carbon nanotubes (CNTs) are also available in the literature preserving semiconducting properties of oligoanilines and high mechanical strength of CNTs.

Earlier we explored the studies[26] on synthesis and corrosion protection abilities of some polyurethane water dispersions blended with polyaniline up to 6 wt %. The blended composites were found to be excellent corrosion resistant coatings. However, instead of blending, the corrosion resistance property can be further improved if the backbone of PU is modified with oligoanilines. To the best of our knowledge there are no reports available on using TriAnis or tetranailines in the synthesis of polyurethanes. In the present investigation, we have exploited the reactivity of amine functionality of trianliline and TAni to modify PU backbone and bring conductivity and electrochemical activity to the polyurethanes. The results are presented and discussed.
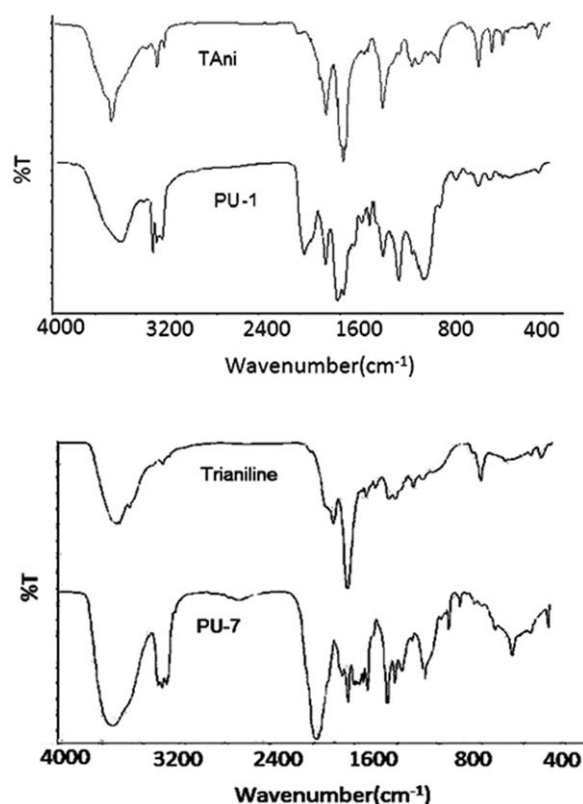
## EXPERIMENTAL

### Materials

Polypropylene glycol (PPG)$-$2000 $M_n = 2000$, PPG-425 $M_n = 425$], trimethylol propane (TMP), N-phenyl-1,4-phenylenediamine were obtained from Aldrich Chem Co. and used as such. P-phenylene diamine (LOBA Chemie Co., India)



**TAni terminated PU(PU-TAnis)**

| PU synthesized | Isocyanate | polyol |
|---|---|---|
| PU-1 | TDI | PPG-425 |
| PU-2 | TDI | PPG-2000 |
| PU-3 | IPDI | PPG-425 |
| PU-4 | IPDI | PPG-2000 |
| PU-5 | HDI | PPG-425 |
| PU-6 | HDI | PPG-2000 |

**Trianiline containing PU(PU-Trimers)**

| PU synthesized | Isocyanate | polyol |
|---|---|---|
| PU-7 | TDI | PPG-425 |
| PU-8 | TDI | PPG-2000 |
| PU-9 | IPDI | PPG-425 |
| PU-10 | IPDI | PPG-2000 |
| PU-11 | HDI | PPG-425 |
| PU-12 | HDI | PPG-2000 |

**Scheme 1.** Synthetic routes for PU-1 to PU-12.

**Figure 1.** FT-IR spectra of representative samples PU-1 (above) and PU-7 (below) along with the tetranailine and trianiline spectra.

was used as received. Toluene-2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethlene diisocyanate (HMDI) were purchased from Alfa Aesar. Methylethylketone (MEK) and methylisobutylketone (MIBK), hydrochloric acid (36%), ammonium hydroxide, and 1-methyl-2-pyrrolidone (NMP) chemicals were purchased from SD FINE Co. (India).

### Characterization

Fourier transform infrared (FT-IR) spectra were recorded using a Perkin Elmer Spectrum-100 spectrometer (Perkin-Elmer Instrument) using KBr pellet technique. Ultraviolet–visible (UV–Vis) spectral measurements were carried out on a Spectro UV–Vis Double Beam PC-8 Scanning Auto cell, LABOMED.

Thermogravimetric analyses (TGAs) of polymer samples were carried out using TA Instruments (TGA Q500 V20.8) from ambient to 600°C under nitrogen atmosphere at a heating rate of 10°C min$^{-1}$. Differential scanning calorimetry analyses of polymer samples were carried out using TA Instruments (DSC Q100 EXFO Series 2000). Cyclic voltammetry (CV) was performed using IM6 eX. ZAHNER® Elektrik in a three-electrode electrochemical cell using saturated calomel electrode (SCE) as the reference electrode and platinum wire as the counter electrode. The working electrode was prepared by casting NMP/MIBK solution of the TAni-terminated polymer onto the surface of the platinum plate electrode (1 cm $\times$ 1 cm). The CV experiments were carried out in 1.0 $M$ sulfuric acid aqueous solution at a scan rate of 100 mV s$^{-1}$. Powder of oligoanilines was pressed into a tablet (13 mm diameter and 1.5 mm thickness) under a pressure of 120 kg cm$^{-2}$ for conductivity measurements. Resistance of the pellet was measured by four probe method using 6220 constant current source and 2182A voltmeter (Keithley, Cleveland, OH). Morphological studies for films/powder were performed using Hitachi 3000N, Tokyo, Japan scanning electron microscope operating at 10 kV. The sample was mounted on a double-sided adhesive carbon disk and sputter coated with a thin layer of gold to prevent sample from possible charging. TEM experiments were conducted on PHILIPS TECHNAI FE12 instrument at 120 kV after casting a drop of well dispersed dilute samples in water on copper grids.

Amine capped-TAni was synthesized according to the known procedure from the literature.[27] The molecular structure of the TAni was confirmed as TAni by mass, nuclear magnetic resonance (NMR), and FT-IR spectroscopy. Diamine-capped TriAni was synthesized and confirmed by following the procedure available in the literature.[28,29]

### Synthesis of TAni-Terminated Polyurethanes (PU-1 to PU-6)

To a round bottom flask containing a solution of 0.0218 mol of isocyanate [toluene diisocyanate (TDI) or IPDI or HMDI in 10 mL of MIBK], added dropwise, a solution mixture of 0.00575 mol of PPG (2000 or 425) and 0.0127 mol of TMP (in 10 mL of MIBK) and this mixture was stirred in oil bath under a N$_2$ atmosphere at 60°C. After stirring 2 h 0.0022 mol of TAni (dissolved in 5 mL of NMP) was added dropwise to the

**Table I.** FT-IR Spectral Data of Tani-Terminated Polymers

| Characteristic absorption bands | Peak position (cm$^{-1}$) | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | PU-1 | PU-2 | PU-3 | PU-4 | PU-5 | PU-6 |
| N–H str. vibrations | 3277.13 | 3289.29 | 3311.32 | 3314.83 | 3441.57 | 3419.02 |
| C–H stretching vibrations | 2927.75–2969.61 | 2871.24–2971.35 | 2923.15 | 2925.34–2970.49 | 2932.89 | 2969.87 |
| Amide I(C=O) stretching vibrations | 1667.59–1707.23 | 1711.82 | 1683.6 | 1705.39 | 1664.89 | 1682.68 |
| Amide II ($\delta_{N-H} + \gamma_{C-N} + \gamma_{C-C}$) | 1537.54 | 1535.88 | 1510.93 | 1525.14 | 1506.64 | 1504.19 |
| $\gamma_{C-N}$ | 1375.3 | 1374.27 | 1380.03 | 1343.31 | 1371.76 | 1374.56 |
| Amide III | 1225.49 | 1226.12 | 1240.63 | 1241.45 | 1263.87 | 1263.51 |
| Amide IV | 751.17 | - | 746.26 | 743.53 | 746.28 | 747.44 |
| Amide V | 695.51 | - | 691.41 | 694.15 | 658.88 | 690.46 |

**Table II.** FT-IR Spectral Data of Trianiline Segmented CPUs

| Characteristic absorption bands | Peak position (cm$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | PU-7 | PU-8 | PU-9 | PU-10 | PU-11 | PU-12 |
| N–H (str) vibrations | 3435.73 | 3450.09 | 3438.57 | 3438.75 | 3434.51 | 3437.00 |
| C–H stretching vibrations | 2931.28 | 2971.06 | 2932.01 | 2969.77 | 2934.19 | 2931.84 |
| Amide I(C=O) stretching vibrations | 1652.00 | 1663.43 | 1666.73 | 1671.65 | 1667.30 | 1673.35 |
| Amide II ($\delta_{N-H} + \gamma_{C-N} + \gamma_{C-C}$) | 1537.91 | 1506.23 | 1506.06 | 1505.59 | 1506.64 | 1505.38 |
| $\gamma_{C-N}$ | 1369.02 | 1375.02 | 1363.53 | 1343.20 | 1371.6 | 1343.47 |
| Amide III | 1227.76 | 1228.69 | 1263.70 | 1263.34 | 1263.74 | 1263.78 |
| Amide IV | 749.01 | 746.28 | 746.26 | 746.28 | 743.5 | 740.79 |
| Amide V | 658.89 | 658.7 | 658.85 | 658.23 | 658.16 | 658.20 |

flask using dropping funnel. The total reaction mixture was stirred over night at room temperature by which time the NCO% was zero and TAni-terminated polyurethane (PU-TAnis) was formed. The PU-TAni was casted in Teflon dishes for free standing films or precipitated as sticky powdered material from 1 *M* aqueous HCl solution fallowed by dedoping in aq.NH$_4$OH solution.

**Synthesis of TriAni-Segmented Polyurethanes (PU-Trimers; PU-7 to PU-12)**

These polymers were synthesized by one step reaction. The reaction mixture containing 0.0218 mol of isocyanate (TDI or IPDI or HMDI in 10 mL of MIBK), 0.00575 mol of PPG (M.Wt. 2000 or 425), 0.0127 mol of trimethylolpropane (TMP), and TriAni (0.001675 in 5 mL of NMP) was stirred in oil bath
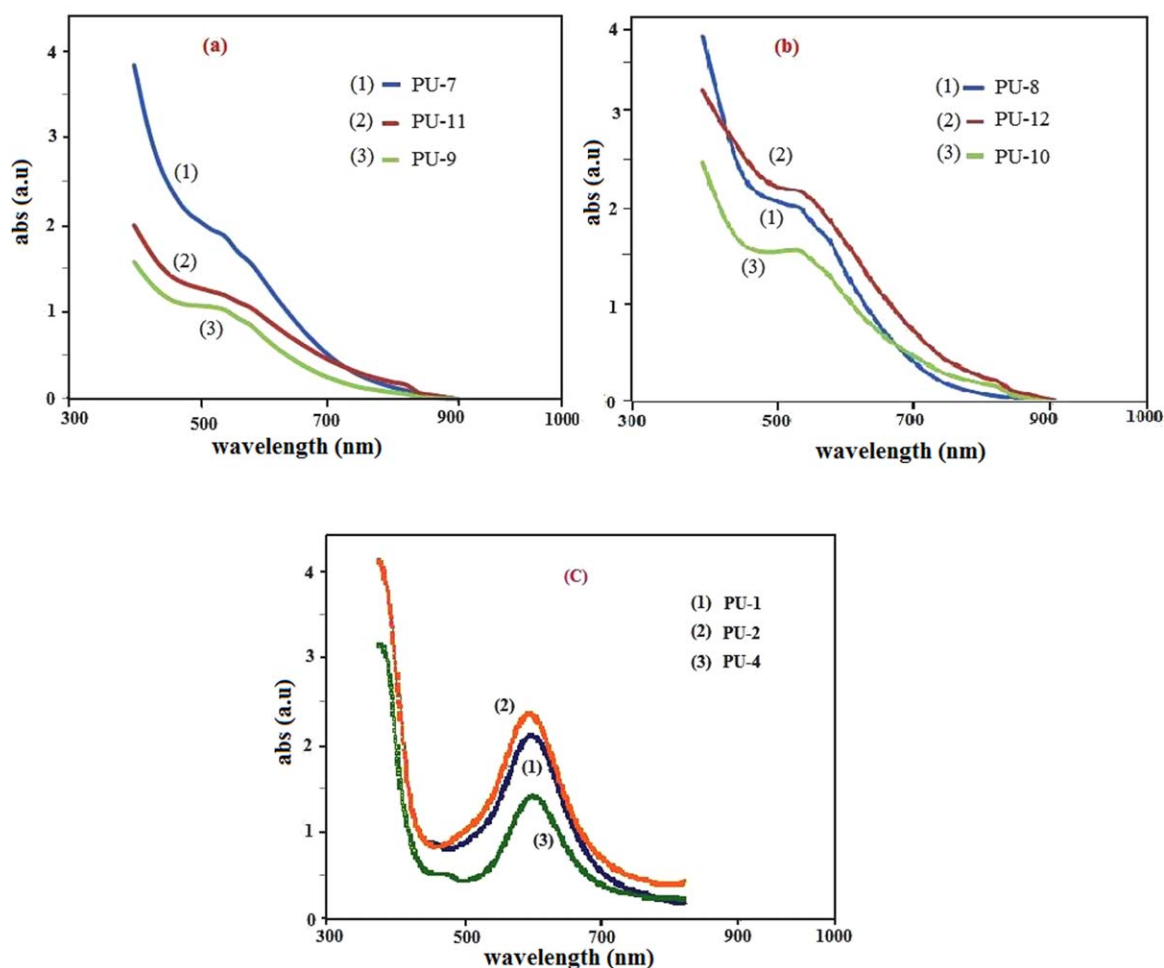


**Figure 2.** UV–Vis spectra of PU-trimers and PU-tetraanilines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** UV–Vis Data of the Polymers in DMF Solvent

| Polymer | UV–Vis, $\lambda_{max}$ (nm)[a] | Conductivity (measured as film; S cm$^{-1}$) |
|---------|------------------|-----------------------------------|
| PU-1    | 420, 597         | $1.21 \times 10^{-5}$             |
| PU-2    | 423, 603         | NM                                |
| PU-3    | 596              | NM                                |
| PU-4    | 594              | $0.48–1.77 \times 10^{-3}$        |
| PU-5    | 460, 591         | NM                                |
| PU-6    | 450sh, 580       | $1.01 \times 10^{-3}$             |
| PU-7    | 537              | $5.5–6.7 \times 10^{-3}$          |
| PU-8    | 533              | $0.3–3.75 \times 10^{-3}$         |
| PU-9    | 517              | $2.8–9.49 \times 10^{-3}$         |
| PU-10   | 532              | $0.21–9 \times 10^{-3}$           |
| PU-11   | 527              | $0.1–7.7 \times 10^{-3}$          |
| PU-12   | 530              | NM                                |

NM, not measured due to in proper drying of the film.
[a] The concentration for the measurements is about 0.3 g of polymer sample in 5 g of DMF solvent.

under a $N_2$ atmosphere at 60°C for 2 h. The total reaction mixture was further stirred over night at 40°C temperature by which time the NCO% was zero as confirmed by FT-IR. The TriAni-segmented polyurethane was casted in Teflon dish for free standing films or precipitated as sticky powdered material from 1 $M$ aqueous HCl solution fallowed by dedoping.

## RESULTS AND DISCUSSION

### Synthesis of Conducting Polyurethanes

The conducting species which are introduced into the backbone of polyurethane, amine capped TAni in the oxidation state of EB was synthesized according to the method of Zhang et al.[27] by the oxidative coupling reaction of aniline dimer. The reaction yields only TAni, because its EB state cannot be further oxidized to longer oligomers in the presence of excess oxidizing agent. The NMR and mass spectral results confirmed the TAni structure. Diamine capped TriAni was prepared by oxidative coupling of $p$-phenylenediamine with aniline and confirmed by comparing with available data from the literature.[28,29]

The structures and synthetic procedure of conducting polyurethanes (CPUs) obtained from TAni (PU-1 to PU-6) and TriAni (PU-7 to PU-12) are shown in Scheme 1.

Mixture of isocyante, PPG, and TMP were reacted at 60°C for 2 h, and TriAni segments were introduced into the backbone by adding solution of this TriAni in NMP solvent. After about 12 h, reaction yielded dark-colored PU-urea. Free standing films were obtained by casting. It took few days for formation of films in complete dry condition from the reaction mixtures at room temperature. Powdered samples can also be obtained from the reaction mixture by pouring into large volume of aqueous HCl solution fallowed by dedoping in aqueous ammonia solution.

### FT-IR Characterization

The polymers PU-1 to PU-12 were characterized by FT-IR analysis. The representative spectra are shown in Figure 1 and the data are collected in Tables I and II. The N–H stretching vibrations originating from urethane segment are seen between 3277 and 3441 cm$^{-1}$ and 3412 and 3450 cm$^{-1}$, respectively, for PU-TAnis and PU-Trimers. The amide I mode is a complex vibration and involves the contribution of the –C=O stretching, the –CN stretching and the –C–C–N deformation vibrations. The complexity and multiplicity of inter- or intramolecular
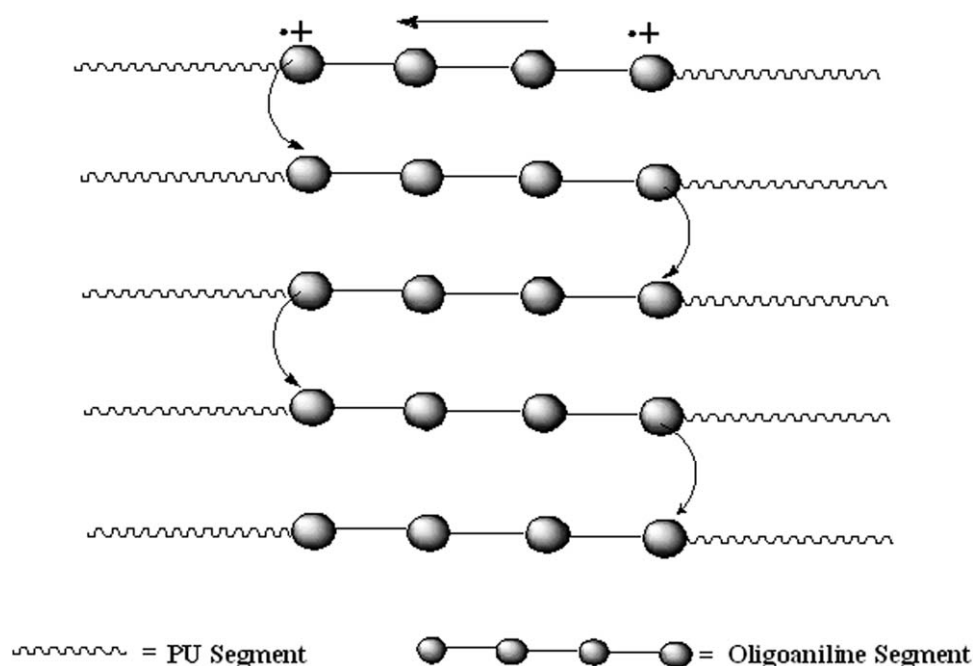


**Scheme 2.** Conducting mechanism in CPUs.

〜〜〜〜〜 = PU Segment            ●—●—●—● = Oligoaniline Segment
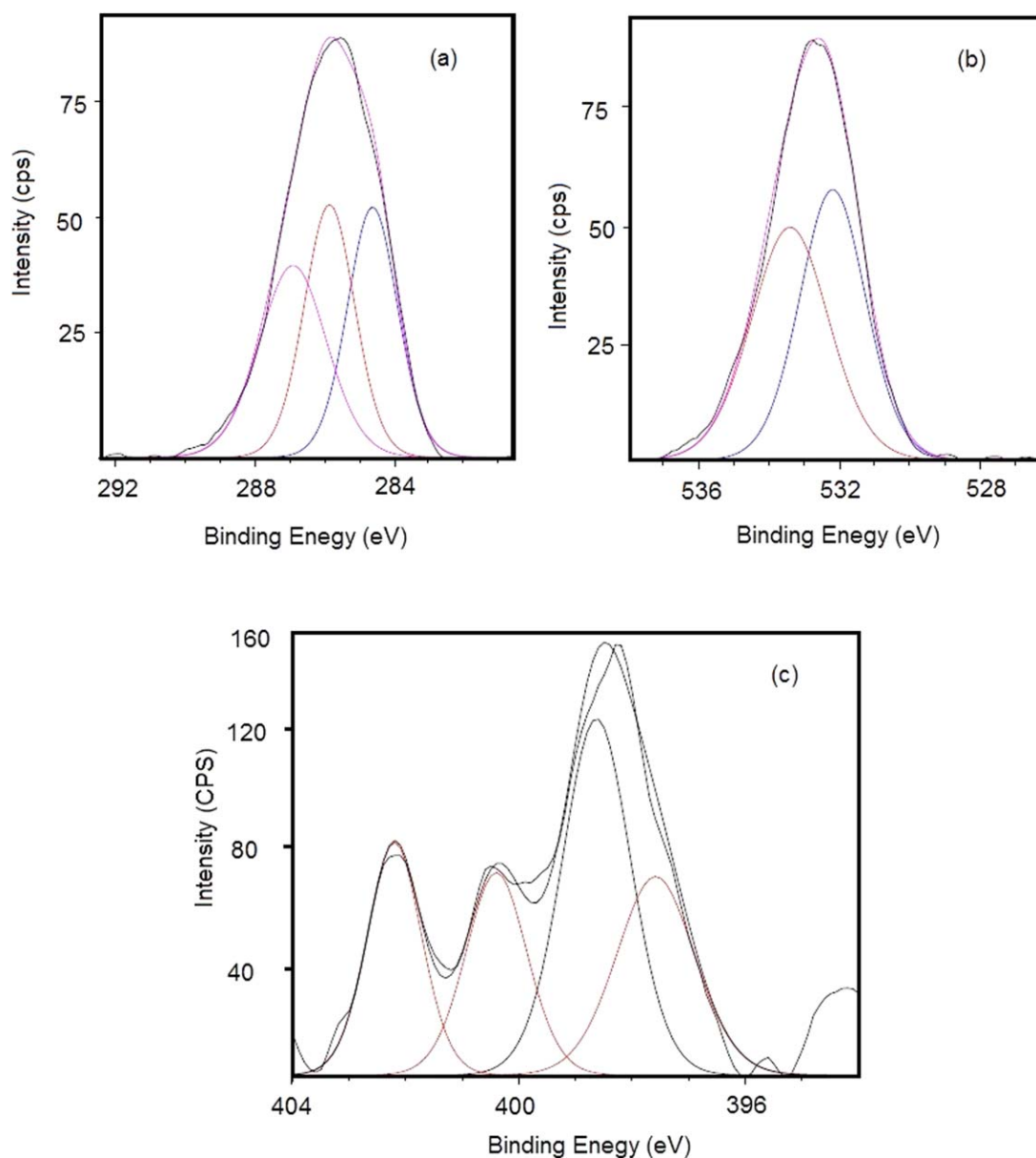
**Figure 3.** The deconvoluted XPS spectra of (a) C1s carbon, (b) O1s oxygen, and (c) N1s nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

environments surrounding the carbonyl groups in polymers make the amide I range considerably broader in polymers which occur in the region 1600–1800 $cm^{-1}$. In the present case the band is seen between 1664 and 1711 and 1652 and 1673 $cm^{-1}$ for PU-TAnis and PU-Trimers. Amide II mode is observed

between 1530 and 1506 $cm^{-1}$ for both type of polymers and is believed to be result of mixed contribution of $\delta_{N-H} + \gamma_{C-N} + \gamma_{C-C}$ vibrations. It is sensitive to both chain conformation and intermolecular hydrogen bonding. Amide III mode involves the stretching vibration of the $-C=N$ group. Amide III is highly

**Table IV.** DSC Data of the Synthesized Polymers

| Polymer | PU-1 | PU-2 | PU-3 | PU-4 | PU-5 | PU-6 |
|---|---|---|---|---|---|---|
| $T_{g1}$ (°C) | −33.18 | NCP | −24.40 | −25.46 | −24.2 | −25.9 |
| Polymer | PU-7 | PU-8 | PU-9 | PU-10 | PU-11 | PU-12 |
| $T_{g1}$ (°C) | −22.84 | −25.5 | −24.7 | −24.35 | −0.97 | −24.8 |
| MP | 80.6 | 90.8 | 86.6 | 98.7 | – | – |

NCP, no clear peak.

**Table V.** TGA Data of the Polymers

| Decomposition temperature | PU-1 | PU-2 | PU-3 | PU-4 | PU-5 | PU-6 |
|---|---|---|---|---|---|---|
| $T_{decom}$ | 151.44 | 242.22 | 195.31 | 280.21 | 263.51 | 241.70 |
| $T_{decom}$10% | 218.29 | 292.00 | 250.59 | 299.66 | 296.54 | 299.89 |
| $T_{decom}$50% | 328.37 | 374.32 | 331.72 | 344.65 | 340.33 | 346.80 |
| Wt % remaining at 450°C | 19.45 | 11.06 | 20.77 | 8.52 | 13.30 | 13.42 |
| Decomposition temperature | PU-7 | PU-8 | PU-9 | PU-10 | PU-11 | PU-12 |
| $T_{decom}$ | 230.2 | 250.68 | 258.57 | 250.65 | 250.23 | 250.56 |
| $T_{decom}$10% | 248.20 | 282.61 | 263.10 | 295.93 | 228.55 | 306.85 |
| $T_{decom}$50% | 310.34 | 354.08 | 340.00 | 350.05 | 359.54 | 370.78 |
| Wt % remaining at 480°C | 15.0 | 10.14 | 10.0 | 5.10 | 14.9 | 9.5 |

mixed and complicated by coupling with –NH deformation modes and is observed between 1227 and 1263 cm$^{-1}$ in the present polyurethane polymers. Amide IV, V, and VI bands are produced by highly mixed modes containing a significant contribution from the –NH out-of-plane deformation mode. They are expected to be in the 800–400 cm$^{-1}$ region.[30–32]

**UV–Vis Absorption Spectra and Conductivity Measurements**
UV–Vis electronic spectroscopy is a valuable tool for conducting polymers and their composites for identifying the conducting and insulating states. All the polymers were characterized by electronic absorption spectroscopy in the range 300–900 nm. The spectra are shown in Figure 2 and the data is collected in Table III. The trimer containing polyurethanes PU-7 to PU-12 showed two UV–Vis absorption bands one nearly at 420 nm and another between 517 and 533 nm in dimethyl formamide solvent. Pure trimer showed a UV–Vis band at 572 nm in DMF.[28] When incorporated into polyurethane prepolymer segments, the band shifted to lower wavelength at 530 nm. This is owing to the fact that after inclusion into polyurethane, the trimer is attached to electron withdrawing acyl groups. This observation is similar to TAni incorporated in (ANI)$_4$-b-PEO600-b-(ANI)$_4$.[33]

TAni showed two visible absorption bands at 310 nm and 580 nm in NMP solvent. Upon doping with HCl solution, two new bands for TAni at 430 and 800 nm emerged which are attributed to the delocalized polaron bands, as observed in the literature.[33] The PU-TAni polymers also exhibited two bands at 300 nm and another at 580–595 nm. Upon doping with HCl (or PTSA), however, there is new absorption appeared at about 420 nm and there is no significant shift of second band at 590 nm. This observation suggests that TAni blocks in the PU-TAni polymers are not protonated under the experimental conditions. Similar phenomenon was observed[33] in (ANI)$_4$-b-PEO2000-b-(ANI)$_4$ triblock copolymer and the tolyl isocyanate-capped TAni, (ANI)$_4$-TDI-(ANI)$_4$. This may possibly due to the reason that NMP is a basic solvent which would compete against aniline units for protonation.[33,34] In addition, the connection to electron-withdrawing acyl groups would reduce the basicity of nitrogen atoms in the TAni blocks of the polymer, which in turn may hinder their protonation. However, it was noticed that the initial dark blue color of the undoped CPU changes to green color after doping with HCl or PTSA partially also.

The conductivity behavior of the samples PU-1 to PU-12 is understood by measuring current and voltage responses (hence resistance) of the samples after doping by stochiometric amounts of PTSA. The conductivity of the polymers was determined for their films using Van der Pauw eq. (1) by four probe method

$$\sigma = \frac{\ln 2}{\pi d} \times \frac{i}{v} \qquad (1)$$

where $\sigma$ is the surface electronic conductivity, $d$ the thickness of the film (which should be less than distance between two probes), and $i$ and $v$ are the current and voltages applied and measured.
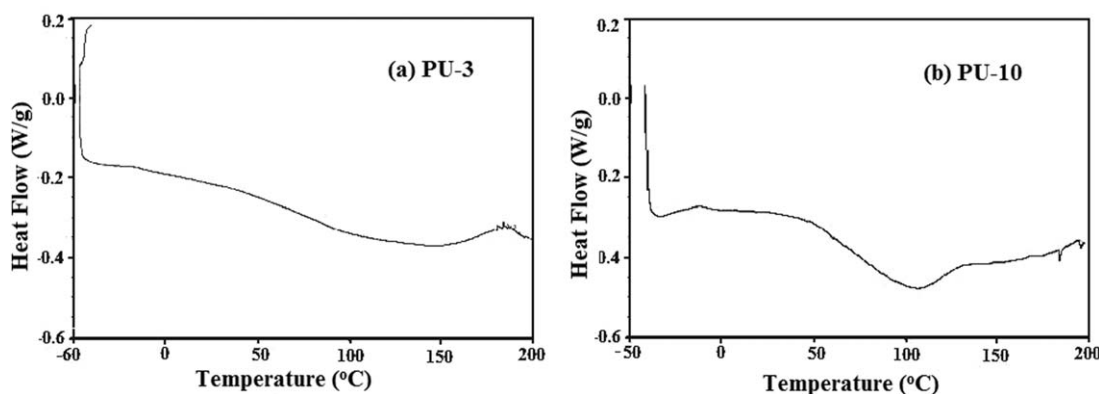


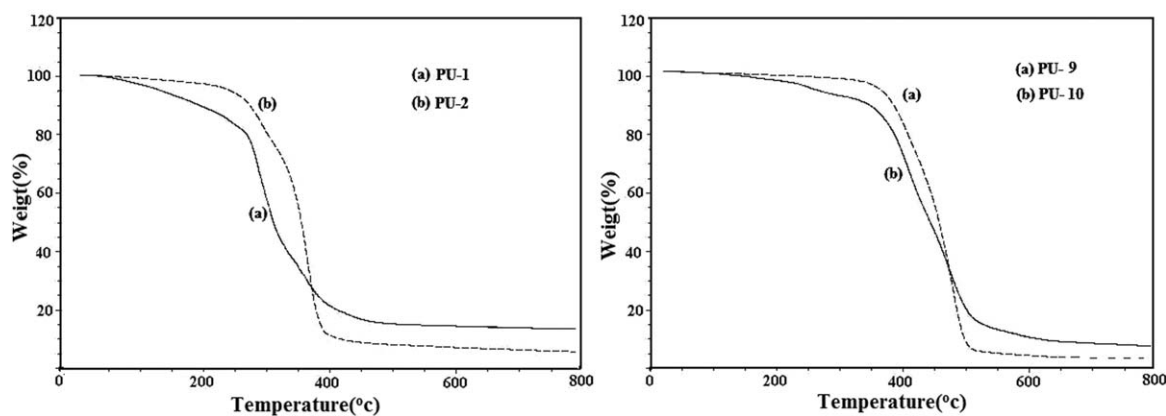**Figure 4.** DSC profiles of (a) PU-3 and (b) PU-10.

**Figure 5.** TGA profiles of PU-1, PU-2, PU-9, and PU-10.

The conductivity data of the films is collected in Table III. A maximum conductivity of $1.77 \times 10^{-3}$ S cm$^{-1}$ is exhibited by PU-4 polymer against $1.9 \times 10^{-1}$ S cm$^{-1}$ pure TAni demonstrating that the achievable conductivity is about 1/100 only. When the conductivity of a particular film was measured on different locations, variations in surface conductivity for both type of polymers was observed. This is due to the fact that the conducting units, viz., TriAni or TAni segments, from the polymer chains are not uniformly distributed throughout the film while film formation.
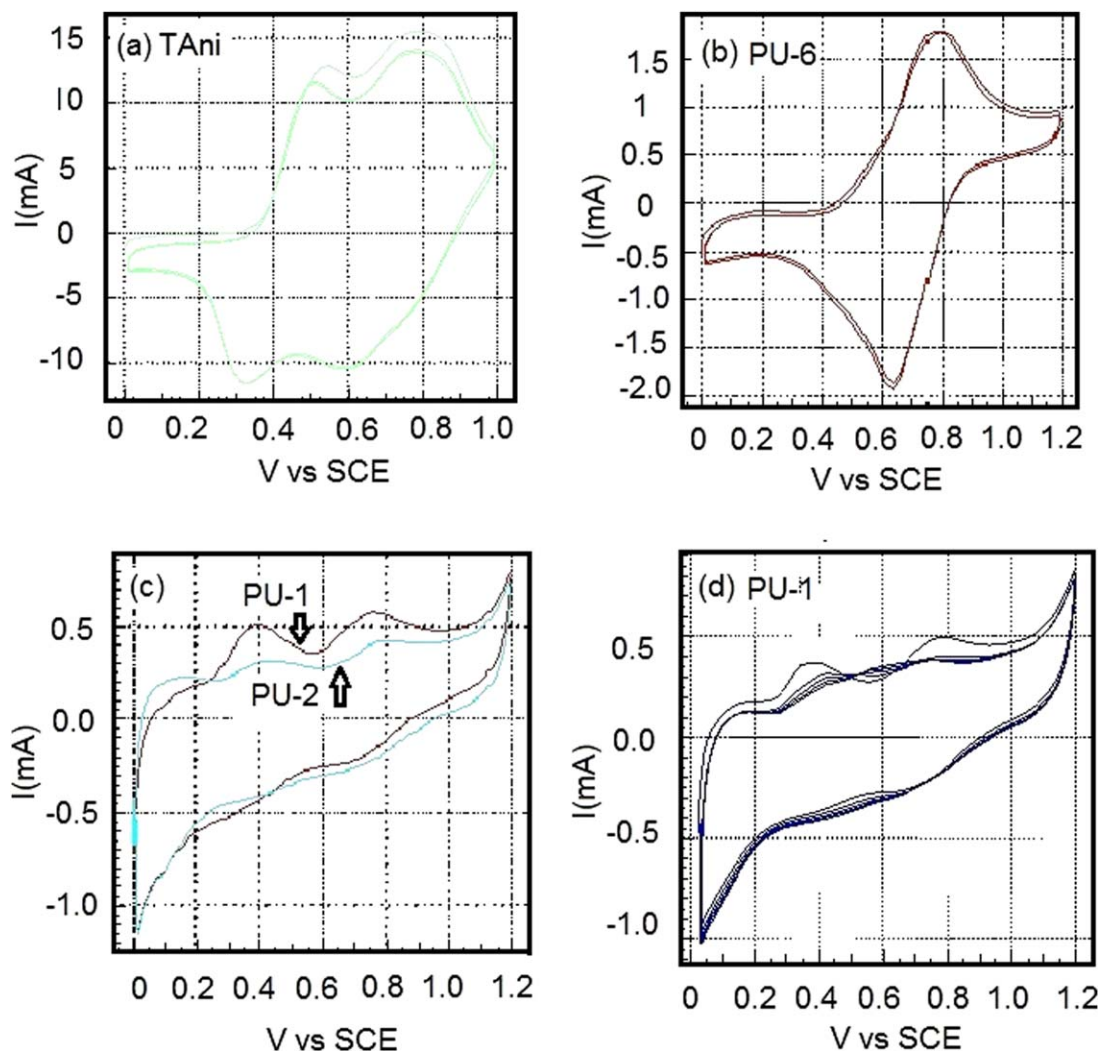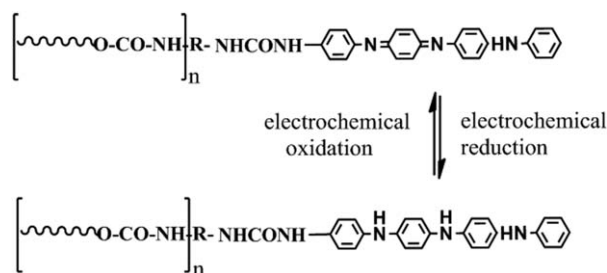


**Figure 6.** Cyclic voltammograms of pure TAni and CPUs at Pt electrode in 1 $M$ sulfuric acid at a scan rate of 100 mV s$^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Scheme 3.** Electrochemical switching of emeraldine base(EB) (above) oxidation state to leucoemeraldine (reduced) state (below).

The observed conductivity values for PU-trimers also varied between $1.2 \times 10^{-5}$ and $9.5 \times 10^{-3}$ S cm$^{-1}$. These values are not close, but 100–1000 times lower than the conductivity of the pure TriAni doped by PTSA (i.e., $5.19 \times 10^{-2}$ S cm$^{-1}$). As the conjugation of TriAni (or TAni) is interrupted by nonconjugated urethane segments, conducting mechanism of the polymer is solely by hopping mechanism, as shown in Scheme 2. Hence the conductivity is reduced in the polymers. Thus, all the polyurethane samples prepared are electronically conducting after doping with PTSA.

### X-ray Photoelectron Spectroscopy Characteristics

X-ray photoelectron spectroscopy (XPS) is a widely used method for surface analysis of coating materials. Due to its surface sensitivity and chemical specificity, XPS is an ideal technique for analyzing the surface segregation nature in PU based coatings. From the XPS spectra, the elements present and their chemical state

(valence) can be determined. The undoped polymers were analyzed by XPS using PU-2 as an example. The XPS spectra for C1s, O1s, and N1s are shown in Figure 3. The C1s spectra of all PU samples contain broad peak centered at 286 eV. This can be deconvoluted to three peaks assignable to aliphatic/aromatic carbon at 284.6 eV, aminocarbon at 285.88, and ether carbon at 286.89 eV [Figure 3(a)]. The O1s peak is broad and observed at 534 eV. Deconvolution of this peak resulted in two peaks at 532.22 and 533.4 eV which can be assigned to oxygen atoms of carbonyl and ester type [Figure 3(b)].

In general PU displays one N1s XPS peak, corresponding to the –NH– (398.9 eV) of the urethane linkage.[35] In the present case, this peak is observed at 398.65. This new nitrogen species belongs to the urea type group formed by the reaction of Tani with prepolymer having NCO groups. Thus, the polymer displayed a total of four peaks, which were assigned to the imine nitrogen (397.59 eV), amide nitrogen (398.65 eV), and charged nitrogen –N$^+$– (400.42 and 402.21 eV). These values are very close and in agreement with the corresponding data published for polyaniline and its network with polyurethane.[35–38]

### Thermal Characteristics

The polymers were studied for their thermal properties such as decomposition/degradation with temperature and glass transition behavior. The differential scanning calorimetric (DSC) data and TGA data are collected in Tables IV and V, respectively.

The samples were analyzed by DSC technique (Figure 4). The technique is informative about physical phenomenon that occur
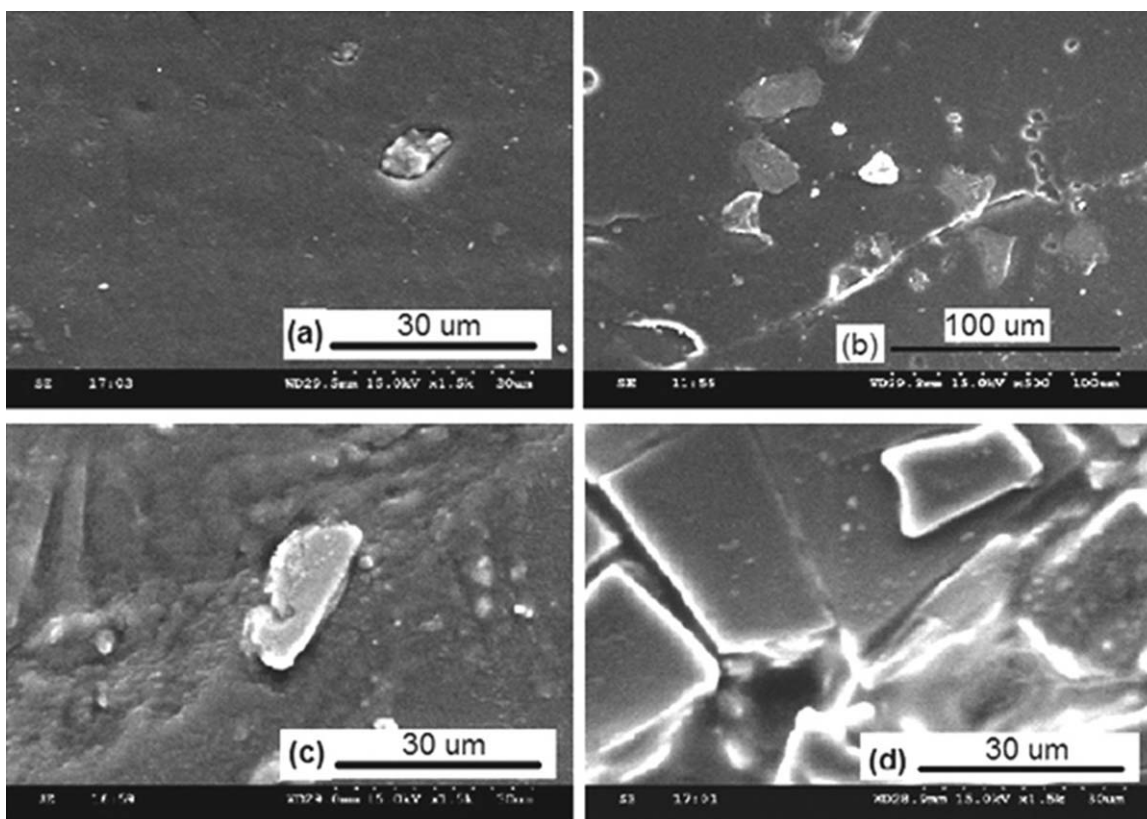


**Figure 7.** Scanning electron micrographs of (a) PU-1 (undoped), (b) PU-4 (undoped), (c) PU-2 (undoped), and (d) PU-2 (doped).
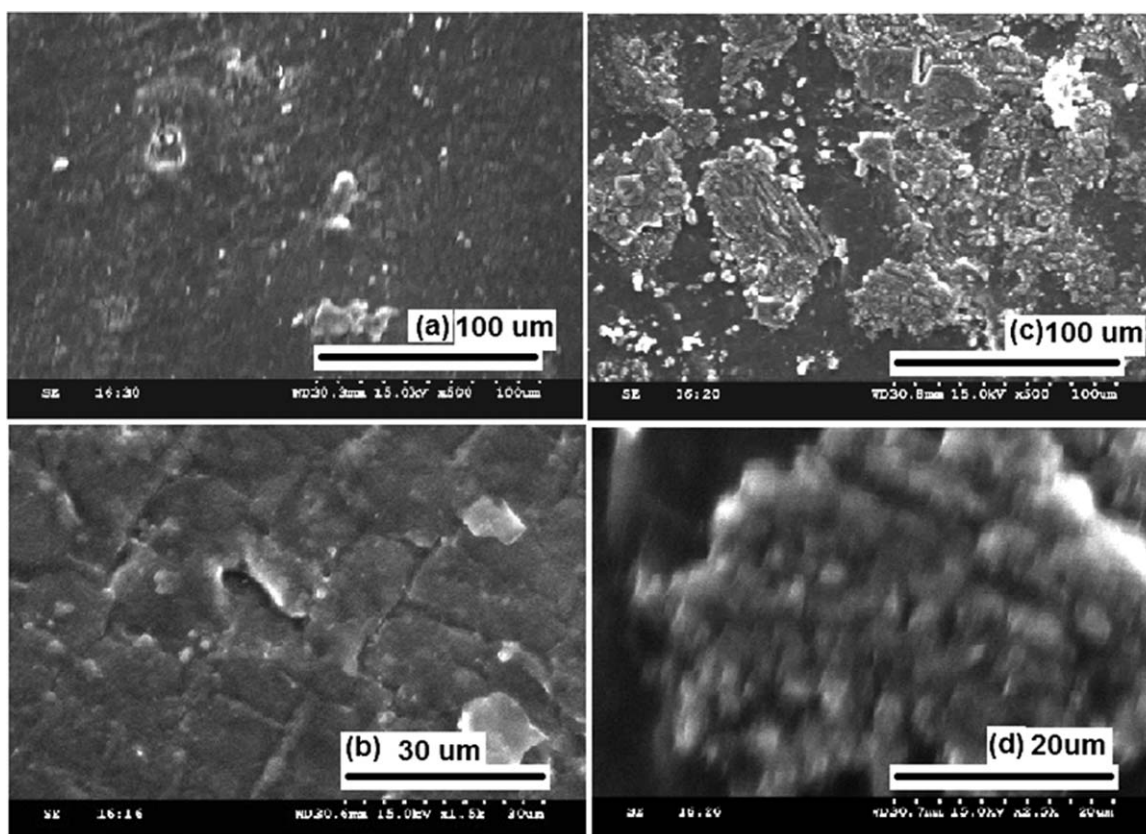
**Figure 8.** Scanning electron micrographs of (a) PU-4 undoped (×500), (b) PU-4 undoped (1.5k), (c) PU-4 doped (×500), and (d) PU-4 doped (2.5k).

during the heating/cooling the sample such as glass transition, cold crystallization or melting. In general, the DSC study of a polyurethane demonstrates two glass transition temperatures one due to soft segment and another due to hard segments. The soft segments give rise a low lying $T_g$ while the hard segment gives $T_g$ in positive temperature region. The latter is seldom observed in a DSC profile, but will be clearly traceable in DMTA study. The PU-trimer polymers showed a $T_{g1}$ around −21 to −26°C which is due to the soft segments derived of PPG components. The polymers of TDI, IPDI are semicrystalline as suggested by the presence of an endothermic melting peaks in the range 80–99°C. Polymers PU-1 to PU-6 exhibited very similar glass transition temperatures that of PU-trimers.

TGA (Figure 5) on TriAni segmented PUs (PU-7 to PU-12) showed their decomposition at 230–262°C and the decomposition continues up to 480–500°C. Polymers showed 50% decomposition between 310 and 360°C. All the polymers showed a residual/remaining mass of 5–15 wt % at 500°C.

PU-TAni polymers showed more or less similar thermal behavior as those of TriAni segmented polymers. The main difference is that the onset of the degradation which starts at lower temperature between 150 and 280°C for these polymers (Table V). The major decomposition continues up to 400°C which is lower by about 80–100°C compared to the TriAni polymers. The residual wt % remaining at 450°C is in the range 9.5–19.5%. Over all, these polymers are less stable than PU-trimer analogues.

## Electrochemical Properties

The signature property of the conducting polyaniline is its tunable electrical conductivity and electrochemical properties. The present polymers were investigated for their electrochemical activity by CV using Pt disc or Pt foil electrodes in a three electrode cell. Pure TAni showed successive one electron oxidations at 0.450 and 0.80 V vs. SCE [Figure 6(a)]. These oxidations are corresponding to the transitions from LEB to EB oxidation state and EB to pernigraniline oxidation state, respectively.[39] The PU-TAni-terminated polymers exhibited lower degree of electrochemical activity. The polymers PU-5 and PU-6 exhibited only single one electron oxidation at 0.803 V and on reversal of the scan showed a single reduction at 0.637 V [Figure 6(b)]. The polymers PU-1 and PU-2 exhibited two oxidations at 0.384 V and 0.768 V vs. SCE [Figure 6(c)]. These potentials are close to the pure TAni. However, the oxidations are irreversible, that is, the corresponding reductions are not observable. Upon several cycles the two oxidation peaks coalescence to one broad peak centered at 0.6 V [Figure 6(d)]. This shows that the polymer behaves as a capacitative material. TriAni showed one oxidation at 0.85 V and a reduction at 0.450 V at Pt electrode. The switching of oxidation states involved in PU-TAnis is illustrated in Scheme 3. In contrast to the PU-TAni polymers, PU-Trimer polymers are not electrochemically active. This may be arising due to decrease in electron donating character (basicity) significantly as these groups are connected to two acyl groups, unlike
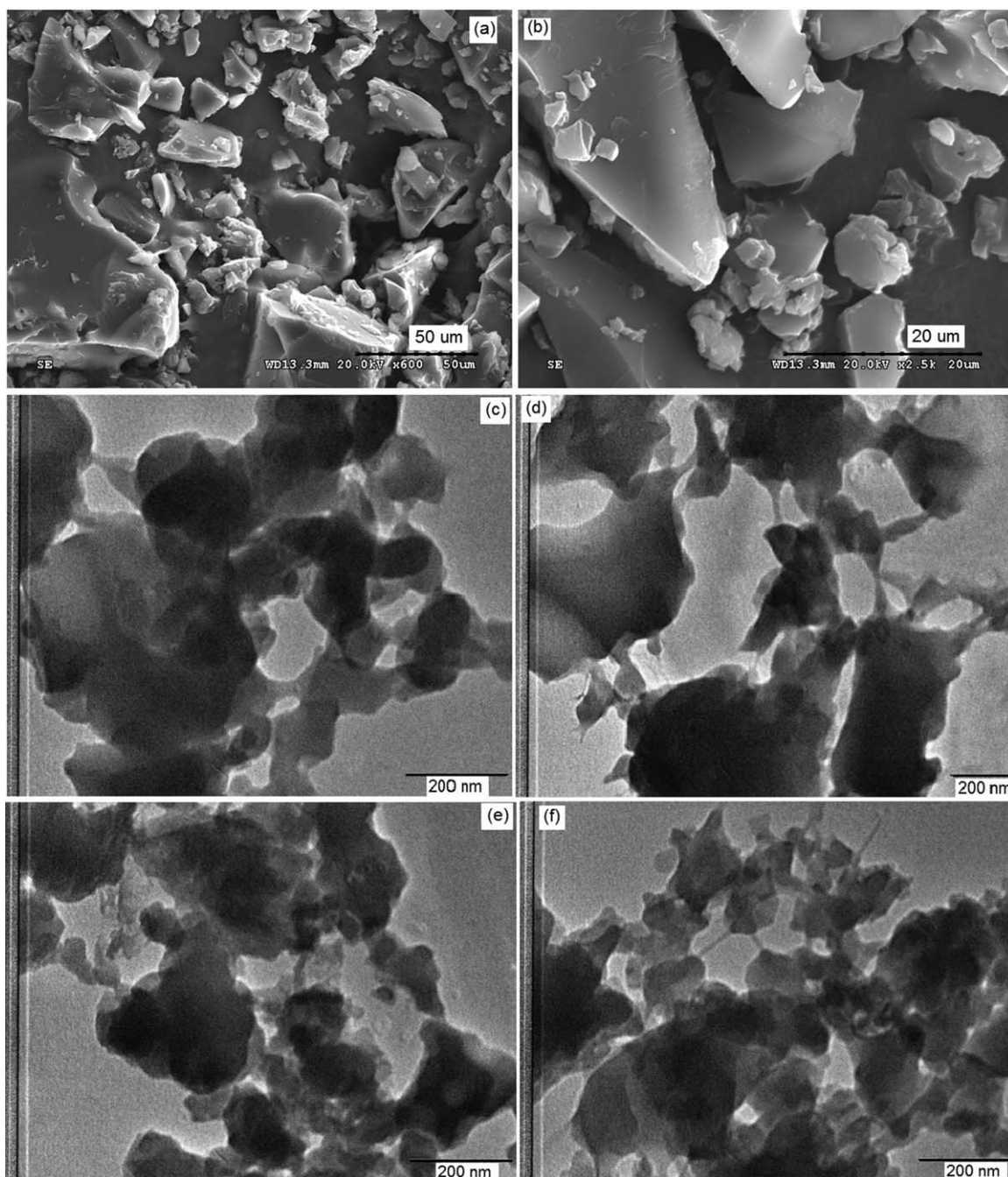
**Figure 9.** FESEM of (a and b) PU-1 and TEM pictures of (c and d) PU-1 and (e and f) PU-9.

"TAni" segments in PU-1 or PU-2 which are linked to one acyl group. Another reason could be that inaccessibility of TriAni units to the electrode surface due to their remote position somewhere in the backbone, unlike PU-TAnis which are available terminally.

**Surface Morphology and Structure**

The morphology of the polymers as films and powders was examined by SEM, FESEM, and TEM techniques. The films of PU-Tani polymers are smooth in undoped state [Figure 7(a–c)] with very few particles agglomerated on the films. The polymers

were doped by PTSA and the cast film showed rectangular flakes of some PTSA deposited on the films [Figure 7(d)]. The films of the PU-trimers showed lesser smoothness than PU-TAni polymers (Figure 8). Upon magnification, the

**Table VI.** Corrosion Data from Tafel Polarization Study

| Polymer | $I_{cor}$ ($\mu$A cm$^{-2}$) | $E_{cor}$ (mV, SCE) | $R_p$ (k$\Omega$ cm$^{-2}$) | CR (mm year$^{-1}$) |
|---------|------------------------------|---------------------|------------------------------|---------------------|
| PU-2 | 9.0 | −425 | 15.8 | 0.104 |
| PU-8 | 34.1 | −301.9 | 7.57 | 0.390 |
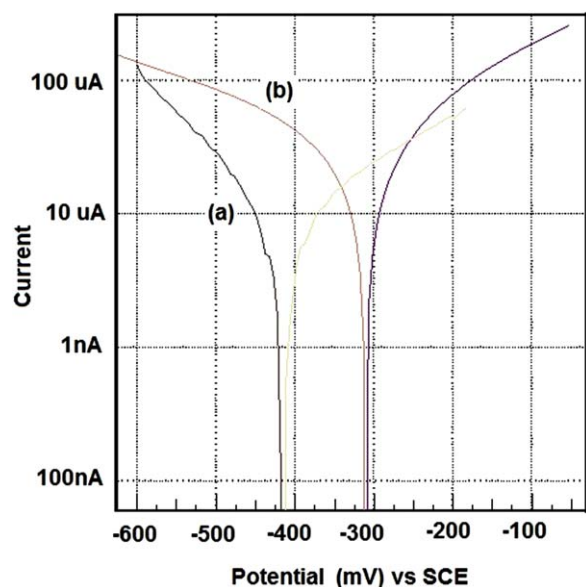
**Figure 10.** Potentiodynamic (Tafel) diagram exhibited by (a) PU-2 and (b) PU-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

undoped film of PU-10 showed rectangular type segments. This film when doped with PTSA showed irregular structure of islands of PTSA crystallized on the surface of the films [Figure 8(c,d)].

The precipitated CPU PU-1 and PU-9 powder samples were analyzed by FESEM and TEM analyses (Figure 9). FESEM picture surfaces [Figure 9(a,b)] suggests that the powder sample precipitated is indeed lumps with varying sizes with very smooth surfaces. Hence the powder was finely ground, dispersed in water and analyzed by TEM technique. The micrographs [Figure 9(c,d)] show that the polymer is dispersed into thin layers of large size (more than 200 nm × 200 nm) aggregates. Under the same conditions PU-9 formed lower size aggregate [Figure 9(e,f)].

**Electrochemical Corrosion Studies**
Adhesion plays a major role in the protection of the metals. It has been found that polyurethane adheres strongly to steel.[40] Very good adhesion on carbon steel was observed even after one year exposure to the 0.5 $M$ NaCl solution.[40] The present polymers also exhibited very good adhesion property on mild steel panels. It has been well established in the literature[41,42] that conducting and electroactive polymers are excellent materials for corrosion protection. The corrosion protection by conducting polymers was first proposed by MacDiarmid[43] and was investigated by others.[44]
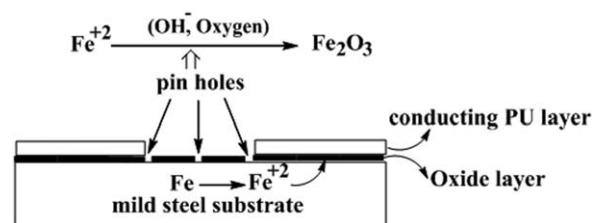


**Scheme 4.** Corrosion protection mechanism by CPUs.

Corrosion protection efficiency of the CPUs was investigated by Tafel polarization studies by taking representative CPUs namely PU-2 and PU-10 as coating material. For this purpose mild steel panels (1 in$^2$) were coated with the above CPUs and subjected for polarization studies in a 3.5-wt % NaCl aqueous solution. $R_p$ was evaluated from the obtained Tafel plots, according to the Stearn–Geary eq. (2).[45] Corrosion rate ($C_R$, in mm per year) was calculated using eq. (3).[46]
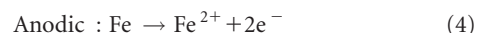
$$Rp = \frac{ba \times bc}{2.303(ba + bc)Icorr} \qquad (2)$$

$$CR = \frac{Icor\left(\frac{A}{cm^2}\right) \times M(g)}{D\left(\frac{g}{cm^3}\right) \times V} \times 3270 \qquad (3)$$

where $I$ is the current (A cm$^{-2}$), $M$ is the molecular weight, $V$ is valence (2 here), 3270 is constant, and $D$ is the density (g cm$^{-3}$) and $b_a$ and $b_c$ are anodic and cathodic slopes from Tafel curves.

The values of the corrosion potential ($E_{corr}$), polarization resistance ($R_p$), and corrosion current density ($I_{corr}$) are given in Table VI. The potentiodynamic polarization curves are shown in Figure 10. It was observed that $I_{corr}$ changed from 12 $\mu$A cm$^{-2}$ for pure MS to 34.1 $\mu$A cm$^{-2}$ for PU-10 and further reduced to 9 $\mu$A cm$^{-2}$ for PU-2. This is also reflected in $E_{corr}$ values which increased to −0.301 and −0.425 V vs. SCE from pure mild steel showing $E_{corr}$ at −0.534 V. Calculation of corrosion rate from eq. (2) showed that PU-Tani polymer (PU-2; CR = 0.104 mm year$^{-1}$) is better corrosion resistant than PU-Trimer (PU-10; CR = 0.39 mm year$^{-1}$). The better corrosion-resistance property of PU-2 is due to the presence higher concentration of TAni in the polymer with its better conducting and redox properties.

The proposed mechanism for corrosion protection by the CPUs PU-2 and PU-10 is similar to the conducting polyaniline[43] or some oligoaniline-epoxy system[40] which is shown in Scheme 4. The conducting segments in the polymer chain act as barrier coating or active coating participating in the reactions taking place across the polymer–metal–electrolyte interface.[47] Elsenbaumer[48] and Wessling[49] reported that conducting polymers form a complex with Fe which improves the corrosion protection. In the present case also the oligoaniline segments maintain a protective oxide coating (Scheme 4). The corrosion protection in neutral chloride media can be represented by eqs. (4–6). The first and second reactions are electrochemical in nature and the third one is chemical precipitation fallowed by oxidation to form oxide layer.

$$\text{Anodic}: Fe \rightarrow Fe^{2+} + 2e^- \qquad (4)$$

$$\text{Cathodic}: 1/2\,O_2 + 2e^- + H_2O \rightarrow 2OH^- \qquad (5)$$

$$\text{Chemical}: 2OH^- + Fe^{2+} \rightarrow Fe(OH)_2 \rightarrow Fe_2O_3 \qquad (6)$$

However, in acid media, the passivation of pin holes takes place by the cathodic complementary reaction of $[Ani]_{oligo}(ES) \rightarrow [Ani]_{oligo}(LS)$. Due to the formation of $[Ani]_{oligo}(LS)$ in acid media, the coating may be changed from conducting to nonconducting type.

**SUMMARY AND CONCLUSION**

The work in the present study described the synthesis, characterization and evaluation of new type of polyurethanes containing oligoanilines exhibiting electronic conductivity and some electrochemical

activity. Amine capped TAni and TriAni oligomeric units in EB oxidation state have been used as chain terminator or extendor. The PU-TAnis exhibited irreversible two electron transfers whereas the PU-TriAnis did not show electrochemical activity. The conductivity of the films of these new polymers is lower to their oligomeric analogues. The corrosion protecting ability is more for TAni containing polyurethane compared to TriAni containing polyurethane. Owing to their conducting nature, these polymers may also be useful in ESD or EMI applications.

## ACKNOWLEDGMENTS

## REFERENCES

1. Shacklette, L. W.; Wolf, J. F.; Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955.

2. Wei, Y.; Yang, Ch.; Wei, G.; Feng, G. *Synth. Met.* **1997**, *84*, 289.

3. MacDiarmid, A. G.; Zhou, Y.; Feng, J. *Synth. Met.* **1999**, *100*, 131.

4. Gao, J.; Li, K.; Zhang, W.; Wang, C.; Wu, Z.; Ji, Y.; Zhou, Y.; Shibata, M.; Yosomiya, R. *Macromol. Rapid Commun.* **1999**, *20*, 560.

5. Wei, W.; MacDiarmid, A. G. *Synth. Met.* **2002**, *129*, 199.

6. Franzen, P. L.; De Boni, L.; Santos, D. S. Jr.; Mendonca, C. R.; Zilio, S. C. *J. Phys. Chem. B* **2004**, *108*, 19180.

7. Kulszewicz-Bajer, I.; Rozalska, I.; Kurylek, M. *New J. Chem.* **2004**, *28*, 669.

8. Wei, Z.; Faulz, Ch. F. *J. Macromol. Rapid Commun.* **2008**, *29*, 80.

9. Oertel, G. Polyurethane Handbook; Hanser: New York, **1985**, p 629.

10. Szycher, M. Handbook of Polyurethanes; CRC: MA, **1999**, p 696.

11. Chattopadhyay, D. K.; Raju, K. V. S. N. *Prog. Polym. Sci.* **2007**, *32*, 352.

12. Huang, L.; Hu, J.; Lang, L.; Wang, X.; Zhang, P.; Jing, X.; Wang, X.; Chen, X.; Lelkes, P. I.; MacDiarmid, A. G.; Wei, Y. *Biomaterials* **2007**, *28*, 1741.

13. Huang, L.; Hu, J.; Lang, L.; Chen, X.; Wei, Y.; Jing, X. *Macromol. Rapid Commun.* **2007**, *28*, 1559.

14. Hu, J.; Zhuang, X.; Huang, L.; Lang, L.; Chen, X.; Wei, Y.; Jing, X. *Langmuir* **2008**, *24*, 13376.

15. Wang, H.; Guo, P.; Han, Y. *Macromol. Rapid Commun.* **2006**, *27*, 63.

16. Wang, H.; Han, Y. *Macromol. Rapid Commun.* **2009**, *30*, 521.

17. Wang, Z. Y.; Yang, C.; Gao, J. P.; Lin, J.; Meng, X. S.; Wei, Y.; Li, S. *Macromolecules* **1988**, *31*, 2702.

18. Chao, D.; Ma, C.; Lu, X.; Cui, L.; Mao, H.; Zhang, W.; Wei, Y. *J. Appl. Polym. Sci.* **2007**, *104*, 1603.

19. Han, D. H.; Yang, L.-P.; Zhang, X.-F.; Pan, C.-Y. *Eur. Polym. J.* **2007**, *43*, 3873.

20. Liu, Y.; Hu, J.; Zhuang, X.; Zhang, P.; Chen, X.; Wei, Y.; Wang, X. *Macromol. Biosci.* **2011**, *11*, 806.

21. Chao, D.; Jia, X.; Liu, H.; He, L.; Cui, L.; Wang, C.; Berda, E. B. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1605.

22. Chen, R.; Benicewicz, B. C. *Macromolecules* **2003**, *36*, 6333.

23. Liu, S.; Kaizheng, Z. T.; Zhang, Y.; Zhu, Y.; Xu, T. X. *Mater. Lett.* **2005**, *59*, 3715.

24. Anantharaj, V.; Wang, L. Y.; Canteenwala, T.; Chiang, L. Y. *J. Chem. Soc. Perkin Trans.* **1999**, *1*, 3357.

25. Chiang, L. Y.; Anandakathir, R.; Hauck, T. S.; Lee, L.; Canteenwala, T.; Padmawar, P. A.; Pritzker, K.; Bruno, F. F.; Samuelson, L. A. *Nanoscale* **2010**, *2*, 535.

26. Gurunathan, T.; Rao, C. R. K.; Narayan, R.; Raju, K. V. S. N. *Prog. Org. Coat.* **2013**, *76*, 639.

27. Zhang, W. J.; Feng, J.; MacDiarmid A. G.; Epstein, A. *J. Synth. Met.* **1997**, *84*, 119.

28. Wei, Y.; Yang, Ch.; Zhong Ding, T. *Tetrahedron Lett.* **1996**, *37*, 731.

29. Lokshin, N. A.; Pyshkina, O. A.; Golubev, V. B.; Sergeyev, V. G.; Zezin, A. B.; Kabanov, V. A. *Macromolecules* **2001**, *34*, 5480.

30. Mido, Y. *Spectrochim. Acta A: Mol. Spectrosc.* **1972**, *28*, 1503.

31. Coleman, M. M.; Lee, K. H.; Skrovanek, D. J.; Painter, P. C. *Macromolecules* **1986**, *19*, 2149.

32. Wilhelm, C.; Gardette, J. L. *Polymer* **1998**, *39*, 5973.

33. Yang, Z.; Wang, X.; Yang, Y.; Liao, Y.; Wei, Y.; Xie, X. *Langmuir* **2010**, *26*, 9386.

34. Chen, S. A.; Lee, H. T. *Macromolecules* **1993**, *26*, 3254.

35. Matsuda, H. *Macromol. Chem.* **1975**, *176*, 573.

36. Rodrigues, P. C.; Lisboa-Filho, P. N.; Mangrich, A. S.; Akcelrud, L. *Polymer* **2005**, *46*, 2285.

37. Masinlanis, B.; Zielinski, R. *J. Appl. Polym. Sci.* **1985**, *30*, 2731.

38. Reddy, S. V.; Joseph, K. T.; Aminabhavi, T. M. *Polym. Plast. Technol. Eng.* **1993**, *32*, 501.

39. Chen, L.; Yu, Y.; Mao, H.; Lu, X.; Zhang, W.; Wei, Y. *Mater. Lett.* **2005**, *59*, 2446.

40. Huang, T.-C.; Su, Y.-A.; Yeh, T.-C.; Huang, H.-Y.; Wu, C.-P.; Huang, K.-Y.; Chou, Y.-C.; Yeh, J.-M.; Wei, Y. *Electrochim. Acta* **2011**, *56*, 6142.

41. Tallman, D. E.; Spinks, G.; Dominis, A. J.;Wallace, G. G. *J. Solid State Electrochem.* **2002**, *6*, 73.

42. Spinks, G. M.; Dominis, A. J.;Wallace, G. G.; Tallman, D. E. *J. Solid State Electrochem.* **2002**, *6*, 85.

43. Ahmad, N.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 103.

44. Kinlen, P. J.; Silverman, D. C.; Jeffreys, C. R. *Synth. Met.* **1997**, *85*, 1327.

45. Stern, M.; Geary, A. L. *J. Electrochem. Soc.* **1957**, *104*, 56.

46. Weng, Ch. J.; Jane-Yu, H.; Kuan-Yeh, H.; Yu-Sian, J.; Mei-Hui T.; Jui-Ming, Y. *Electrochim. Acta* **2010**, *55*, 8430.

47. D. Sazou, *Synth. Met.* **2001**, *118*, 133.

48. Lu, W.-K.; Elsenbaumer, R. L.; Wessling, B. *Synth. Met.* **1995**, *71*, 2163.

49. Wessling, B. *Synth. Met.* **1997**, *85*, 1313.