NOTE

Oxidative Polymerization of Aniline and Pyrrole by Isopolymetallates of Vanadium

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INTRODUCTION

Specialty polymers such as polyaniline (PANI) and polypyrrole (PPY) have been widely investigated in the field of conducting polymers with a variety of end applications.[1–6] Pyrrole (PY) is one of the most easily oxidizable specialty monomers, and a variety of oxidizing agents is available for the oxidative polymerization of PY. These include halogens, $FeCl_3$, $Fe(NO_3)_2$, $Fe(BF_4)_3$, $Fe(ClO_4)_3$, $K_3Fe(CN)_6$, FeOCl, 2,3-dicholoro-5,6-dicyano-p-benzoquinone, ammonium perdisulfate (PDS), $CuCl_2$, and $Cu(ClO_4)$ in bulk, aqueous, and nonaqueous media.[7] As with PY, various oxidant systems, such as PDS, $FeCl_3$, FeOCl, $CuCl_2$, $Cu(BF_4)_2$, $Cu(ClO_4)_2$, and $K_2Cr_2O_7$,[7] have been investigated for the oxidative polymerization of aniline (ANI). Among the transition-metal ions, vanadium salts have been used in several systems. V_2O_5 was reported by Biswas et al.[8] to be an efficient heterogeneous catalyst for the polymerization of *N*-vinylcarbazole in bulk and in a toluene solvent. Kanatzidis et al.[9,10] described the intercalative polymerization of ANI and PY in host matrices such as V_2O_5 xerogels or FeOCl and ascribed a redox reaction between V^{5+} centers and Fe^{3+} ions and the respective monomers, which led to the formation of PANI or PPY, respectively. Liu and Kanatzidis[11] also reported the polymerization of ANI and PY in some layered phosphates where O_2 acted as the oxidant. Izumi and Toshima[12] showed that bis(acetylacetonato)(oxo)vanadium (IV) failed to polymerize PY in acetonitrile in the presence of O_2 at room temperature. However, the addition of $AlCl_3$ to the dispersed solution resulted in the formation of a brown precipitate with a much lower electrical conductivity ($<10^{-10}$ S/cm). Similarly, another oxidant system, $CuCl–AlCl_3–O_2$, was used to polymerize PY, and the product PPY also showed a very low conductivity value ($<10^{-10}$ S/cm).

With this background, we recently developed a pH-controlled oxidant system based on isopolyvanadate (IPV) for the aqueous polymerization of ANI and PY. To the extent we searched the relevant literature, reports involving the procedure that we developed (IPV oxidant system) do not seem to exist. Some salient features of the ANI–IPV and PY–IPV polymerization systems are described in this note.

EXPERIMENTAL

Materials

ANI (Merck-Schuchardt, Hohenbrunn, Germany) and PY (Lancaster Synthesis, Morecambe, UK) were distilled under reduced pressure and stored in the dark before use. V_2O_5 (Aldrich, Milwaukee, WI) was used as such. All of the other reagents were of analytical grade and were used after necessary purification by standard procedures.

Polymerization of ANI and PY

A weighed amount of V_2O_5 powder was dissolved in aqueous NaOH (12–20%) to produce a colorless solution to which a known amount of monomer (ANI or PY) was added. The solution was stirred magnetically and 6N HCl was added dropwise. At a pH of less than 3, a black precipitate appeared, and the addition of HCl was continued in each of the polymerization system until the precipitation was completed. The precipitated mass that was formed was filtered off and repeatedly washed with dilute HCl followed by methanol, and finally, the residue was dried *in vacuo* at 50°C for 5 h until a constant weight was reached. The mass thus obtained was subsequently characterized as PANI or PPY.

Characterization

Fourier transform infrared (FTIR) spectra of the PANI and PPY homopolymers were taken with KBr pellets on a PerkinElmer (model 883; Wellesley, MA) instrument. pH variation was monitored by a digital pH meter (SYSTRONICS 335, Bangalore, India). Thermogravimetric analyses (TG)

TABLE I
Some Typical Data on ANI and PY Polymerization

Entry No.[a]	V_2O_5/ANI	V_2O_5/PY	PDS/ANI	$FeCl_3$/PY	Polymer yield (%)	Reference
1	0.51	—	—	—	45	This study
2	0.77	—	—	—	78	This study
3	1.20	—	—	—	>90	This study
4	—	1.50	—	—	51	This study
5	—	2.00	—	—	70	This study
6	—	2.50	—	—	>90	This study
7	—	—	0.80	—	78	Ref. 14
8	—	—	1.20	—	>90	Ref. 14
9	—	—	2.00	—	>90	Ref. 14
10	—	—	1.25	—	>90	Ref. 13
11	—	—	—	1.0	52	Ref. 15
12	—	—	—	2.0	>90	Ref. 15

[a] In each entry set, the molar ratio between the oxidant and monomer was taken in the initial feed.

and differential thermal analyses (DTA) were performed on a Shimadzu DT 40 instrument (Kyoto, Japan). Ultraviolet–visible (UV–vis) absorption spectra were obtained with a Hitachi U 3210 spectrophotometer. Conductivity measurements were conducted on pressed pellets by the conventional four-probe method.

RESULTS AND DISCUSSION

General features of polymerization

In this study, the addition of ANI or PY to an alkaline solution of V_2O_5 (pH > 12) did not lead to polymer formation and any change in the color of the solution. However, the dropwise addition of 6N HCl to the system containing ANI or PY gradually changed the color of the solution from colorless to pale yellow orange and finally to brown with a parallel change in the pH of the solution (up to pH ≈ 3). With the continued addition of HCl to the system, the ANI solution gradually turned violet to deep blue violet, and a blackish green precipitate appeared at (pH < 2), which was subsequently characterized as PANI. With the PY solution, the same addition led to a change of color from bluish green to black with the appearance of a black precipitate (pH < 2), which was subsequently characterized as PPY. These conversions occurred at pH values of less than 3, and thereafter, a sharp decrease in pH (<1) was noted in both systems. The entire polymerization process was almost instantaneous at room temperature.

Table I (entries 1–6) presents some typical polymer conversion data that revealed that with increasing $[V_2O_5]$/[Monomer] molar ratios at a certain pH, the percentage conversion increased and attained a value as high as 90% or more in both systems almost instantaneously at room temperature. For comparison, some of the percentage conversion data of PANI and PPY realized with the conventional oxidants PDS[13,14] and $FeCl_3$,[15] respectively, are also given in Table I.

FTIR spectral analyses

The formation of PANI and PPY in this study with IPV as the oxidant was endorsed by FTIR spectroscopic analyses.

Table II shows the various peaks actually observed in the FTIR spectra of PANI and PPY obtained from the ANI–IPV and PY–IPV systems, respectively. These data matched the characteristic FTIR values obtained with PDS[14] and $FeCl_3^{16}$ oxidant systems, respectively.

UV–vis absorption studies

UV–vis absorption revealed no characteristic absorption for the IPV solution (pH < 2) in the region 540–560 nm. However, in the presence of ANI, the IPV solution assumed a deep blue coloration, signifying charge transfer vis-a-vis PANI formation, and a broad ultraviolet (UV) absorption peak at 560 nm manifested. The corresponding IPV–PY system, which produced a deep green coloration due to charge-transfer initiation leading to PPY formation, revealed a UV absorption at 540 nm. This relative shifting of UV absorption was indicative of the formation of reduced IPV species (V^{4+}) in the corresponding polymerization systems.

Thermogravimetric stability studies

Table III compares the thermal stability of PANI and PPY obtained by IPV and by conventional oxidants, respectively. The overall thermal stabilities of PANI prepared by IPV and

TABLE II
FTIR Band Assignments

Material	Peaks (cm^{-1})	Assignment
PANI	1232–1292	C–N stretching mode
	1475–1594	N–H bending mode
	3426	>N–H stretching mode
PPY	798	1, 3, 4 trisubstitution of the pyrrole ring
	918	1, 3, 4 trisubstituion of the pyrrole ring
	1065	C_β–H deformation of 1, 2, 5 or 1, 3, 5 trisubstituion of the pyrrole ring
	1572	1, 2 disubstitution or trisubstituion of the pyrrole ring

TABLE III
Thermogravimetric Stability Data

Polymer	Oxidant system	Initial decomposition	Temperature (°C) for		
			50% weight loss	Complete weight loss	DTA exothermic peak
PANI	IPV	235	325	600	344 (shoulder), 512
PANI	PDS	230	375	600	363 (shoulder), 533
PPY	IPV	270	700	750 (60%), limiting	422
PPY	FeCl$_3$	235	500	750 (70%), limiting	468

PDS oxidants were similar. However, PPY prepared by IPV oxidant showed a somewhat improved overall thermal stability than PPY obtained with FeCl$_3$ oxidant.

DTA scans revealed manifestation of exothermic oxidative degradation peaks at 363 and 422°C for PANI and PPY, respectively, obtained by IPV. These values were in good agreement with those reported for PDS and FeCl$_3$ oxidant systems. Thus, these thermogravimetric stability patterns endorsed that the behavior of IPV-induced PANI and PPY systems was fairly consistent with that of conventional oxidant systems such as PDS[14] or FeCl$_3$.[15]

Conductivity characteristics

The direct-current conductivity values of PANI and PPY obtained from IPV oxidant system were in the order of 10^{-1} and 10^{-2} S/cm, respectively. These values compared reasonably well with the reported conductivity values for a few other PANI- and PPY-based samples (Table IV). As is well known for PANI, nonconducting blue emerelidine base is converted to a protonated PANI salt, which is highly conducting. In this system, the polymers were doped with the protons, which led to the formation of a conducting protonated emerelidine salt. This notion was supported by the observation that the surface treatment of these polymers with alkali reduced the conductivity level dramatically to less than 10^{-6} S/cm. Pertinently, the conductivity values realized with our IPV-based systems compared satisfactorily with the corresponding data for PDS- or FeCl$_3$-induced PANI or PPY, respectively.

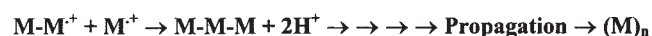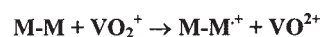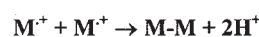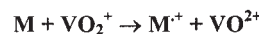**Mechanism for the oxidative polymerization of ANI and PY**

A distinctive aspect of the chemistry of vanadium (V), molybdenum (Mo), tungsten (W), niobium (Nb), tantalum (Ta),

and chromium (Cr)[17] is the formation of polymeric species collectively known as isopolyanions/cations or isopolymetallates. Greenwood and Earnshaw[18] pointed out that when a colorless solution obtained by the dissolution of V$_2$O$_5$ in strong aqueous alkali is gradually acidified with dilute acids, it first deepens in color, becoming orange to red as the neutral point is passed; then, it darkens further to produce a brown precipitate of hydrated V$_2$O$_5$ at a pH of less than 3, which redissolves at a still lower pH to give a pale yellow solution. Spectrophotometric investigations have established that the predominant species in the initial colorless solution is the tetrahedral VO$_4^{3-}$ ion, and in the pale yellow solution, it is the angular VO$_2^+$ ion.[17] In the intervening orange red solution, a complicated series of hydrolysis/polymerization reactions occur, leading to the formation of IPV. Notably, in this case, the oxidation number of vanadium (V) did not change. With the background of this information, the idea occurred to us that the formation of an electron-deficient VO$_2^+$ species in aqueous solution at a pH of about 2–3 might participate in a charge-transfer interaction with ANI or PY containing a nitrogen (N) heteroatom, thereby leading to the oxidative polymerization of ANI or PY. However, in the presence of acid, the formation of oxovanadium ions (VO^{2+}) was also possible through the mild reduction of VO$_2^+$ ions:[18]

$$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O \quad E^0 = 1.0V$$

where E^0 is the standard reduction potential.

The source of this electron in this case might have been the N lone pairs in ANI or PY, which resulted in the formation of [ANI]$^+$ or [PY]$^+$, which would propagate as usual[19] and be followed by the formation of PANI or PPY, respectively. The possible charge-transfer initiation and oxidative polymerization is shown in Scheme 1.

TABLE IV
Direct-Current Conductivity Values of Various PANI and PPY Samples

Polymer	Oxidant system	Conductivity (S/cm)	Reference
PANI	IPV	10^{-1}	This study
PANI	S$_2$O$_8^{2-}$	10^{-3}	Ref. 14
PPY	IPV	10^{-2}	This study
PPY	FeCl$_3$	10^{-5}	Ref. 15

$$M + VO_2^+ \rightarrow M^{·+} + VO^{2+}$$

$$M^{·+} + M^{·+} \rightarrow M\text{-}M + 2H^+$$

$$M\text{-}M + VO_2^+ \rightarrow M\text{-}M^{·+} + VO^{2+}$$

$$M\text{-}M^{·+} + M^{·+} \rightarrow M\text{-}M\text{-}M + 2H^+ \rightarrow \rightarrow \rightarrow \rightarrow Propagation \rightarrow (M)_n$$

$$M = ANI \text{ or } PY; (M)_n = PANI \text{ or } PPY$$

Scheme 1

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