

Thermal Analysis of Chemically Synthesized Polyemeraldine Base

S. S. PANDEY,* MANJU GERARD, AMIT L. SHARMA, B. D. MALHOTRA

Biomolecular Electronics and Conducting Polymer Research Group, National Physical Laboratory,
Dr. K. S. Krishnan Road, New Delhi 110012, India

Received 26 June 1998; accepted 4 June 1999

ABSTRACT: Thermal characteristics of chemically synthesized polyemeraldine base have been experimentally investigated using differential scanning calorimetry and thermogravimetric analysis (TGA), UV-visible, and Fourier transform IR techniques, respectively. Results of the TGA measurements have revealed that the chemically synthesized emeraldine base is thermally stable upto about 400°C. The effect of temperature on time taken for crosslinking in the polyemeraldine base has also been studied. Analysis of reaction kinetics of crosslinking in polyemeraldine base reveals that a pseudo first-order thermodynamic reaction occurs in this conducting polymer.
© 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 149–155, 2000

Key words: polyaniline; polyemeraldine base; differential scanning calorimetry; thermogravimetric analysis; crosslinking

INTRODUCTION

Recent years have seen increased interest in the research and development of conducting polymers. This has been attributed to the many technological applications of conducting polyanilines such as solid-state light-weight rechargeable batteries, electrochromic displays, solid-state electronic devices, and sensors.^{1–2} Among the various organic conducting polymers, polyaniline has attracted the maximum attention because of its high electrical conductivity and interesting redox properties associated with the presence of a nitrogen heteroatom in the main polymeric backbone

wherein the lone pair of heteroatom is in conjugation with the π electrons of the polymeric chain.³ The commercial utilization of conducting polyaniline has been closely linked with the thermal, electrical, and environmental stability of this organic electronic material.^{4–6}

Many reports on electrochemical stability and thermal degradation of conducting polyanilines have recently been published.^{7–16} Yue et al. have shown that the sulphonation of polyaniline results in increased thermal stability of the parent polyaniline.⁷ Rodrigue et al. have reported the results of their interesting photoelectronic and spectroscopic studies on the oxygen exposure dependence and thermal treatment of electronic structure of polyaniline.⁸ Lacroix and Diaz¹² have proposed that thermal decomposition of polyaniline occurs in two stages. The first stage is attributed to the loss of moisture whereas the second stage is associated with the breakdown of polymer backbone. Patil et al. have proposed a three-step sequence for the thermal degradation of doped polyaniline.¹⁵ Noeh et al. have shown that the emeraldine base of polyaniline is stable up to

* Present address: Department of Computer Science and Electronics, Kyushu Institute of Technology, Iizuka, Fukuoka 820, Japan.

Correspondence to: B. D. Malhotra (bansi@csnpl.ren.nic.in).

Contract grant sponsor: European Economic Community; contract number: CT I*-CT-92-0102.

Contract grant sponsor: India–U.S. Fund; contract grant number: DST/INT/US/404/93.

Journal of Applied Polymer Science, Vol. 75, 149–155 (2000)

© 2000 John Wiley & Sons, Inc.

CCC 0021-8995/00/010149-07

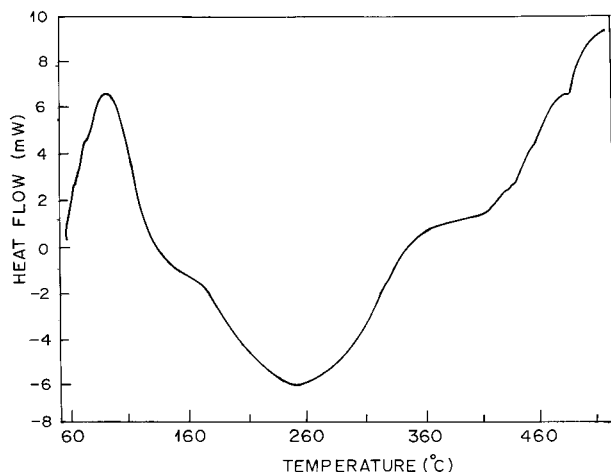


Figure 1 A DSC thermogram of chemically prepared polyemeraldine base.

about 500°C.¹⁷ Fossong et al. have observed an increase in the crystallinity in the polyemeraldine base when its temperature is increased to 150°C.¹⁸

In this paper, we report the results of our thermal studies undertaken on the chemically synthesized polyemeraldine base using differential scanning calorimetric (DSC), thermal gravimetric analysis (TGA), UV-visible, and Fourier transform IR (FTIR) techniques, respectively. Attempts have also been made to delineate the reaction kinetics of thermal processes like crosslinking and thermal degradation of the polymeric backbone of the polyemeraldine base.

EXPERIMENTAL

Polyaniline was chemically synthesized by oxidative polymerization of aniline using ammonium perdisulphate as an oxidant. Distilled aniline (0.2M) was dissolved in 300 mL of 1.0M HCl pre-cooled at 5°C. Oxidant was gradually added to this solution at 1.0 mL/min. The dark green precipitate resulting from this reaction was washed repeatedly with 1M HCl until the green color disappeared. This precipitate was further extracted with tetrahydrofuran using a soxhlet extractor and was dried under dynamic vacuum.

The thermal characterization was performed using a Perkin-Elmer DSC-7. The measurements were conducted up to 500°C at a heating rate of 20°C/min in inert (nitrogen) atmosphere. Kinetic calculations were performed using the kinetic software available with the Perkin-Elmer DSC-7.

For thermogravimetry studies, the Mettler (TA 3000) system was used. Ten milligrams of sample was heated at a rate of 15°C/min and the TGA thermogram was recorded up to 800°C in nitrogen atmosphere. UV-visible spectra on different annealed samples of the emeraldine base were recorded using a Shimadzu (Model 160 A) spectrophotometer. FTIR measurements on annealed and unannealed samples of emeraldine base were conducted on a Nicolet FTIR (Model 510 P). The results of the electrical conductivity measurements carried out using the four-point probe method indicate the value of the electrical conductivity of undoped polyaniline (polyemeraldine base) as 3.27×10^{-10} S/cm.

RESULTS AND DISCUSSION

A DSC thermogram (Figure 1) obtained for a chemically synthesized polyemeraldine base sample shows an endothermic peak at 100°C and an exothermic peak at 250°C. The peak seen at 100°C is attributed to the loss of water. The 250°C exothermic peak may arise either due to the polymer chain degradation or to the interchain crosslinking. To confirm the phenomenon of crosslinking, detailed TGA studies on the chemically synthesized polyemeraldine base have been performed. A typical TGA thermogram obtained for the polyemeraldine base has been shown in Figure 2. It can be seen (Fig. 2) that about 4% weight loss occurs between 30 and 125°C whereas the weight loss of 3% is found between 125 and 400°C. As soon as the sample crosses 400°C, there is a tremendous weight loss of about 35%. Such a weight loss can be attributed to the degradation of

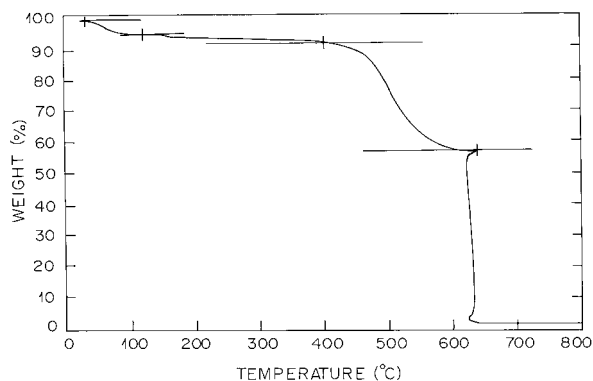


Figure 2 A TGA thermogram obtained for a chemically prepared polyemeraldine base.

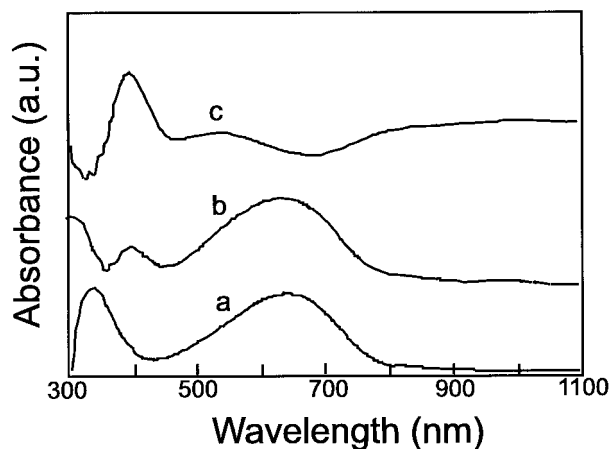


Figure 3 UV-visible spectra obtained in NMP solution on different 250°C annealed (curve a, 5 min; curve b, 20 min; curve c, 50 min) samples of a chemically prepared polyemeraldine base.

polyemeraldine base. The small weight loss observed in the temperature range of 125–400°C can be assigned to crosslinking of chains in the polyemeraldine base. In the light of these results, it can be inferred that polyemeraldine remains thermally stable up to about 400°C. To further confirm the hypothesis of crosslinking, the polyemeraldine base was heated at 300°C in a vacuum oven for about 50 min after which a DSC thermogram was recorded. Interestingly, the resulting DSC thermogram showed the absence of the 250°C exothermic peak, suggesting that the crosslinking in the polyemeraldine base has been completed.

To experimentally investigate the structural changes resulting from crosslinking, we have performed the UV-visible studies on the chemically synthesized polyemeraldine base when it is annealed in vacuum oven at 250°C for different durations of time. Typical electronic absorption spectra recorded in the N-methyl pyrrolidone (NMP) solution on some of the annealed (5, 20, and 50 min) samples of the polyemeraldine have been shown in Figure 3. It can be seen that there is a dramatic decrease in the peak intensity around 630 nm associated with the $n - \pi^*$ transition. Besides this, a new peak begins to develop after about 700 nm. This new peak has been attributed to the free carrier absorption in the doped polyemeraldine film. The doping of the polyemeraldine base occurs due to the thermal deprotonation of its aromatic ring in the polymer chain crosslinking it to the imine nitrogen. The proportion of the tertiary nitrogen atoms in-

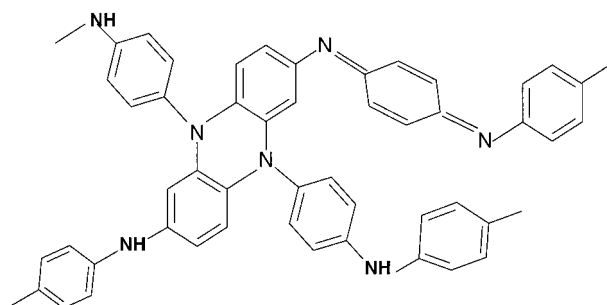


Figure 4 Tentative structure of a chemically prepared crosslinked polyemeraldine base.

creases with the degree of crosslinking. It appears that this thermal deprotonation is likely to dope some of the imine nitrogen in the polyemeraldine base chain resulting in the observed free carrier absorption (Fig. 3). The observed decrease in the value of the electrical conductivity coupled with the decreased insolubility of the annealed polyemeraldine base sample is consistent with these results. The tentative structure of the uncrosslinked and crosslinked (doped) emeraldine base has been shown in Figure 4. In the light of these results, it can be concluded that the inter-chain crosslinking (Fig. 5) in the annealed polyemeraldine base results in the increased dimensionality (from one to two/three). Such a type of thermal crosslinking has also been investigated by Rodrigue et al. using XPS technique.⁸

Results of the FTIR measurements undertaken on unannealed (curve a) and 250°C annealed (50 min, curve b) samples of chemically prepared polyemeraldine base under vacuum have been

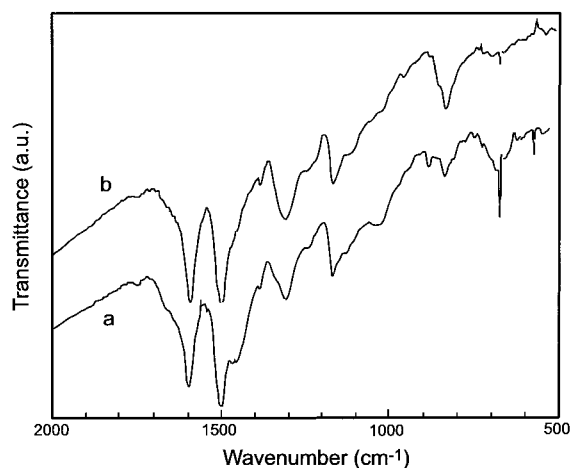


Figure 5 FTIR spectra of a unannealed and annealed chemically synthesized polyemeraldine base.

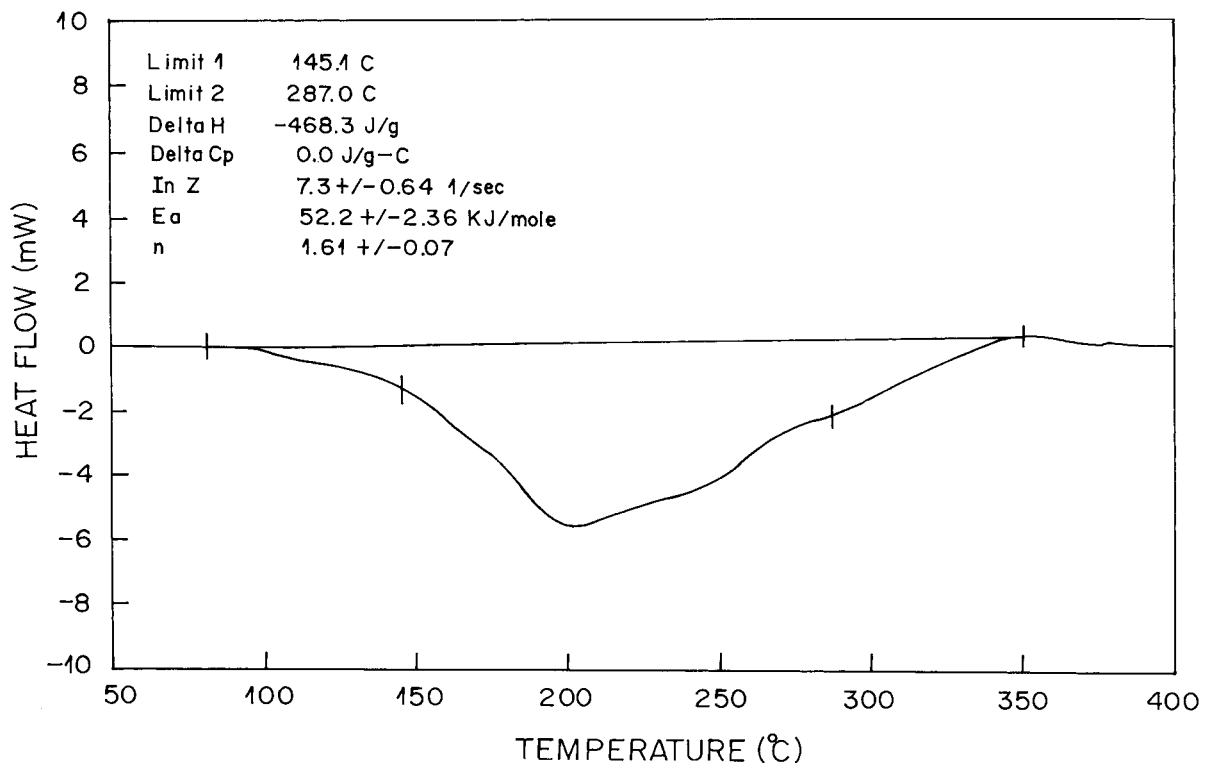


Figure 6 Reaction kinetics of crosslinking in a chemically prepared polyemeraldine base.

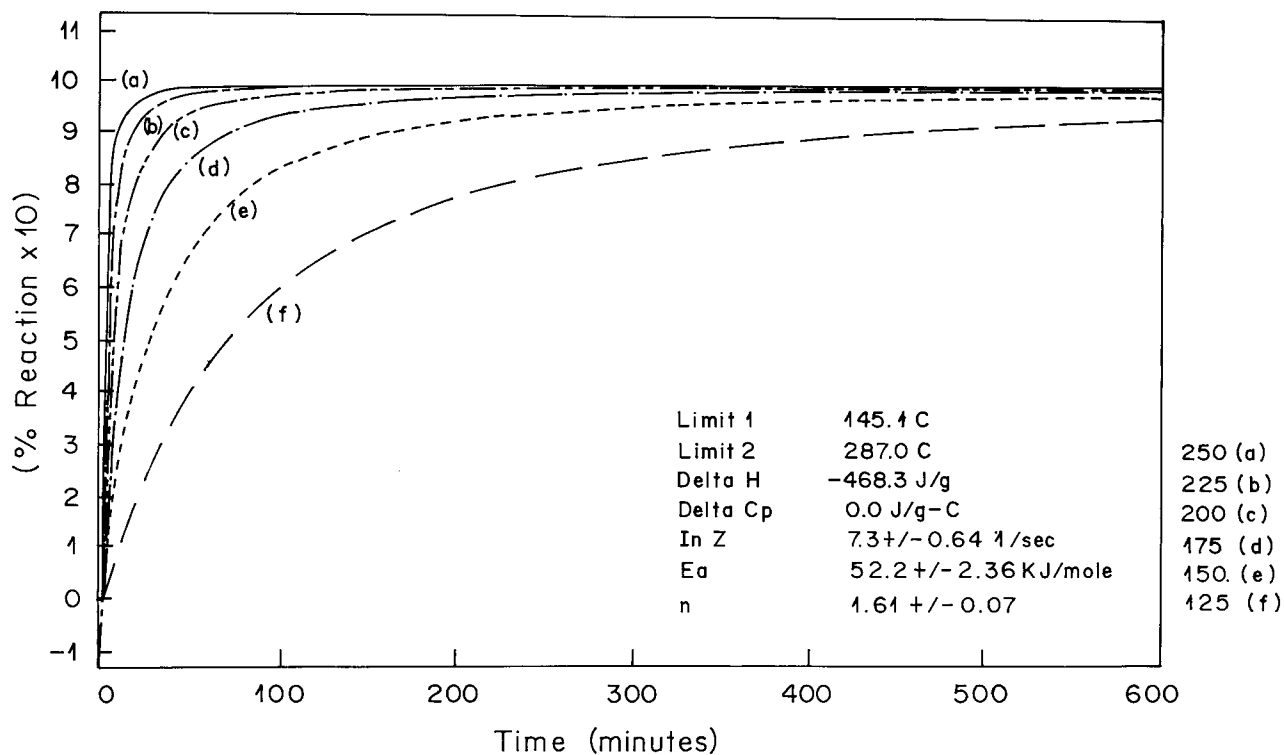


Figure 7 Percentage of crosslinking as a function of time at various temperatures in chemically synthesized polyemeraldine base.

Table I Effect of Temperature (°C) on Crosslinking Time (s) for 90% Conversion of a Chemically Synthesized Polyemeraldine Base

Temperature (°C)	Time Taken for 90% Conversion (s)
125	30,000
150	9840
175	4440
200	2057
225	1028
250	343

shown in Figure 5. The 1500 and 1300 cm^{-1} vibration bands have been associated with the C=C (benzenoid ring) and C—N group of tertiary nitrogen in the structure of the polyemeraldine base (Fig. 5). It is envisaged that the imine nitrogen atoms in polyemeraldine get linked to the carbon atoms of benzene ring (Fig. 4) resulting in the increase in the tertiary nitrogen atoms in the polyemeraldine chain. This is likely to result in the increase in the relative proportion of the benzenoid ring as compared to the quinoid ring as a

function of extent of crosslinking brought by thermal annealing. This will lead to further increase in the relative ratio of C—N and C=N groups in the crosslinked polyemeraldine base. These results are in agreement with the observed decrease in the relative peak area of the 1500 and 1300 cm^{-1} peaks (Fig. 5) with increased annealing time indicating the higher dimensionality in the polyemeraldine base as indicated earlier.

It is significant to note that Wei et al.²⁰ have recently reported the crosslinking in polyaniline and observed a pronounced redox peak at 0.5 V vs Standard Calomel Electrode (SCE) after annealing the emeraldine base at 300°C. This redox peak has been associated with the oxidative degradation of polyaniline.²¹

The results of the kinetic studies undertaken on the chemically synthesized polyemeraldine base have been shown in Figure 6. The area under the curve from 145 to 290°C has been chosen for the study of kinetics of crosslinking. The percentage of crosslinking plotted as a function of time at various temperatures (Fig. 7) indicates that the rate of crosslinking is faster at higher temperatures. Time taken for the 90% crosslinking of

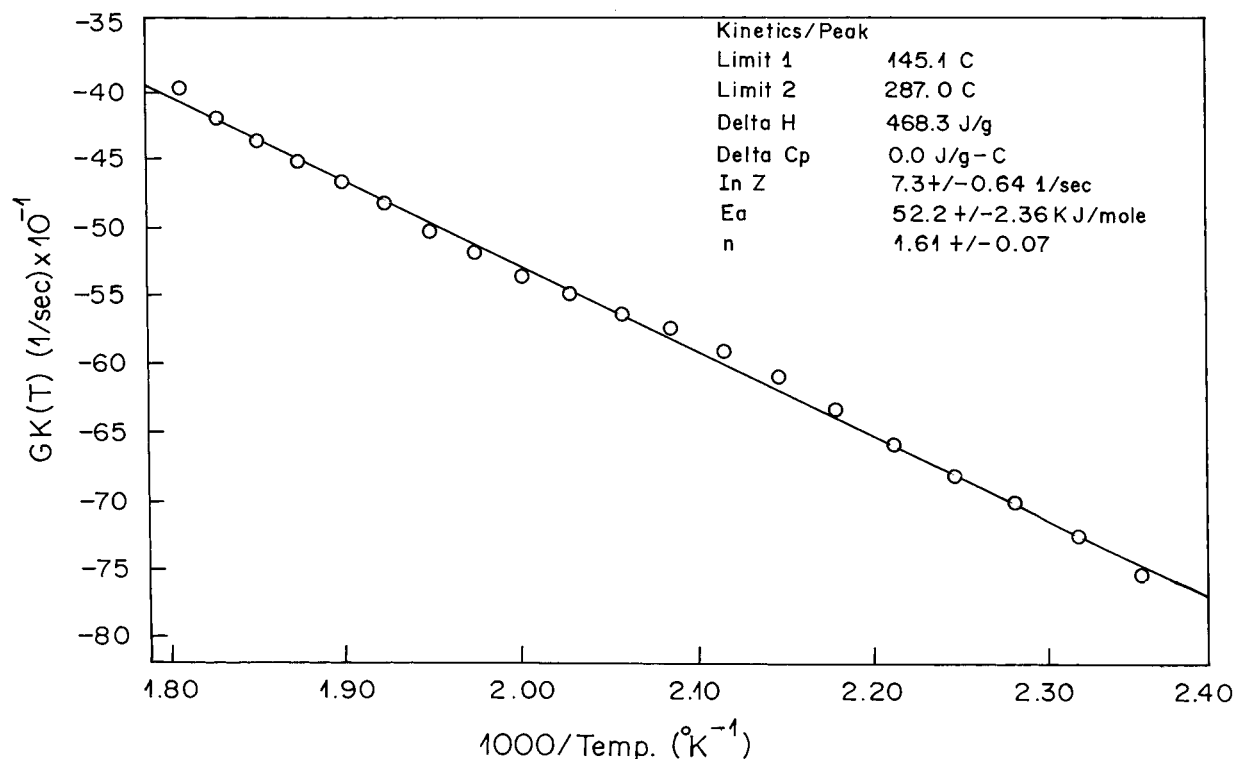


Figure 8 Arrhenius plot obtained for crosslinking in a chemically synthesized polyemeraldine base.

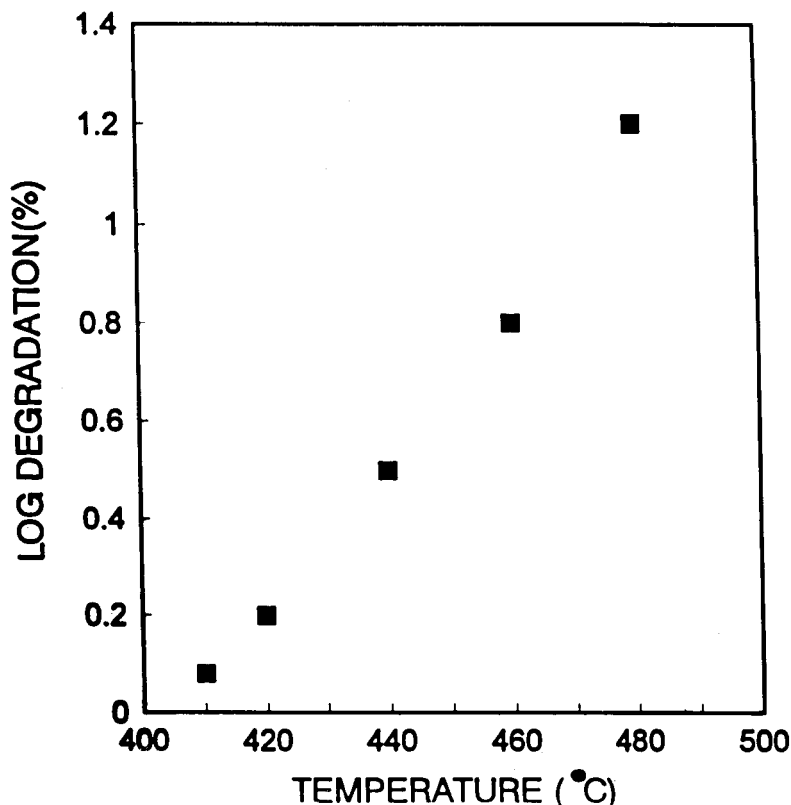


Figure 9 Log (%) of degradation obtained as a function of temperature for a polyemeraldine base.

polyemeraldine base at different temperatures has been computed. These results (Table I) reveal that the crosslinking is a temperature-dependent kinetic phenomenon. The increase in annealing temperature leads to the increased rate of crosslinking. The analysis of the Arrhenius plot (Fig. 8) obtained in the temperature range of 145–290°C yields the values of the kinetic parameters associated with crosslinking. Using the peak integration method associated with crosslinking, the order of crosslinking process has been found to be 1.61, suggesting that it follows the pseudo first-order kinetics having an enthalpy change of 468.3 J/g and an energy of activation as 52.2 KJ/mole.

A heavy weight loss (>35%) observed after 400°C as seen in the TGA thermogram indicates the degradation of the chemically synthesized polyemeraldine base. The degradation kinetics has been investigated over the temperature range of 400–500°C. The plot of log of percentage weight loss vs the increase in temperature (Fig. 9) yields a straight line, suggesting that the thermal degradation of the chemically synthesized polyemeraldine base follows the first order kinetics.

CONCLUSIONS

It has been shown that thermal degradation in chemically prepared polyemeraldine base occurs in three steps. The annealing (250°C) of the polyemeraldine base has been shown to result in the crosslinking of the polymer chains. The observed large weight loss (35%) soon after 400°C signals the initiation of thermal degradation in the polyemeraldine base. The detailed reaction kinetics of crosslinking in polyemeraldine base suggests that it follows the pseudo first-order kinetics whereas the thermal degradation follows first-order kinetics. Results of structural studies conducted using UV-visible and FTIR studies indicate the change in dimensionality in the crosslinked polyemeraldine.

We are grateful to Prof. A. K. Raychaudhuri, Director NPL, New Delhi, for the encouragement and his interest in this work. We are thankful to Dr. Subhas Chandra for interesting discussions. We thank Professor Keiichi Kaneto and Dr. W. Takashima, Department of Computer Science and Electronics, Kyushu Institute of Technology, Iizuka, Fukuoka, Japan, for many valu-

able discussions. One of us (BDM) is thankful to the Japanese Society for the Promotion of Science (JSPS) for the award of an Invitation Fellowship (ID No. S-67033) during May–June 1999. SSP and MG thank the Council of Scientific and Industrial Research (India) for the award of Research Associateship. Financial assistance received from European Economic Community (Contract No. CT I*-CT-92-0102) and the India–U.S. Fund (DST/INT/US/404/93) is gratefully acknowledged.

REFERENCES

1. MacDiarmid, A. G.; Chiang, J. C.; Hlpern, M.; Mu, S. L.; Somasiri, N. L. D.; Yaniger, Y. I. *Cryst Liq Cryst* 1985, 121, 173.
2. Wudl, F.; Angus, R. O., Jr.; Lu, F. L.; Allemond, P. M.; Vachon, D. J.; Novak, M.; Leu, Z. X.; Heeger, A. J. *J Am Chem Soc* 1987, 109, 3677.
3. Verghese, M. M.; Ramanathan, K.; Ashraf, S. M.; Kamalasanan, M. N.; Malhotra, B. D. *Chem Mat* 1996, 8, 822.
4. Angelopoulos, M.; Dipietro, R.; Zheng, W. G.; MacDiarmid, A. G.; Epstein, A. J. *Synth Met* 1997, 84(1–3), 35.
5. Pandey, S. S.; Ram, M. K.; Malhotra, B. D.; Srivastava, V. K. *J Appl Polym Sci* 1997, 65, 2745.
6. Verghese, M. M.; Ramanathan, K.; Malhotra, B. D.; Ashraf, S. M. *J Appl Polym Sci* 1998, 70, 1447.
7. Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; MacDiarmid, A. G. *Synth Metals* 1991, 43, 765.
8. Rodrgue, D.; Snauwaert, P.; Demaert, J.; Riga, J.; Verbist, J. J. *Synth Metals* 1991, 41–43, 769.
9. Kaba, L.; Hitchens, G. D.; Brockiss, J. O. M. *J Electrochem Soc* 1990, 137, 1341.
10. Smith, C.; Vtley, J. H. P.; Petrescu, M.; Viertler, M. *J Appl Electrochem* 1989, 19, 53.
11. Abell, L.; Pomfet, S. J.; Adams, P. N.; Monkman, A. P. *Synth Met* 1997, 84(1–3), 127.
12. Ansari, R.; Price, W. E.; Wallace, G. G. *Polymer* 1996, 37(6), 917.
13. Chan, H. S. O.; Ng, S. C.; Seow, S. H.; Sin, W. S.; Hor, T. S. A. *J Therm Anal* 1993, 39, 177.
14. Lacroix, J. C.; Diaz, A. F. *J Electrochem Soc* 1988, 135, 1457.
15. Patil, S. F.; Bedekar, A. G.; Agastie, C. *Mater Lett* 1992, 14, 307.
16. Chan, H. S. O.; Ho Pok, H.; Khor, E.; Tan, M. M. *Synth Met* 1989, 31, 95.
17. Neoh, K. G.; Kang, E. T.; Tan, K. L. *J Pure Appl Chem (A)* 1992, 29, 401.
18. Fossong, W.; Jinsang, T.; Lixiang, W.; Hong Fang, Z.; Zhishen, M. *Mol Cryst Liq Cryst* 1988, 160, 175.
19. MacDiarmid, A. G.; Somasiri, N. L. D.; Salaneck, W. R.; Lundstorm, I.; Leidberg, B.; Hassan, M. A.; Erlandson, R.; Koniasson, P. *Spring Ser Solid State Sci* 1985, L3, 218.
20. Wei, Y.; Tang, G. W.; Husch, K. F.; Sherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Polymer* 1992, 33(2), 314.
21. Genies, E. M.; Lapkowski, M. *J Electroanal Chem* 1987, 236, 189.