Novel Oxidants for Polymerization and Crystallization of Aniline

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ABSTRACT: By using novel oxidants, namely, sodium salt of *para*-toluene sulfonic acid, lithium perchlorate, and potassium ferricyanide, and varying the oxidant to monomer ratio from as low as 1/100 to 1/20 in the presence of concentrated HCl, it has been possible to simultaneously polymerize aniline and crystallize the polyaniline at room temperature. The crystals thus obtained have been characterized using FTIR, GPC, XRD, and Optical Microscope. It was found that highly crystalline substituted oligo-polyanilines were obtained. The studies indicate that the use of even weaker oxidants, like pTS-Na, $LiClO_4$, and $K_3[Fe(CN)_6]$, can bring about simultaneous polymerization and crystallization of aniline, as we observed earlier using ammonium persulphate. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 640–646, 2005

Key words: conducting polymers; crystallization; FTIR; GPC

INTRODUCTION

Polyaniline (PANi) is one of the most interesting electroactive conducting polymers and is studied intensely.[1,2] Four different forms of PANi, oligomer formation, and crystal structure have been reported.[3,4] It has been our aim to develop crystals of PANi so that better conduction can be achieved because of better interchain hopping of electrons. However, PANI being intractable once it is formed, it was felt that there needs to be another route of polymerization wherein crystals could be grown.

We have earlier reported[5] that it is possible to simultaneously polymerize and crystallize aniline by using very small concentrations of ammonium persulphate as the oxidant. However, ammonium persulphate is a strong oxidizing agent, and it was anticipated that better control of reaction rates could be obtained by using the same procedure using milder oxidizing agents. In this paper we report on very slow polymerization and crystallization using milder oxidizing agents like pTS-Na, $LiClO_4$, and $K_3[Fe(CN)_6]$. It should be noted that pTS is in the salt form, acting as an oxidant, unlike use in the acid form as reported in literature[6] where it acts as a secondary dopant.

EXPERIMENTAL

Materials

Aniline, concentrated HCl, sodium salt of *para*-toluene sulfonic acid (pTS-Na), lithium perchlorate ($LiClO_4$), potassium ferricyanide ($K_3[Fe(CN)_6]$), ammonium persulphate (APS), and sodium hydroxide were obtained from S. D. Fine Chemicals Ltd, Maharashtra, India. All the chemicals purchased were of A. R. grade quality. Aniline was twice distilled before use.

Methods of analysis

The infrared absorption spectra of the various samples were recorded in the range of 500–4000 cm^{-1} using a Perkin–Elmer FTIR Spectrophotometer Model Paragon 500 by the KBr disk method at a resolution of 4 cm^{-1} for 120 scans.

GPC analysis was done using Polymer Laboratories PL Logical GPC Software. The experimental conditions were as follows: a mixed bed column of 2 feet, with the mobile phase being N, *N*-Dimethylformamide (DMF). The sample concentration used was 1% in the mobile phase at a flow rate of 1 mL/min and a temperature of 35°C. The standard used was polystyrene, and the calibration was done using Narrow Standards. The detector was a refractive index detector.

The XRD patterns were recorded using a Philips X-ray Generator PW 1729 and automatic X-ray diffractometer model PW 1710 unit. A Cu K_α line from a

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sealed tube having copper anode served as a source of radiation. The specimen samples were crushed to form fine powders and were palletized, by using a press, in an aluminum holder, which was then mounted on the rotating stage of the diffractometer. Nickel filtered Cu K_a radiation ($\lambda = 1.542$ Å) was incident on the sample, which was scanned at the rate of $1.2°$/min in reflection mode over a range of $2\theta = 5°$ to $70°$.

The optical micrographs were recorded in the transmission mode with and without a polarizer and analyzer combination using an Olympus Optical Microscope attached with a CCD black and white camera. The analysis of the images was done using Soft Imaging System GmbH's "analysis 3.0" software.

Method of crystallization

Traditionally, polymers are crystallized from the melt by slow cooling. Many simple, low molecular weight materials crystallize from a fairly saturated solution as it cools. Single crystals of many polymers can be produced by crystallization from a very dilute solution, typically 0.01% by weight.[7] The method of crystallization is as reported earlier.[5] However, the procedure is described here briefly. In this method the monomer is allowed to polymerize in a strong acidic medium by the addition of a suitable oxidizing agent, and the solution is slowly allowed to evaporate, resulting in crystals of oligo-polyaniline. The degree of polymerization could be controlled, by varying the type of oxidant and their concentrations.

Aniline monomer (10 mL, $5.476M$ w. r. t. total solution volume) was taken in an optically flat petri dish, and concentrated HCl (5.0 mL) was added and stirred thoroughly to redissolve the aniline hydrochloride salt formed. Then a solution of c.f. pTS-Na (1.0634 gms pTS-Na, $0.2738M$ w. r. t. aniline) pTS-Na in 5.0 mL concentrated HCl was added to it and stirred thoroughly (5% pTS-Na). The petri dish was kept covered under a bell jar, and the solvent was allowed to evaporate slowly. We could clearly see the formation of small, transparent crystals as the HCl was evaporating from the surface of the liquid. These smaller crystals slowly covered the surface and drastically reduced further evaporation of the solvent, thereby allowing sufficient time for the crystals to grow inside the liquid. The product obtained was filtered after 12 days. The samples were subjected to visual examination on each day during the crystallization. The duration was based on the observation that the solvent is appreciably evaporated and the color of the system also changes. Similarly, crystals were grown using a concentration of 1% of pTS-Na. The crystals were observed to be in the shape of a backbone or like the leaf of a coconut tree in the initial stages. The growth pattern of the substance obtained was similar to that of substituted oligo-polyanilines obtained by our earlier reported procedure.[5] The growth pattern and the reaction rate of the crystals were similar to the case in which the ammonium persulphate to aniline ratio was only 1/1000, thus suggesting that it was indeed oligo-polyaniline, the only difference being in the color of the crystals, which were now a light green. It was observed that, as the reaction progressed, the heat of reaction liberated was sufficient to accelerate the evaporation of HCl.

Similar reactions to grow crystals were carried out with only 5 and 1% of LiClO$_4$ as the oxidant. Also, crystals were grown using only 0.1% K$_3$[Fe(CN)$_6$] as the oxidant. The reason for employing such a low concentration of K$_3$[Fe(CN)$_6$] is that it is only partly soluble in concentrated HCl and hence also the lower concentration of acid, namely, $3.33M$ HCl. Since the concentration of HCl was reduced, the rate of evaporation also was reduced, and it was observed that, even after 12 days, these had not crystallized. Hence, an external source of heating was employed, by focusing a 60 W lamp over the solution in the petri dish, and it took an additional week for crystallization to complete. These crystals were deep blue in color at the top and light blue in color at the base, and the overall growth looked like a coral sheaf. All the samples were prepared under ambient conditions and were preserved in a desiccator.

RESULTS AND DISCUSSION

Properties of crystals obtained with various oxidants at different concentrations

The properties of the crystals obtained by varying the oxidants and their concentration with respect to aniline on the percentage yield, Cl/N ratio, percentage oxidation, and the percentage crystallinity are tabulated in Table I. It can be seen that the percentage yield of the crystals decreased as the concentration of pTS-Na decreased, but the percentage oxidation seems to have increased. The percentage yield of the samples obtained with LiClO$_4$ doesn't seem to change with concentration. On the other hand, the PANi-pot0.1 showed unusually high yield as compared to other samples but the percentage of oxidation was about the same. This may be due to efficient conversion into polymeric species. Further, it may be noted from Table I that the Cl/N ratio increased as the oxidant concentration decreased. This might be due to free HCl molecules, as re-

TABLE I
Effect of Different Oxidant Concentrations on the Properties of Oligo-PANi

Oxidant	Oxidant/aniline mole ratio	Oxidant concentration (in % moles) w. r. t. aniline	Sample	% yield[a]	Cl/N ratio[b]	Degree of oxidation[c] %	% crystallinity
PTS-Na	1/20	5.0	PANi-pTS5	35.2	0.89	35.80	95.19
PTS-Na	1/100	1.0	PANi-pTS1	28.4	0.96	41.80	87.52
$LiClO_4$	1/20	5.0	PANi-$ClO_4$5	28.5	0.85	33.00	96.52
$LiClO_4$	1/100	1.0	PANi-$ClO_4$1	28.5	1.03	34.15	96.53
$K_3[Fe(CN)_6]$	1/1000	0.1	PANi-pot0.1	66.2	1.01	34.43	93.90

[a] % yield was calculated by using the formula
yield = (wt. of product/wt of aniline + wt. of oxidant + wt. of HCl in conc. acid).
[b] from elemental analysis.
[c] Degree of oxidation was calculated by using the formula Degree of oxidation = $[A_{1599}/(A_{1599} + A_{1493})] \times 100$, where A_{1599} corresponds to absorbance of the Quinoid peak at 1599 cm^{-1} in the FTIR spectrum, similarly, A_{1493} corresponds to absorbance of the Benzenoid peak at 1493 cm^{-1} in the FTIR spectrum.

ported in literature, for PANi-HCl where N^+/Cl^- is close to unity, and for phosphonic acid doped PANis, where the P/N ratio is reported to be more than 1.[8,9]

Pouget et al.[4] have reported that, as the Cl/N ratio increases, the crystallization of PANi increases in going from the EB-I base (neutral) form (Cl/N ~ 0) to the ES-I (acidic) salt form (Cl/N ~ 0.5) of PANi. At a Cl/N ratio of 0.5, the maximum crystallinity reported is about 50%.

The increase in the Cl/N ratio on going from the sample with a higher concentration of oxidant to a lower one indicates that ring substitution might be occurring, which is confirmed by FTIR studies as reported earlier.[5]

FTIR studies

FTIR spectra of the three representative samples, namely, PANi-pTS1, PANi-$ClO_4$1, and PANi-pot0.1 are given in Figure 1. The overall spectra of the three samples are quite similar, showing characteristic bands of PANi as reported in literature and also earlier.

The relative intensities of the two peaks, at 1597 cm^{-1} and 1493 cm^{-1}, suggest that the benzenoid ring repeat units are more in number as compared to the quinoid ring repeat units, thereby indicating that the degree of oxidation is less, as compared to the standard method, which is expected because of the low concentrations of oxidants in all the samples. The degree of oxidation is shown in Table I.

The C-H in-plane (i/p) bending vibrations are observed at 1405.7 cm^{-1}[10] in the spectra, which are not well resolved. This can be explained by comparing the degree of polymerization of these samples with that of oligo-polyanilines prepared with APS, as reported earlier.[5] Because the number of repeat units is more in samples prepared with APS as compared to samples

prepared with the weaker oxidants, the C-H (i/p) bending vibrations are relatively more prominent in the former.

The peaks at 1140.8, 1140.8, and 1145.7 cm^{-1} in the three respective spectra of PANi-pTS1, PANi-$ClO_4$1,
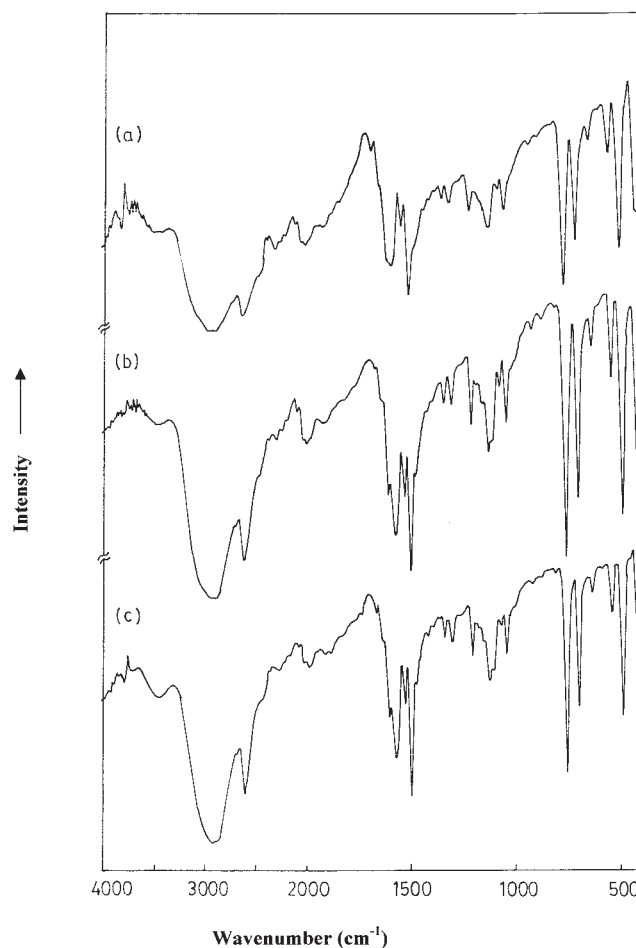

Figure 1 FTIR spectra of (a) PANi-pTS1, (b) PANi-$ClO_4$1, and (c) PANi-pot0.1

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TABLE II
Molecular Weight Distribution Results for the Representative Samples PANi-pTS1, PANi-ClO$_4$1, and PANi-pot0.1

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Mx	PANi-pTS1		PANi-ClO$_4$1		PANi-pot0.1	
	Mx values	D. P.*	Mx values	D. P.*	Mx values	D. P.*
Mp	1912	21	1276	14	1729	19
Mn	1567	17	822	9	1032	11
Mw	2163	24	1643	18	1935	21
Mz	2813	31	2278	25	5592	61
Mz + 1	3761	41	3281	36	15871	174
Mv	2077	23	1458	16	1715	19
P. D.	1.380		1.240		1.875	
P. A. (A. U.)	435027		412596		78135	

* Molecular weight of repeat unit (C$_6$H$_5$N) has been taken as 91.13.

and PANi-pot0.1 can be ascribed to the electronic like absorption of Q = NH$^+$-B or B-NH$^+$-B[11] (Q—Quinoid form of benzene ring, B—Benzenoid form of benzene ring), whereas the peaks at 1194.0, 1194.3, and 1194.0 cm^{-1} in the respective spectra of PANi-pTS1, PANi-ClO$_4$1, and PANi-pot0.1 can be assigned to the N = Q = N stretching vibrations.[12] The small size of the peak at 1140.8 cm^{-1} is due to the small degree of electron delocalization,[12] which was expected because of the smaller degree of polymerization and oxidation as compared to standard PANi, for which the peak is broad, showing extensive delocalization. The peak at 1103.0 cm^{-1} in the spectra of PANi-pTS1 is seen to have split into two and is observed at 1111.6 cm^{-1} and 1113.9 cm^{-1} in the spectra of PANi-ClO$_4$1 and PANi-pot0.1, respectively, and can be assigned to C-H i/p on the 1,2,4 ring,[11] which shows that chlorination is occurring at the *ortho* positions on the aromatic ring. This is also consistent with the high Cl/N ratios, suggesting that more chlorination is occurring as the oxidant concentration is reduced.

It is to be noted that, as the rate of reaction increases, chlorination on the ring decreases. Although there is substitution occurring, it seems that the polymerization is occurring at the *para* position only and chlorination is occurring at the *ortho* position. This is confirmed by ^{1}H-NMR studies, as reported earlier where it is seen that head to tail coupling is occurring. Thus, FTIR studies confirm the formation of substituted oligo-polyanilines even by the use of weaker oxidizing agents in low concentrations and concentrated HCl.

GPC studies

Gel Permeation Chromatography of the samples was carried out by dissolving 1% wt/vol of solid in HPLC grade N,N dimethylformamide (DMF). The solution obtained was filtered through a Phenomenex PP filter paper having pore size of 4μ, and then

about 100μL was injected into the column. GPC results are shown, for the sample prepared with the lowest concentrations of the oxidants as representative, in Table II. The table shows a narrow distribution of molecular weights (polydispersity = 1.380 and 1.240) for PANi-pTS1 and PANi-ClO$_4$1, respectively, while it shows a broader distribution of molecular weights (polydispersity = 1.875) for PANi-pot0.1. The polydispersity value is always higher than 1 for polymers; and the closer the value of polydispersity to 1, the narrower is the distribution of molecular weight.[7] This confirms that, even at very low concentrations of weaker oxidants (as compared to ammonium persulphate) with respect to aniline, polymerization takes place. Unlike in the sample prepared with 1% APS,[5] where the presence of a smaller peak at shorter elution time is seen (showing that higher molecular weight PANis, that is, with a higher degree of polymerization, is also present), these samples show only one peak in the chromatographs.

Table II lists the values of the different molecular weights obtained for the three samples. From Table II it can be seen that the molecular weight distribution ranges from a minimum of 17 repeat units to about 41 repeat units for PANi-pTS1, while the molecular weight distribution ranges from a minimum of 9 repeat units to about 36 repeat units for PANi-ClO$_4$1, and for PANi-pot0.1 it ranges from 11 to 174. This proves the idea that, for a catalytically initiated reaction, the molar ratio of the catalyst need not be equal to that of the monomer as in many organic reactions. This also suggests that very low concentrations of weaker oxidants are sufficient to initiate polymerization of aniline. From the molecular weights and their distribution results, one can say that these samples are mainly oligo-polyanilines. This shows that different degrees of polymerization can be achieved by varying the oxidants and their concentrations. The difference may be due to the
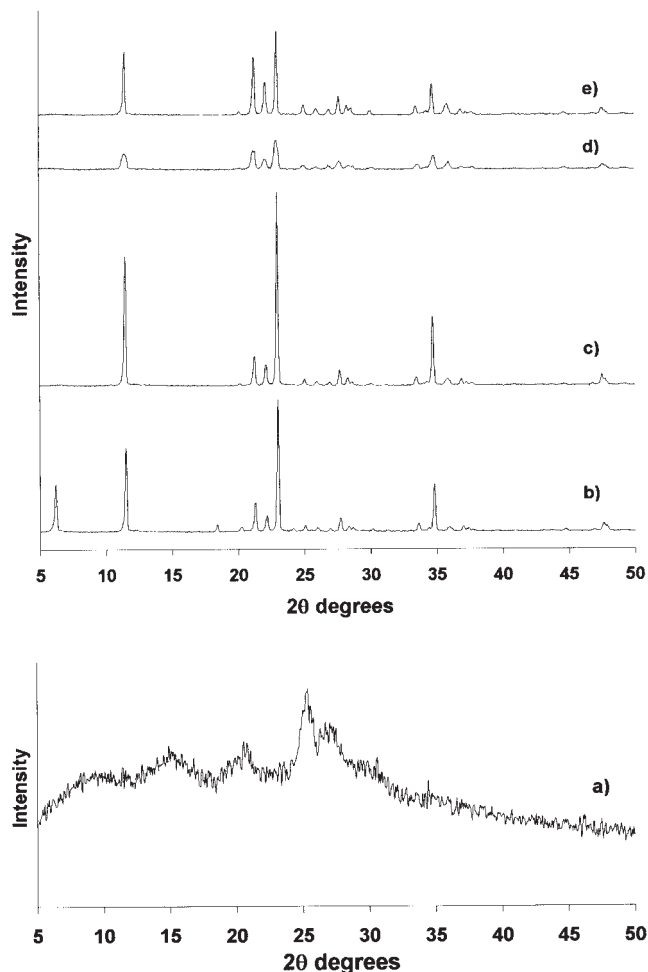
Figure 2 XRD patterns of (a) PANi-Std, (b) PANi-aps1, (c) PANi-pTS1, (d) PANi-ClO$_4$1, and (e) PANi-pot0.1.

class of oxidants, namely, organic, inorganic, and coordination complex, respectively.

Thus, the elemental analysis, FTIR, and GPC results show that the use of even low concentrations of weaker oxidizing agents leads to crystals of substituted oligo-polyanilines.

X-ray diffraction studies

The percentage crystallinities calculated for these samples were found to be 87–97%. It may be noted that, in comparison to the crystals obtained using ammonium persulphate, these crystals have slightly lower crystallinity, but nevertheless, very high percentage crystallinity as compared to PANi prepared by the standard method.

X-ray diffractograms of oligo-PANi prepared using APS by our procedure and with pTS-Na, LiClO$_4$, and K$_3$[Fe(CN)$_6$] are depicted in Figure 2. In general, the XRD peaks are similar except the peak at $2\theta = 6°$

that is present in oligo-PANi prepared using APS. Even in the various samples with different percentages of APS, it was found that this peak at 6° could be correlated to a higher degree of polymerization. The most important point to be noted here is that neither in the standard method of polymerization of aniline nor in the lower concentrations of oxidants did we observe the diffraction peak at 6° corresponding to d = ~ 14 Å. As the normality of acid is raised from 1N in the standard method to 11.3N in our procedure, we have reason to believe that the chlorine substitution also occurs on the ring leading to substituted oligo-polyanilines; these have higher crystallization behavior with extended chains, which cannot be fitted into the conventional model for pure PANi. A detailed analysis based on this concept is being communicated.[13]
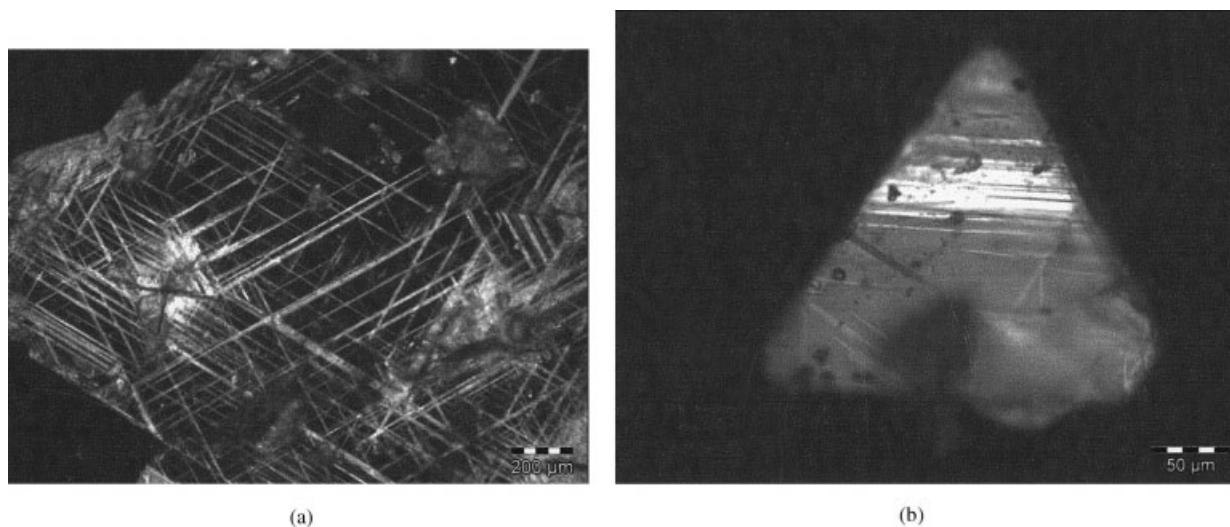
Optical microscopic studies

The optical micrographs (Figs. 3–5) show that the crystals are flaky plate-like with overgrowths, thereby making it polycrystalline. On the surface of the crystals, many tiny flakes originating all over and growing further were observed.

PANi-pTS—There is no definite growth feature at high concentrations of pTS but thin platelet-like formations are visible. When seen under cross polar, a large number of parallel rod-like lines are visible (Fig. 3a). The width of these lines is about 3.54 μm to 31.32 μm, with the mean width being 10.74 μm. At lower concentrations, occasionally the growth habit is triangular platelet-like in shape (Fig. 3b). The length of the triangular flakes is about 234.65 μm and varies between 226.68 μm to 241.83 μm.

PANi-ClO$_4$—No triangular growth was observed (Fig. 4). Many small crystals grow, and the shape of a single crystal looks like an elongated parallelogram. Many rod-like structures are also seen, with the width or thickness about 3.54 μm to 23.72 μm, the average value being 8.32 μm. From Figure 4 it can be clearly seen that there are many layers of lamellae growing one over the other, resulting in thicker and polycrystalline samples. With lower concentrations of LiClO$_4$, the growth habit is again like a parallelogram (rather than triangular), and the length of the sides varies between 166.68 μm to 250.77 μm. There are no rod-like straight line structures. Under cross polar, some black particles or patches are seen.

PANi-pot—More like triangular crystal growth. These triangles have their sides varying in length between 113.64 μm to 1236.96 μm, with the mean value being 435.89 μm. The crystal has a non-uniform appearance, with regions that are transparent and nontransparent (Fig. 5). This nontransparency may result from thicker regions or deeper blue color on account of polymerization.

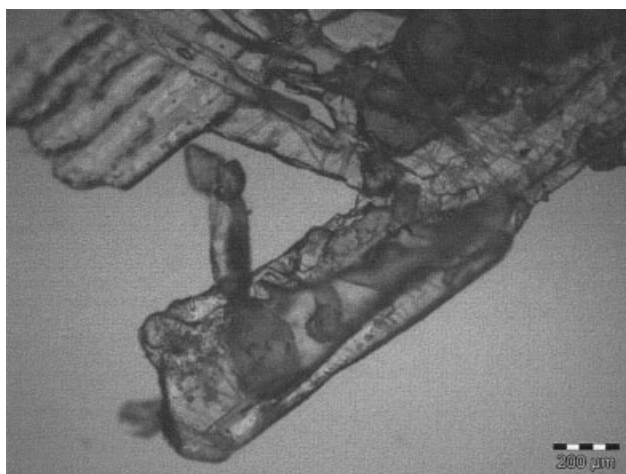**Figure 3** Optical microscope images of substituted oligo-polyaniline crystals (PANi-pTS).

Thus, from the optical microscopic studies, it can be seen that, even though the morphology varies with the oxidant and their concentration, these are all basically flaky in nature. It might be noted that the substituted oligo-polyanilines obtained using APS also were flaky in nature.

CONCLUSION

This study shows that the polymerization and crystallization of aniline can be achieved in a single step at room temperature using novel oxidants at very low concentrations. The resultant material is highly crystalline substituted oligo-polyanilines having a flaky plate-like growth. An important outcome of this study, in conjunction with that reported earlier, is that, by controlling the amount of oxidant, the molecular weight distribution, degree of oxidation, and degree of crystallinity can be controlled, and hence the properties of the crystals. The studies indicate that the use of even weaker oxidants, like pTS-Na, $LiClO_4$, and $K_3[Fe(CN)_6]$, can bring about simultaneous polymerization and crystallization of aniline as we observed earlier using APS.

Figure 4 Optical microscope image of substituted oligo-polyaniline crystals (PANi-ClO_4).
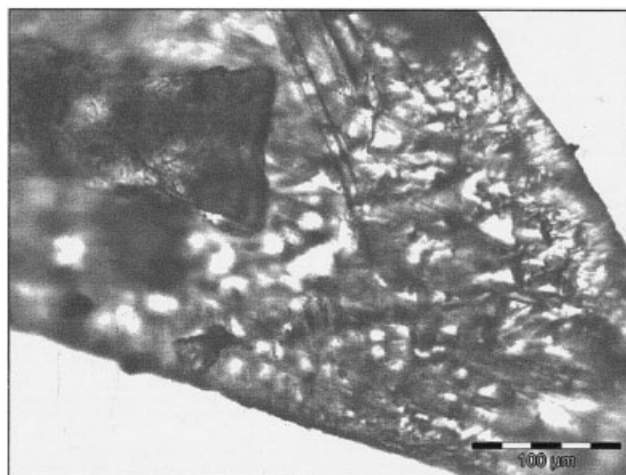
Figure 5 Optical microscope image of substituted oligo-polyaniline crystals (PANi-pot).

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