

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Investigation of Spectroscopic and Thermal Properties of Poly(o-toluidine) Doped with Polymeric Acids

Milind V. Kulkarni<sup>a</sup>; Annamraju Kasi Viswanath<sup>a</sup>; P. K. Khanna<sup>a</sup>

<sup>a</sup> Photonics and Advanced Materials Laboratory, Center for Materials for Electronics Technology (C-MET), Pune, India

**To cite this Article** Kulkarni, Milind V. , Viswanath, Annamraju Kasi and Khanna, P. K.(2006) 'Investigation of Spectroscopic and Thermal Properties of Poly(o-toluidine) Doped with Polymeric Acids', Journal of Macromolecular Science, Part A, 43: 1, 197 – 203

**To link to this Article:** DOI: 10.1080/10601320500406073

**URL:** <http://dx.doi.org/10.1080/10601320500406073>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Investigation of Spectroscopic and Thermal Properties of Poly(*o*-toluidine) Doped with Polymeric Acids

MILIND V. KULKARNI, ANNAMRAJU KASI VISWANATH,  
AND P. K. KHANNA

Photonics and Advanced Materials Laboratory, Center for Materials  
for Electronics Technology (C-MET), Panchawati, Pune, India

*Single step polymerization of poly(o-toluidine) was carried out by using ammonium persulphate as an oxidizing agent. Formation of the conducting emeraldine salt phase of the polymer was confirmed by the UV-visible and FT-IR spectroscopic analysis. The elemental composition of the polymer was evaluated by using a CHNS analyzer. Thermal stability of these polymers was investigated by the thermogravimetric analysis. Among the three polymeric acids used for doping purposes, poly(acrylic acid) doped material was found to show less thermal stability compared to poly(styrene sulphonic acid) and poly(vinyl sulphonic acid) doped poly(o-toluidine).*

**Keywords** polymers, chemical synthesis, spectroscopy, thermal stability

## Introduction

Electroactive polymers have attracted a great deal of attention during the past decades because of their unusual electrical/electronic properties. Among them, polyaniline is one of the best candidates for various technological applications due to its moderately high conductivity, good environmental stability and facile synthesis process (1–4). However, it has been observed in recent investigations that, the substituted derivatives of polyaniline could also serve as a good alternative for unsubstituted polyaniline with comparable conductivities.

Polymerization of aniline derivatives has been widely investigated for the improvement of processability and other properties of conductive polyaniline. The use of some aniline derivatives causes improvements in some of the physical and chemical characteristics, such as stability and solubility. A good conductivity could be achieved when polyaniline is doped or protonated with acids like HCl, H<sub>2</sub>SO<sub>4</sub>, or some organic sulphonic acids. Also, there has been many reports on the use of polymeric acid dopants for polyaniline (5–8). However, little attention has been given to the substituted

Received November 2004; Accepted June 2005.

Address correspondence to Annamraju Kasi Viswanath, Photonics and Advanced Materials Laboratory, Center for Materials for Electronics Technology (C-MET), Panchawati, Off Pashan Road, Pune 411 008, India. Tel.: 91-020-25898390, 25899273; Fax: 91-020-25898085, 25898180; E-mail: v\_kasi@hotmail.com

derivatives of polyaniline synthesized using polymeric acid dopants. We have taken up a systematic investigation of conducting polymers (9–14) and polymers doped with suitable molecules for the development of humidity sensors (15–17).

In the present work, we have synthesized poly(*o*-toluidine) doped with polymeric acids [like poly(styrene sulphonic acid) PSSA, poly(vinyl sulphonic acid) PVSA, and poly(acrylic acid) PAA] by the chemical oxidative polymerization method. The physico-chemical properties of the polymers were investigated by studying their spectroscopic and thermal analysis. The effects of the substituent on the properties of the polymer are also discussed.

## Experimental

All chemicals used were of Analytical reagent (AR) grade and used as received. The polymerization of the monomer, (*o*-toluidine) was initiated by the dropwise addition of the oxidizing agent (ammonium persulphate) in an acidified solution prepared using doubly distilled water under constant stirring at 0–5°C. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 24 h. The precipitated polymer was filtered and washed with distilled water until the filtrate was colorless. Finally, the polymer was dried in an oven at 70°C for 12 h.

The UV-visible spectra of the polymer solution in *m*-cresol were recorded by using a Hitachi-U3210 spectrophotometer in the range of 300–900 nm. FT-IR spectra of the polymer were taken on a Perkin-Elmer-Spectrum 2000 spectrophotometer between 400–4000 cm<sup>-1</sup>. The samples were prepared in the pellet form using spectroscopic grade KBr powder. The elemental composition of the material was estimated by using a CE Instruments EA-1110 CHNS analyzer. A thermogram of the polymer sample was recorded using a Mettler-Toledo 851 thermogravimetric analyzer in the presence of N<sub>2</sub> atmosphere from RT to 900°C at a heating rate of 10°C/min.

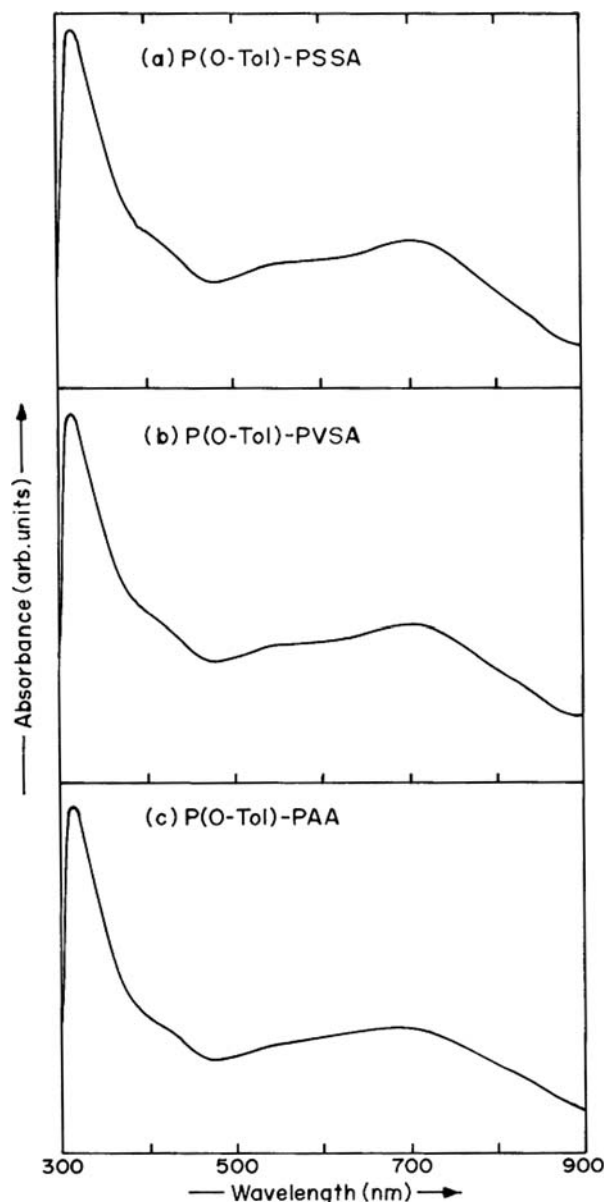
## Results and Discussion

Figure 1(a–c) shows the optical absorption spectra of poly(*o*-toluidine) synthesized by using different polymeric acids. The spectra were recorded by using *m*-cresol as a solvent. As seen from the figure, in *m*-cresol, all three polymers exhibit a strong peak at 320 nm and a broad peak at 720 nm, together with small shoulders at 420 nm and 540 nm.

The sharp peak at 320 nm corresponds to the  $\pi$ - $\pi^*$  transition of the benzenoid rings, while, the broad peak at 720 nm is due to the conducting emeraldine salt phase of the polymer. The absorption band appearing as a shoulder at 420 nm can be assigned to the localized polarons, which is characteristic of the protonated polyaniline, whereas the shoulder at 540 nm represents the insulating pernigraniline phase of the polymer (18, 19).

In poly(*o*-toluidine), the bands in UV-visible spectra, corresponding to the different oxidation states of the polymer, are found to appear at a shorter wavelength as compared with polyaniline. This blue shift in the optical bands can be attributed to the different molecular orientations and to the decrease of conjugation in the polymer chains.

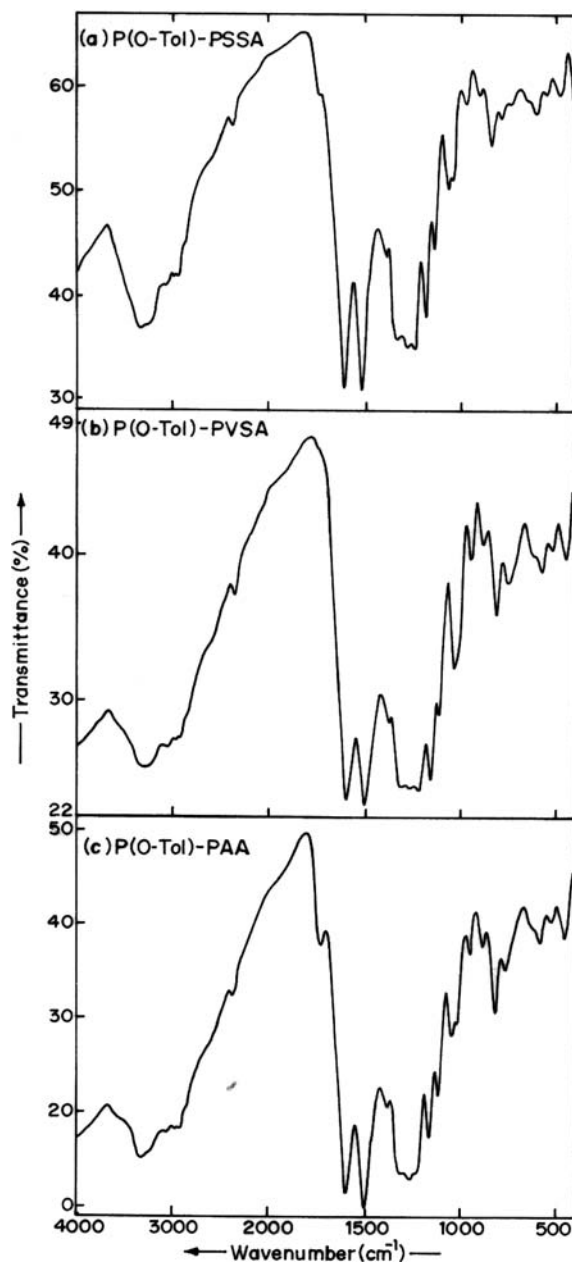
It has been reported in the literature that not only the electronic effect of the methyl substituent is responsible for the blue shift of the absorption maxima, but also the steric effect, the electronic effect of the substituent must also be taken into account (20). Bredas et al. (21) have reported that the presence of some substituents can induce some



**Figure 1.** UV-Visible spectra of poly(*o*-toluidine) doped with a) PSSA, b) PVSA, and c) PAA.

non-planar conformations that decrease the conjugation length and hence, the blue shift in the absorption spectra. The presence of different bands in the spectrum clearly shows that the polymer is composed of different oxidation states (insulating and conducting phase) of the polymer.

Figure 2(a–c) represents the FT-IR spectra of the poly(*o*-toluidine) doped with polymeric acids, and the peak locations related to the corresponding chemical bonds are listed in Table 1. The key bands observed from the figure, as well as from Table 1, are in good agreement with the IR frequencies of poly(*o*-toluidines) (22, 23).



**Figure 2.** FT-IR spectra of poly(o-toluidine) doped with a) PSSA, b) PVSA, and c) PAA.

The presence of strong bands corresponding to quinoid and benzenoid ring and the bands for the dopant ion clearly indicate the formation of a conducting emeraldine salt phase of the polymer and supports the UV-visible spectroscopic results.

Table 2 represents the % composition of the various elements (viz. C, H, N and S) present in the polymer. The presence of sulphur in PSSA and PVSA doped

**Table 1**  
Characteristic frequencies of chemically synthesized polymeric acid doped poly (o-toluidine)

Wavenumber (cm <sup>-1</sup> )			Band characteristics
PSSA	PVSA	PAA	
577.26	574.96	575.341	C–H out of plane bending vibration
750.24	750.23	—	SO <sub>3</sub> <sup>-</sup> attached to the aromatic rings
813.21	823.16	812.48	Paradisubstituted aromatic rings indicating polymer formation
875.57	879.26	879.21	Due to the methyl group attached to the phenyl ring
1113.69	1115.20	1111.23	C–H in plane bending vibration
1158.69	1157.46	1156.67	Vibration band of the dopant anion
1212.91	1219.83	1268.03	$\nu$ (C–N) in QB <sub>c</sub> Q, QBB and BBQ
—	—	1407.03	$\delta$ (OH) + $\nu$ (C–O) of COOH
1499.74	1498.72	1497.22	$\nu_s$ (CO <sub>2</sub> ) of carboxylate group
1592.22	1591.21	1592.46	C–N stretching of benzenoid rings
—	—	1716.12	C–N stretching of quinoid rings
2350.74	2354.24	2354.18	$\nu$ (C=O) of polyacrylic acid
2925.37	3033.21	2966.78	$\nu$ (N–H) <sup>+</sup> unsaturated amine
3334.98	3250.91	3330.75	C–H stretching due to substituent methyl group
			>N–H stretching vibration

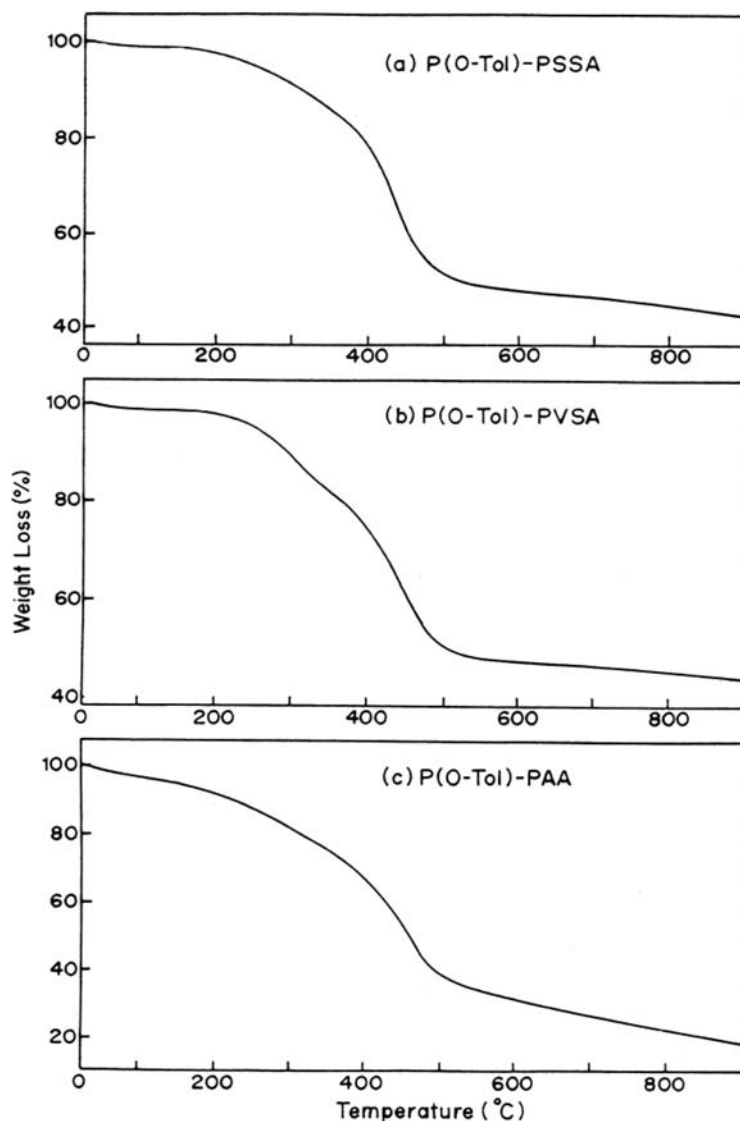
poly(o-toluidine) confirms the efficient doping of the iminic nitrogen atom of the polymer, which is responsible for the conducting phase of the polymer.

Figure 3(a–c) displays the thermal profiles of poly(o-toluidine) doped with polymeric acids. They exhibit a typical three-step decomposition pattern similar to the thermal degradation of HCl doped poly(o-toluidine). The first step starting almost from room temperature and going up to 130°C, corresponds to the expulsion of water molecules from the polymer matrix. The second step, from 220°C to 270°C is associated with the elimination of the dopant (dedoping) and degradation of the small chain fragments. The third step, starting from 270°C onwards, represents the degradation and decomposition of the polymer backbone. This kind of TGA pattern is generally observed in substituted polyanilines (24, 25).

On comparison, among the thermograms for the three different polymeric acids, it is observed that, in the case of polyacrylic acid doped poly(o-toluidine), more weight

**Table 2**  
Elemental composition of the poly(o-toluidine) doped with polymeric acids

Polymer	%C	%H	%N	%S
P(o-tol)-PSSA	64.15	5.73	8.76	2.68
P(o-tol)-PVSA	64.37	5.80	9.64	3.34
P(o-tol)-PAA	66.60	5.78	9.42	—



**Figure 3.** Thermograms of poly(*o*-toluidine) doped a) PSSA, b) PVSA, and c) PAA.

loss is observed in the first step of weight loss than that of PSSA and PVSA doped poly(*o*-toluidine). However, the second step loss associated for the dedoping is very slow and extending over a broad temperature range in the case of PSSA doped poly(*o*-toluidine). On the other hand, a very rapid and fast weight loss is observed in the PVSA and PAA doped polymer. In PSSA and PVSA, 50% wt loss is observed up to 520°C, while, in poly(acrylic acid) doped polymer 50% wt loss is observed only up to 460°C, indicating the less thermal stability of the poly(acrylic acid) doped material compared to PSSA and PVSA doped poly(*o*-toluidine). This could be due to the less thermal stability of polyacrylic acid moiety, which undergoes fast thermal decomposition at a very early temperature range.

## Conclusions

From the spectroscopic (UV-vis. and FT-IR studies) it is observed that the presence of conducting emeraldine salt phase of the polymer, confirms that the polymeric acids efficiently dope the iminic nitrogen site of the poly(o-toluidine). Thermal properties are also found to be affected by the nature of the dopant ions. Among the three acids used for the doping purpose, poly(o-toluidine) doped with PSSA and PVSA shows good thermal stability. Where as, poly(acrylic acid) doped material is found to be less thermally stable.

## References

1. Skotheim, T.J. (ed.) (1986) *Handbook of Conducting Polymers*; Marcel Dekker: New York.
2. Syed, A.A. and Dinesan, M.A. (1991) *Talanta*, 3 (8): 815.
3. Patil, A.O., Heeger, A.J., and Wudl, F. (1988) *Chem. Rev.*, 88: 183.
4. Roncali, J. (1992) *Chem. Rev.*, 92: 711.
5. Shannon, K. and Fernandez, J.E. (1994) *J. Chem. Soc. Chem. Commun.*, 643.
6. Orata, D. and Buttry, D.A. (1988) *J. Electroanal. Chem.*, 257: 71.
7. Hwang, J.H. and Yang, S.C. (1989) *Synth. Met.*, 29: E271.
8. Liu, J.M. and Yang, S.C. (1991) *J. Chem. Soc. Chem. Commun.*, 1529.
9. Kulkarni, M.V. and Viswanath, A.K. (2004) *European Polymer Journal*, 40: 379.
10. Kulkarni, M.V., Viswanath, A.K., Marimuthu, R., and Seth, T. (2004) *Polymer Engineering and Science*, 44: 1676.
11. Kulkarni, M.V., Viswanath, A.K., Marimuthu, R., and Seth, T. (2004) *J. Polymer Science A: Polymer Chemistry*, 42: 2043.
12. Kulkarni, M.V., Viswanath, A.K., and Mulik, U.P. (2005) *Materials Chemistry and Physics*, 89: 1.
13. Kulkarni, M.V., Viswanath, A.K., Marimuthu, R., and Mulik, U.P. (2004) *Journal of Materials Science: Materials in Electronics*, 15: 781.
14. Kulkarni, M.V. and Viswanath, A.K. (2004) *Journal of Macromolecular Science, Part A, Pure and Applied Chemistry*, 41: 1173.
15. Somani, P.R., Viswanath, A.K., Aiyer, R.C., and Radhakrishnan, S. (2001) *Sensors and Actuators B*, 80: 141.
16. Somani, P.R., Viswanath, A.K., Aiyer, R.C., and Radhakrishnan, S. (2001) *Novel Organic Electronics*, 2: 83.
17. Somani, P.R., Marimuthu, R., Viswanath, A.K., and Radhakrishnan, S. (2003) *Polymer Degradation and Stability*, 79: 77.
18. Athawale, A.A., Kulkarni, M.V., and Chabukswar, V.V. (2002) *Mater, Chem. and Phys.*, 73: 106.
19. Athawale, A.A., Deore, B.A., and Kulkarni, M.V. (1999) *Mater, Chem. and Phys.*, 60: 262.
20. D'Apramo, G., Leclerc, M., and Zotti, G. (1993) *J. Electroanal. Chem.*, 351: 145.
21. Bredas, J.L., Street, G.B., Themans, B., and Andre, J.M. (1985) *J. Chem. Phys.*, 83: 1323.
22. Palaniappan, S. and Narayana, B.H. (1994) *J. Polym. Sci. A Polym. Chem.*, 32: 2431.
23. Hu, H., Cadenas, J.L., Saniger, J.M., and Nair, P.K. (1998) *Polym. Int.*, 45: 262.
24. Malmonge, L.F. and Mattoso, L.H.C. (2000) *Polymer*, 41: 8387.
25. Patil, S.F., Bedekar, A.G., Patil, R.C., and Agashe, C. (1994) *Ind. J. Chem.*, 33A: 580.