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Melting transition in the leucoemeraldine form of polyaniline

A. P. Chacko[a], S. S. Hardaker[a], R. V. Gregory[a,*] and T. W. Hanks[b]

[a]School of Textiles, Fiber and Polymer Science, Clemson University, Clemson, SC 29634-1307, USA
[b]Department of Chemistry, Furman University, Greenville, SC 29613-0420, USA

Exploitation of the redox properties of polyaniline has made possible the formation of a meltable crystalline phase in the leucoemeraldine base form of the polymer. Both fibres and films exhibiting the melting transition were prepared from leucoemeraldine base/N,N'-dimethyl propylene urea solutions. This melting behaviour is confirmed by a battery of experimental methods: thermogravimetric analysis, differential scanning calorimetry, optical microscopy, dynamic mechanical analysis and x-ray diffraction. This melting transition raises the possibility of future melt processing of polyaniline. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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Introduction

Polyaniline (PANI) has attracted considerable interest over the last two decades owing to its high degree of electrical conductivity, facile solution processability, and its switching ability between the insulative and conductive states by simple protonation of its emeraldine base oxidation state[1]. Although some work is reported in the literature regarding the formation of fibres and films from PANI in the conductive state, these materials usually have limited mechanical strengths and electrical conductivities[2-6]. Early work by Andreatta and co-workers on blends of PANI in the conductive state with poly(p-phenylene terephthalamide) produced blends with reasonable mechanical strengths but reduced electrical conductivity[3]. Counterion-induced processability reported by Cao et al.[4], and subsequently by Osterholm et al.[5], produced fibres and films with reasonable mechanical and electrical properties but the overall electrical properties tended to be poor. Hsu and co-workers at DuPont produced fibres from PANI in the doped form dissolved in concentrated sulfuric acid; however, the fibres had low mechanical strength and the process was not considered viable for large-scale fibre production[6].

Considerable progress has been made in processing PANI in the undoped emeraldine base (EB) form from solutions of N-methyl-2-pyrrolidinone (NMP) and N,N'-dimethyl propylene urea (DMPU), as well as other organic solvents[7,8]. In the base form, PANI tends to be less rod-like since extensive delocalization of electron density, necessary for conduction, does not occur as in the doped conductive state. This allows solubility in certain solvents that will not solubilize the rigid-rod form of the polymer. Some solvents such as hexafluoroisopropanol (HFIP) will solve both the base and conductive salt form but are very toxic and expensive[9].

Continuous processing of the polymer in the base form for extended periods of time remains a problem since solutions of solids in excess of 8% in NMP and 12% in DMPU are unstable owing to gelation. This precludes many applications which require the formation of polymer from stable solutions at high solids concentrations or where solution storage for some period of time is desired. This gelation results from interactions between the nitrogens and their associated protons on the PANI backbone[10,11]. Stable solutions are desired for the production of fibres or films with segment-to-segment reproducibility of mechanical and electrical properties. These cannot be obtained if the polymer solution is undergoing a dynamic change such as network formation and subsequent gelation. This dynamic change is realized in concentrations of PANI above 6% in NMP and 12% in DMPU as increasing viscosity owing to an elastic network formation[12,13]. Recently, Mattes and co-workers at Los Alamos employed gel inhibitors such as pyrrolidine to increase the EB/NMP solution lifetime at high solids concentrations for processing of films and fibres[14]. These gel inhibitors substantially reduce the elastic network formation but do not eliminate it. Potential uses of PANI on a large scale for electrochromic devices, rechargeable batteries, shielding of electromagnetic interference, light-emitting diodes, etc. will depend on the formation of materials with predictable and reproducible morphologies on a segment-to-segment basis, resulting in reproducible polymer properties. Such reproducibility cannot be obtained if the polymer solution is changing its viscous and elastic properties during polymer formation.

PANI can exist in three distinct oxidation states as shown in *Figure 1*. Of these, only the emeraldine base (EB) form can be doped by acids to form the electrically conductive emeraldine salt. Both the EB and the reduced emeraldine base, called leucoemeraldine base (LEB), are soluble in NMP and DMPU and fibres and films can be processed from these solutions with subsequent doping to varying levels of conductivity. Recently we reported studies on the rheology and viscoelasticity of fibre-forming solutions of PANI/EB and PANI/LEB as well as the mechanical properties of fibres formed from these solutions, to better understand the effect of dynamic changes such as gelation on the mechanical and electrical properties of the formed fibre or film. Work in our laboratory and at IBM by Angelopoulos and co-workers has shown DMPU to be an excellent solvent for higher solids concentrations of PANI and the EB form[11-13]. Viscoelastic studies showed, however, that the
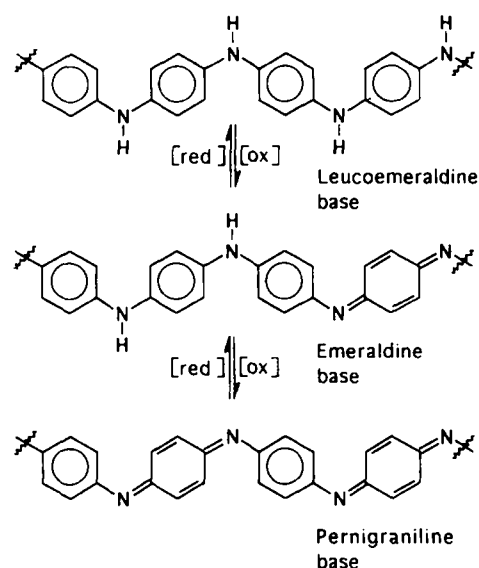
Figure 1 Oxidation states of polyaniline: (a) fully reduced, leucoemeraldine base (LEB); (b) partially oxidized, emeraldine base (EB); (c) fully oxidized, pernigraniline

solution becomes more elastic with time, indicating an unacceptable degree of solution instability at higher solids concentrations. This solution elasticity results from intra- or interchain secondary bond formation between the imine nitrogens and the amine hydrogens on the undoped PANI chains[10]. Reduction to the LEB oxidation state by phenyl hydrazine or other suitable reducing agents produces a stable solution where the increase in solution elasticity is substantially reduced[15]. Interaction between amine moieties on the PANI backbone is substantially weaker than between imine nitrogens and amine hydrogens and can be easily broken up by solvents such as DMPU[12–14]. At the same time, we reported that the electrical properties of PANI fibres formed from either the insulative LEB or EB form, and subsequently doped, have conductivities of 140 to 350 S cm^{-1} or higher and, in the case of fibres formed from LEB solutions, mechanical properties approaching those of some commercially available polyamides such as Nylon 6[14]. This earlier work demonstrated that the electrical properties are dependent on the degree of orientation of the fibres and films and on the stability of the forming solution. In an effort to characterize the fibres and films formed from the more stable LEB/DMPU solutions, several studies to determine the morphologies and the relationship between the polymer microstructures and observed electrical and mechanical properties were conducted.

We report here, for the first time, the observance of crystals in materials formed from LEB/DMPU which melt at elevated temperatures under a nitrogen atmosphere. The surface of this material appears to flow at elevated temperatures, indicating a potential for melt processing of LEB PANI. Annis and MacDiarmid reported crystal formation in PANI formed from EB and subsequently drawn to ratios of 2.5/1 but did not report evidence of crystallite formation in unoriented EB or perform x-ray analysis on LEB materials[15,16].

Experimental

Polyaniline was synthesized by the chemical polymerization of aniline with ammonium persulfate (APS) as the oxidant.

Aniline (49 g) was dissolved in 500 ml of 1.0 M aqueous HCl and the temperature adjusted to − 36°C. LiCl (43 g) was also added to the reaction vessel to prevent freezing. Ammonium persulfate (57 g) and LiCl (43 g) were dissolved in 500 ml of 1.0 M aqueous HCl and added dropwise to the aniline solution over a 4 h period. This is essentially the same method reported by Milton and Monkman[17]. The reaction was allowed to continue for 18 h. Upon completion, the reaction mixture was filtered and washed with water, resulting in the half-oxidized (emeradine) salt form. The emeraldine salt (ES) was deprotonated in excess 3 wt% NH$_4$OH, washed with water and methanol and subsequently dried to yield the emeraldine base powder.

The molecular weight was characterized with a Waters gel permeation chromatograph operating at 75°C with dimethyl sulfoxide (DMSO) and 0.1 wt% LiBr as the eluent. Poly(vinyl pyrridine) standards were used. The number-average molecular weight was found to be $M_n = 78$ kD and the weight-average molecular weight was $M_w = 165$ kD, giving a polydispersity index of 2.13.

Solutions of polyaniline were prepared by dissolving 9–17 wt% emeraldine base in N,N'-dimethyl propylene urea containing phenyl hydrazine (about one-third of the weight of polymer) as the reducing agent. The resulting solutions of leucoemeradine base were dark brown in colour, quite viscous, and contained no particulate matter.

Fibres were spun from 17 wt% solutions of leuco-emeraldine base in DMPU through a single-hole spinnerette ($D = 0.10$ mm, $L/D = 2.0$). The extrusion flowrate was 0.396 cm^3 min^{-1}, and the take-up speed was 30 m min^{-1}. The 2 m long coagulation bath was composed of 27% N-methyl-pyrrolidinone (NMP) and 73% water by weight. Some of the fibres were annealed at 200°C for 30 min.

Dip-coated films were prepared by dipping microscope slides into a 9 wt% solution of leucoemeraldine base followed by coagulation in an NMP/water bath. The NMP concentration of the coagulation bath was varied between 0 wt% NMP and 66 wt% NMP. The dip-coated films reported in this work were coagulated at the same coagulant concentration as the fibres.

A 10 wt% solution of leucoemeraldine base was spin-coated onto silicon wafers at a spin speed of 500 rev min^{-1} for 30 s on a PM101DT-R790 spin coater from Headway Research, Inc. The coated silicon wafers were then heated at ~72°C for 10 min to remove most of the solvent. Some films were annealed at 200°C for 30 min.

Visible light microscopy (in reflection mode) was carried out with a Reichert microscope fitted with a hot-stage. Micrographs were obtained at 70 × magnification (numerical aperture of 0.2) under both nitrogen and air atmospheres as a function of temperature.

X-ray diffraction powder patterns of spin-coated films were obtained on a Scintag XDS 2000 diffractometer with Cu K_α radiation ($\lambda = 1.54$ Å) and operated in step-scan mode (2.0 s per step) with step size $2\theta = 0.03°$. The powder samples were prepared by crushing the spin-coated films after being floated off of the silicon substrates by submersion in water.

Thermogravimetric analysis (t.g.a.) was carried out on a TA Instruments model 2950 TGA at a heating rate of 20°C min^{-1} (5°C min^{-1} for fibres) until degradation under both air and nitrogen atmospheres. Differential scanning calorimetry (d.s.c.) was carried out on a TA Instruments model 2920 DSC at a heating rate of 20°C min^{-1} (5°C min^{-1} for fibres) from room temperature to 450°C under a nitrogen atmosphere. Dynamic mechanical thermal
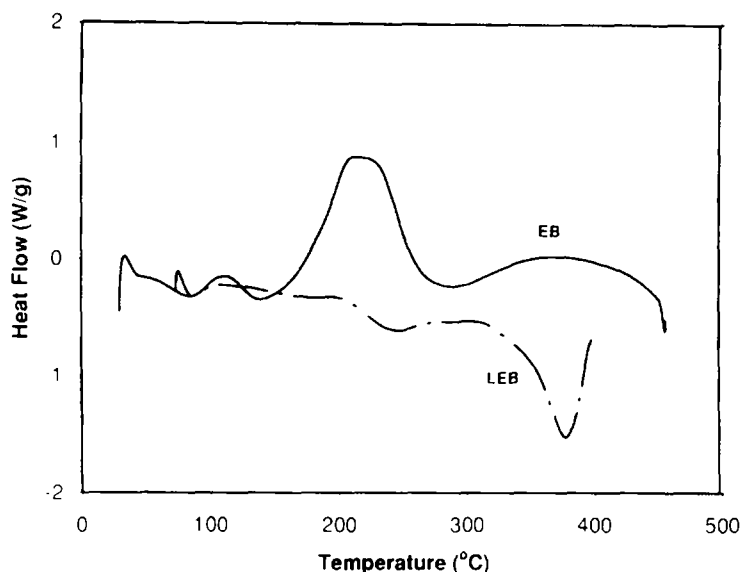
Figure 2 D.s.c. of films formed from EB/NMP and LEB/DMPU solutions (9% wt/wt)
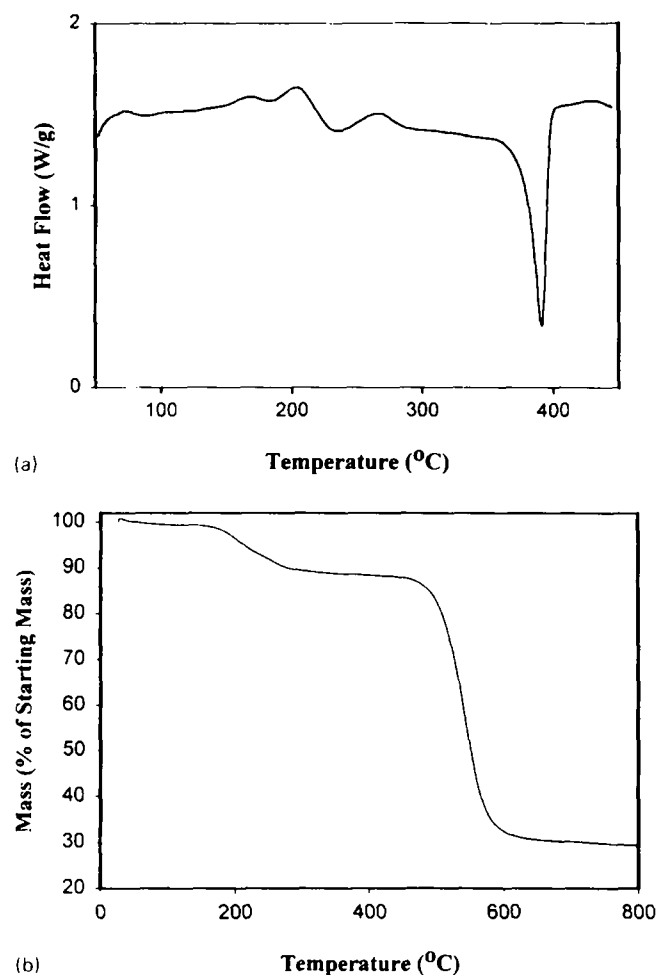

(a)

(b)

Figure 3 Thermal analysis results for spin-coated LEB/DMPU films: (a) d.s.c. of spin-coated LEB/DMPU film with endotherm at 390°C; (b) t.g.a. of film in (a)

analysis (d.m.t.a.) of a bundle of 15 filaments (gauge length of 20 mm) was carried out on a Seiko model DMS 210 DMTA at 1.0 Hz and a heating rate of 2°C min⁻¹ under a nitrogen atmosphere.

Results and discussion

While several workers have studied the thermal transitions of polyaniline, most have concentrated only on the emeraldine base form produced from NMP solutions[18,19]. *Figure 2* contrasts the d.s.c. data of films formed by dip coatings of emeraldine base and leucoemeraldine base produced from DMPU solutions. A broad exotherm at approximately 200°C was observed for the EB films, most probably due to oxidation or crosslinking, consistent with results obtained by others[16,17]. The glass transition temperature (T_g) of the dip-coated LEB films was found to be about 200°C, and an endotherm was observed at approximately 385°C. Thermogravimetric analysis was carried out to confirm that the endotherm was not a consequence degradation, since the films showed no significant weight loss up to a temperature of 450°C in nitrogen.

The specific enthalpy change associated with the endotherm observed for the LEB fibre was ~36 J g⁻¹. Even larger endotherms were observed in films prepared by spin coating LEB/DMPU solutions. *Figure 3* presents the thermal analysis results for the spin-coated film. In *Figure 3a*, the endotherm was observed at about 390°C, with a specific enthalpy change of ~70 J g⁻¹. Thermal transitions were also observed between 175 and 250°C. These transitions are believed to be due to crystallization and/or loss of solvent. The t.g.a. for this film is shown in *Figure 3b*, demonstrating again that the film is not decomposing at the observed endotherm temperature. The film is stable in nitrogen to more than 450°C. There is some weight loss between 175 and 260°C associated with the loss of residual solvent confirmed by both t.g.a. and d.s.c. of annealed film in which no weight loss or thermal transitions were observed between 175 and 250°C.

Figure 4 presents two micrographs of the spin-coated film at 350°C and at 395°C obtained under a nitrogen atmosphere. At the lower temperature, the film surface was found to be somewhat rough; but at the higher temperature the film surface became smoother, more reflective, and began to distort. The dramatic difference between the two micrographs occurred at almost exactly the same temperature as the endotherm observed from d.s.c. After cooling, it was observed that a small amount of polymer had flowed from

Figure 4 Micrographs of LEB spin-coated films formed from DMPU solution (10% wt/wt) at: (a) 350°C, prior to endotherm observed in *Figure 3a*; (b) 395°C, after passing through endotherm
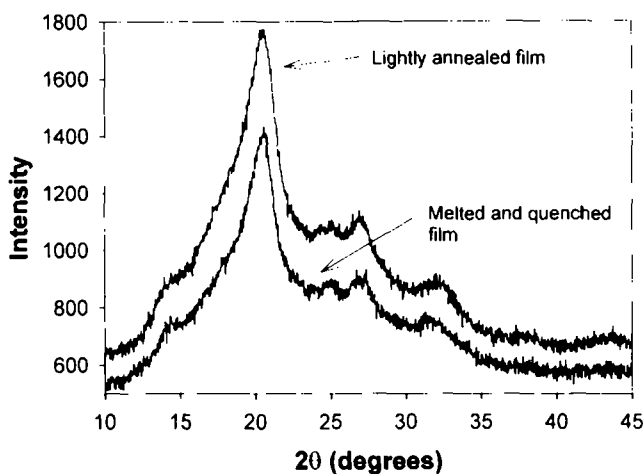

Figure 5 X-ray diffraction of: (a) spin-coated LEB film; (b) spin-coated LEB film heated to 450°C and quenched under nitrogen

Figure 6 D.m.t.a. analysis of LEB fibres: (a) *E'* (storage modulus) and *E"* (loss modulus), showing a significant decrease in the dynamic moduli at the endotherm temperature observed in *Figure 3a*; (b) fibre shrinkage as a function of temperature for the fibre bundle in (a)

between the microscope slides. The above evidence (d.s.c., t.g.a. and microscopy) is consistent with a melting transition at about 390°C.

X-ray diffraction was employed as an independent method to confirm the existence of crystalline structure in the LEB/DMPU spin-coated films. *Figure 5a* shows the diffraction pattern for the spin-coated film. Along with the non-crystalline scattering centred at about $2\theta = 19°$, a number of other peaks are present, characteristic of crystalline structure. In *Figure 5b*, the crystalline scattering of a spin-coated film heated to 450°C and quenched under a nitrogen atmosphere is shown. The much less intense scattering for the heated-and-quenched sample is consistent with the melting of a crystalline phase.

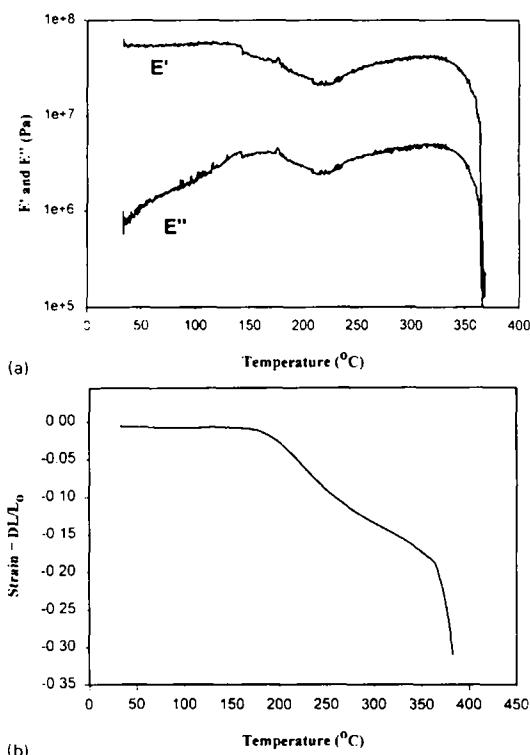The last data to indicate that the endotherm described

above is, in fact, due to melting of crystallites were obtained from dynamic mechanical thermal analysis of a bundle of fibres. *Figure 6a* presents the storage and loss moduli of this fibre bundle. This shows classic behaviour of the moduli

through the glass transition, but an increasing storage modulus from about 225 to 325°C, possibly due to an increase in crystallinity. Above 350°C, both the storage and loss moduli decrease abruptly. Since the sample was not broken at the conclusion of the measurement, the decrease in the dynamic moduli indicates that the fibres experienced a dramatic softening.

In addition to the dynamic moduli, the change in sample length with temperature was obtained and is shown in *Figure 6b* as fibre shrinkage (change in fibre length; $\Delta l/l$) *versus* temperature. Below the glass transition, there was no significant shrinkage as expected for a glassy material. When enough thermal energy was available for large-scale segmental mobility (at the glass transition), an increase in the rate of shrinkage was observed. Since the fibres were partially oriented (coagulation bath draw ratio = 1.5/1), shrinkage occurs in order to maximize the entropy. From the glass transition to approximately 375°C, the rate of shrinkage remained nearly constant; but it increased dramatically above 375°C, consistent with melting.

Experimental evidence obtained to date in our laboratory (x-ray, t.g.a., d.s.c., d.m.t.a. and microcopy) is consistent with the conclusion that the endotherm at approximately 385 to 395°C is due to the melting of a crystalline phase in polyaniline films and fibres produced from solutions of leucoemeraldine base in DMPU. This is believed to be the first report of melting in an electrically conductive homopolymer, and has significant implications for the possibility of melt-processable PANI.

It should be recognized, however, that the PANI is in the reduced form and must be subsequently re-oxidized and protonated to achieve electrical conduction. The two times post-drawn fibres produced from the LEB/DMPU wet spinning process, oxidized with H_2O_2 and doped with HCl exhibit a conductivity of 140 S cm^{-1}, somewhat lower than the 350 S cm^{-1} reported for the fibres produced from spinning EB/DMPU solutions. Optimization of the process is expected to result in improved electrical properties.

Conclusions

An endotherm was observed at approximately 385 to 395°C in both fibres and films that has been shown by x-ray, thermal, microscopic and dynamic mechanical methods to be consistent with melting of a crystalline phase in polyaniline. The formation of a meltable crystalline phase has been made possible by exploitation of the redox and doping processes that are unique to polyaniline. The existence of a meltable crystalline phase raises the possibility of melt processing PANI. Studies are currently

underway to characterize the crystalline phase and enhance the crystal growth. These results will be reported in a timely manner. A substantial increase in the percentage of the crystalline phase may well open new and solvent-free methods of obtaining artefacts and devices made of pure PANI.

References

1. MacDiarmid, A. G., in *Conjugated Polymers and Related Materials*, ed. W. R. Salaneck, I. Lundstrom and B. Ranby. Oxford Scientific, New York, 1993, pp. 73–98.
2. Andreatta, A., Heeger, A. J. and Smith, P., *Polym. Commun.*, 1990, **31**, 275.
3. Andreatta, A., Tokito, S., Moulton, J., Smith, P. and Heeger, A. J., *Science and Applications of Conducting Polymers*. IOP Publishing Ltd. Bristol, 1990.
4. Cao, Y., Andreatta, A., Smith, P. and Heeger, A. J., *Synth. Met.*, 1992, **48**, 91.
5. Ikkala, O. T., Laakso, J., Vakiparta, K., Virtanen, E., Ruohonen, H., Jarvinen, H., Taka, T., Passiniemi, P. and Osterholm, J. E., *Synth. Met.*, 1995, **69**, 213.
6. Hsu, C. H., Cohen, J. D. and Tietz, R. F., *Synth. Met.*, 1993, **59**, 37.
7. Angelopoulos, M., Asturias, G. E., Ermer, S. P., Ray, A., Scherr, E. M., MacDiarmid, A. G., Akhtar, M. A., Kiss, Z. and Epstein, A. J., *Mol. Cryst. Liq. Cryst.*, 1988, **160**, 151.
8. Tzou, K. T. and Gregory, R. V., *Synth. Met.*, 1995, **69**, 109.
9. Hopkins, A. R., Rasmussen, P. G. and Basheer, R. A., *Macromolecules*, 1996, **29**, 7838.
10. Angelopoulous, M., Kiao, Y. H., Furman, B. and Teresita, G., *Macromolecules*, 1996, **29**, 3046.
11. Chacko, A. P., Hardaker, S. S., Huang, B. and Gregory, R. V., *Mater. Res. Soc. Symp. Proc.*, 1996, **413**, 505.
12. Chacko, A. P., Hardaker, S. S., Samuels, R. J. and Gregory, R. V., *Synth. Met.*, 1997, **84**, 41.
13. Chacko, A. P., Hardaker, S. S. and Gregory, R. V., *Proc. SPE ANTEC 97*, 1997, **II**, 1468.
14. Wang, H. L., Yang, D., Zhu, T. T., Blumenthal, W. R. and Mattes, B. R., *Synth. Met.*, 1997, **84**, 37.
15. Chacko, A. P., Hardaker, S. S. and Gregory, R. V., *Polym. Prepr.*, 1996, **37**(2), 743.
16. Annis, B. K., Lin, J. S., Scherr, E. M. and MacDiarmid, A. G., *Macromolecules*, 1992, **25**, 429.
17. Milton, A. J. and Monkman, A. P., *J. Phys. D: Appl. Phys.*, 1993, **26**, 1468.
18. Wei, Y., Jang, G. W., Hsueh, K. F., Scherr, E. M., MacDiarmid, A. G. and Epstein, A. J., *Polymer*, 1992, **33**(2), 314.
19. Kiao, Y. H., Furman, B., Graham, T. and Angelopolulos, M., *Proc. SPE, ANTEC 96*, 1996, **II**, 1363.