Thermal transitions and mechanical properties of films of chemically prepared polyaniline[*]

Yen Wei[†], Guang-Way Jang and Kesyin F. Hsueh
Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA

and Elliot M. Scherr and Alan G. MacDiarmid
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

and Arthur J. Epstein
Department of Physics and Department of Chemistry, The Ohio State University, Columbus, OH 43210-1106, USA
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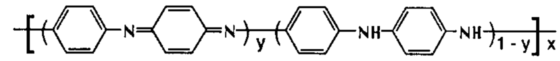
The mechanical and thermal properties of the solution-cast films of chemically prepared polyaniline have been studied by means of dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). The glass transition temperature (T_g) of the polyaniline films in emeraldine base form was determined and characterized for the first time to be in the range of ~105–220°C for the films containing ~16–0% of 1-methyl-2-pyrrolidinone (NMP) residual solvent, respectively, from a decrease in the storage modulus in d.m.a. and from d.s.c. studies. Depending on the content of NMP, the thin films of polyaniline have a storage modulus of ~200 MPa–2 GPa at temperatures below T_g. Other thermal transitions and reactions in the temperature range of ~25–500°C are also characterized by infra-red spectroscopy, X-ray diffraction and cyclic voltammetry and are discussed in relation to the mechanical properties of polyaniline.

(Keywords: polyaniline; electrically conductive polymer; glass transition temperature; thermal analysis; dynamic mechanical analysis; modulus)

INTRODUCTION

Polyaniline, an important member in the family of electrically conductive polymers, has been studied extensively because of its unique electrochemical behaviour and environmental stability[1,2]. Upon doping with a non-oxidizing protonic acid such as hydrochloric acid, polyaniline exhibits a moderately high conductivity (~10 S cm^{-1}). However, like most conductive polymers, the commercial applications of polyaniline have been limited by its poor processability. One item of great importance for potential thermal processing of these materials is the thermal transition temperatures such as the glass transition (e.g. for the amorphous component of polyaniline[3]) and the melting (e.g. for the crystalline component of polyaniline[4–6]) temperatures of the materials. There are many reports on the thermal stability and thermal reactions of polyaniline[7–9], and on the mechanical properties of polyaniline[10]. However, the glass transition temperature (T_g) has not been observed previously; in addition, very little is known about the dynamic mechanical properties of polyaniline. It is generally believed that the base (i.e. undoped) form of polyaniline could be schematically represented by the following formula:



where the value of y represents the oxidation state of the polymers and is 0.5 for polyaniline in the 'emeraldine' oxidation state[11]. This emeraldine base (EB) form of polyaniline can be dissolved in 1-methyl-2-pyrrolidinone (NMP); and free-standing EB films can be cast from the resultant NMP solution[12].

In this paper, we present the first observation and characterization of a well defined T_g for emeraldine base films of polyaniline by means of a series of thermal and mechanical analytical techniques including dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). The effects of the solvent NMP present in the films on the value of T_g are investigated. Other thermal transitions and reactions in the region from room temperature to 500°C have also been studied and are discussed in relation to the mechanical properties of polyaniline.

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[†] To whom correspondence should be addressed

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EXPERIMENTAL

Materials and instrumentation

Aniline (Fisher) was distilled under reduced pressure. Ammonium persulphate, $(NH_4)_2S_2O_8$ (99%, EM Science) was used as received without further purification. All aqueous solutions were prepared using distilled and deionized water. Thermogravimetric analysis and d.s.c. were performed on a Du Pont 9900 thermal analysis system with TGA 951 and DSC 910 modules. The programmed heating rate was 20°C min^{-1}. All the thermal analysis and thermal annealing experiments were conducted under nitrogen or argon atmosphere. Conductivities were measured using the four-probe techniques on powder-pressed polymer pellets and on free-standing films of the polymer. An EG&G PAR model 173 potentiostat/galvanostat was employed as a constant current source. Infra-red (i.r.) spectra of the polymer were recorded on a Perkin-Elmer model 1760X FTIR spectrophotometer. Gel permeation chromatography (g.p.c.) was performed on a Waters GPC model IIA equipped with a model 590 programmable solvent delivery module, a refractometer as detector, and an Ultrastyragel linear column at 35°C using NMP (Aldrich, HPLC grade) as solvent. Dynamic mechanical analysis was performed on a Du Pont 2000 thermal analysis system equipped with the models 983 DMA module. The programmed heating rate was 5°C min^{-1}. A low mass vertical clamp (newly developed at Du Pont) was employed for d.m.a. measurements in which a typical sample size was 1.25 mm long, 8.68 mm wide and 0.07 mm thick, and a fixed frequency of 1 Hz was used. The d.m.a. experiments were performed in purged nitrogen gas. The wide angle X-ray diffraction studies were performed on a Rigaku Geigerflex X-ray diffractometer using a CuKα radiation source. The scan range (2θ) was 5–35° at a scan rate of 2° min^{-1}. Cyclic voltammetry of the polymers before and after thermal ageing was studied with an EG&G PAR model 273 potentiostat/galvanostat. Platinum foils were used as both working and counter electrodes with a saturated calomel electrode (SCE) as reference. The polymer was dissolved in NMP and cast onto the working electrode. The cyclic voltammograms were recorded in 1.0 M HCl aqueous solution in a potential range of -0.2 to 1.0 V *versus* SCE at a scan rate of 25 mV s^{-1}.

Synthesis of polyaniline

Polyaniline in the salt form was prepared by chemical oxidation of aniline with ammonium persulphate as oxidant in 1 M HCl solution. The base form of polyaniline was obtained[11] by treating the salt form with 0.1 M NH_4OH. In a typical procedure, aniline (10.0 ml, 0.107 mol) was dissolved in 600 ml of 1 M HCl and the mixture was precooled to below 5°C in an ice bath. A solution (200 ml) of 5.6 g (0.025 mol) $(NH_4)_2S_2O_8$ in 1M HCl was added to the aniline solution dropwise over a period of 15 min with vigorous stirring. After ~2 h, the precipitate was collected on a Buchner funnel and was washed with four portions of 100 ml of 1 M HCl. The precipitate was then transferred into a beaker containing 400 ml of 1 M HCl. The resulting mixture was stirred at room temperature for ~4 h followed by filtration. Upon drying under dynamic vacuum at room temperature for 48 h, the HCl-doped polyaniline was obtained as a green powder.

Part of the polyaniline in the HCl salt form as synthesized above was converted into the base form by stirring ~3 g of the polymer powder in an excess amount (500 ml) of 0.1 M NH_3–H_2O at room temperature for 3 h. Upon filtering and drying under dynamic vacuum for 48 h, the base form of polyaniline was obtained as a blue powder.

Preparation of free-standing films

The free-standing films of the emeraldine base form of polyaniline were prepared based on the procedures reported by Angelopoulos *et al.*[12]. As a representative procedure, 1 g of finely ground emeraldine base powder was added to 100 ml of NMP and magnetically stirred for at least 1 h at room temperature. The resultant blue solution was filtered through a Buchner funnel using a Whatman no. 2 filter paper. The solution was then cast onto a clean glass plate and the solvent was allowed to evaporate at ~60°C for 15 h. The coated glass plate was then placed in water and the film was lifted off the glass. The free-standing film was then dried under dynamic vacuum at room temperature for 48 h. The EB films prepared by this procedure usually contained ~16% of the solvent NMP which could not be removed completely by heating to 60°C. To prepare the solvent-free film, the film obtained by the above procedure was doped with HCl by immersing the film in 1 M HCl solution for 18 h at room temperature. The resultant film of polyaniline HCl salt was then undoped to its base form by placing the film in 0.1 M NH_4OH for 18 h at room temperature. This doping–undoping process was repeated at least twice. The final undoped film was dried under dynamic vacuum at room temperature for 48 h.

RESULTS AND DISCUSSION

Polyaniline in the HCl salt form was prepared by chemical oxidation of aniline with $(NH_4)_2S_2O_8$ as oxidant in a 1 M aqueous HCl solution. The base form of polyaniline was obtained by treating the salt form with 0.1 M NH_4OH. The molecular weight of the polymer in base form was estimated to be ~10^3–10^5 by g.p.c.[13]. The elemental analysis of the polymer gave C 80.31%, H 4.91% and N 15.67%, which corresponds to the empirical formula $C_{12}H_9N_2$ (calculated values: C, 79.56%; H, 4.97%; N, 15.47%) for the polyaniline base having the emeraldine oxidation state[12].

The free-standing films of the EB were directly cast from its solution in NMP. The films appear blue in reflectance and are quite flexible. The film with a thickness of ~0.04 mm can be folded many times without breaking. The Fourier transform infra-red (*FT*i.r.) spectrum of the film as prepared is shown in *Figure 1a*. All of the characteristic absorption bands for the EB form of polyaniline[14–16] were observed. The strong band at 1597 cm^{-1} is assigned to the quinoid moiety of the polymer. The 1,4-substitution pattern on the benzenoid can be identified by the aromatic C–H in- and out-of-plane bending at 1113 and 834 cm^{-1}. It is apparent from the spectrum that the film still contains residual NMP solvent as indicated by the presence of a strong C=O stretching band at 1671 cm^{-1}. The NMP solvent (b.p. 81–82°C/10 mmHg) could not be completely removed from the films by the drying procedures currently employed[12]. Further increase in the drying temperature might not be advisable because of the possible irreversible thermal reactions such as crosslinking at the elevated temperatures[7–9]. Therefore, a different procedure was developed for the removal of the residual solvent to produce NMP-free EB films. Thus, the EB film containing NMP was first doped with 1 M HCl and then undoped in a 0.1 M NH_4OH aqueous solution. This doping–undoping process was repeated several times. Upon drying, the EB film was obtained free of the NMP solvent. The *FT*i.r. spectrum (*Figure 1b*) showed a lack of the absorption band at 1671 cm^{-1} for the C=O stretching in NMP.

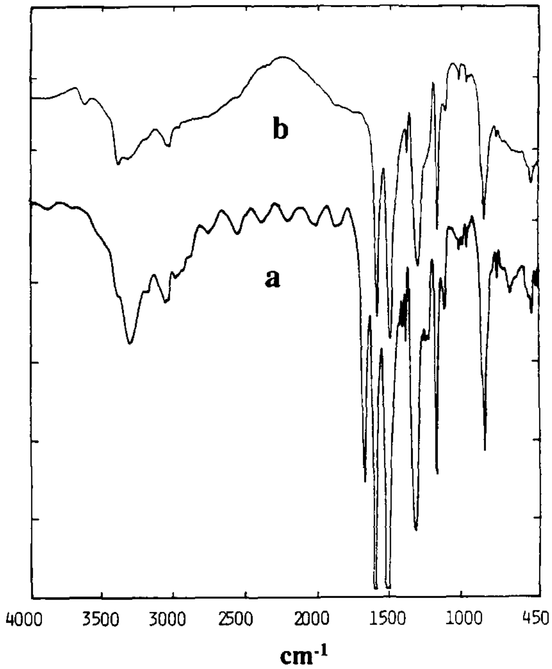

Figure 1 *FT*i.r. spectra of the emeraldine base films of polyaniline containing (a) ~16% of NMP solvent and (b) no NMP solvent

The t.g.a. thermograms for the NMP-free EB film and the EB film without the removal of NMP are shown in *Figure 2*. There is one major weight loss at ~400°C for the NMP-free EB film whereas two major weight losses were observed in the range of ~50–270°C and at ~500°C for the NMP-containing EB film. The major weight loss at 400–500°C is attributed to the structural decomposition of the polymer[9]. A t.g.a. experiment performed on pure NMP indicated that the weight loss at ~110–270°C can be assigned to the evaporation of the NMP solvent. A small amount (<1%) of moisture evaporate at temperatures of ~50–100°C. The amount of NMP in the EB film containing NMP was estimated from the t.g.a. thermogram to be ~16% by weight. These results are consistent with those obtained from the *FT*i.r. studies. The general appearances of the NMP-free EB film are quite similar to those of the NMP-containing EB film. It was noted, however, that the NMP-containing film appeared to be much more flexible than the NMP-free film. Therefore, the thermal and mechanical properties of the both films were investigated, starting with those of the NMP-containing EB film.

Figure 3 shows a typical d.m.a. scan of the NMP-containing EB film with a thickness of 0.07 ± 0.03 mm, in which the storage modulus E', loss modulus E'' and $\tan\delta$ (i.e. E''/E') were determined in the temperature range of 25–350°C at a heating rate of 5°C min^{-1} under a nitrogen atmosphere. At ~25°C, E' of the film was ~200 MPa. The d.m.a. thermograms of the NMP-containing films were very reproducible. Depending on the solvent content in the films, E' varies in the range of ~200 MPa–2 GPa at 25°C.

A glass transition of a polymer is marked by drastic changes in its physical properties. The cooperative motion of large chain segments takes place in the glass transition region which includes T_g. At the temperatures above T_g, the polymer is in a rubbery state while at the temperatures below T_g, it behaves as a glass[17]. For the

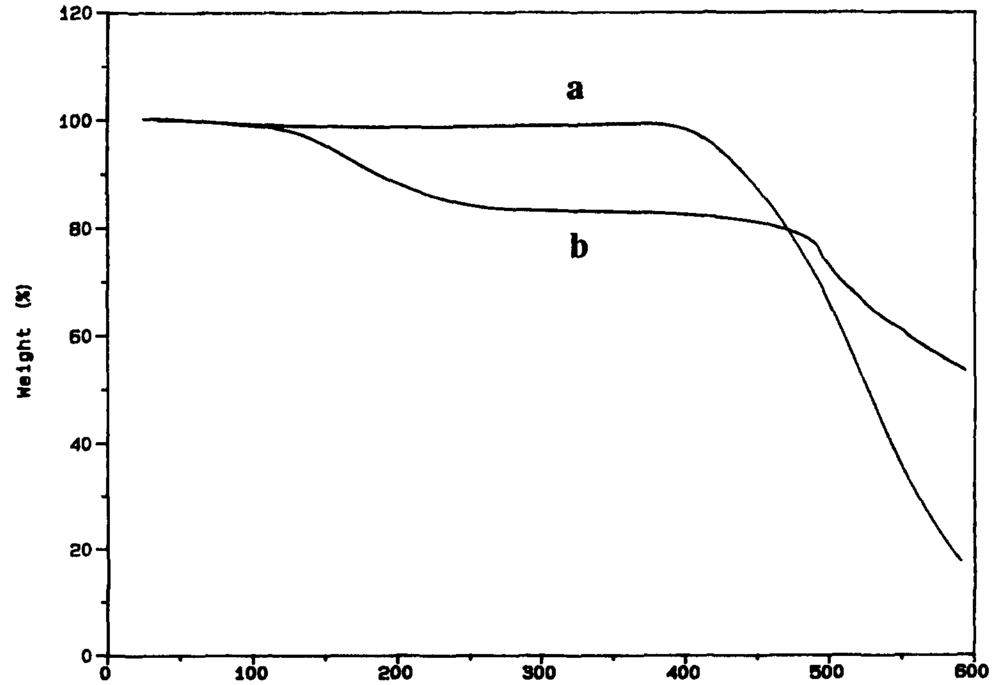

Figure 2 T.g.a. thermograms of the emeraldine base films of polyaniline containing (a) no NMP solvent and (b) ~16% of NMP solvent

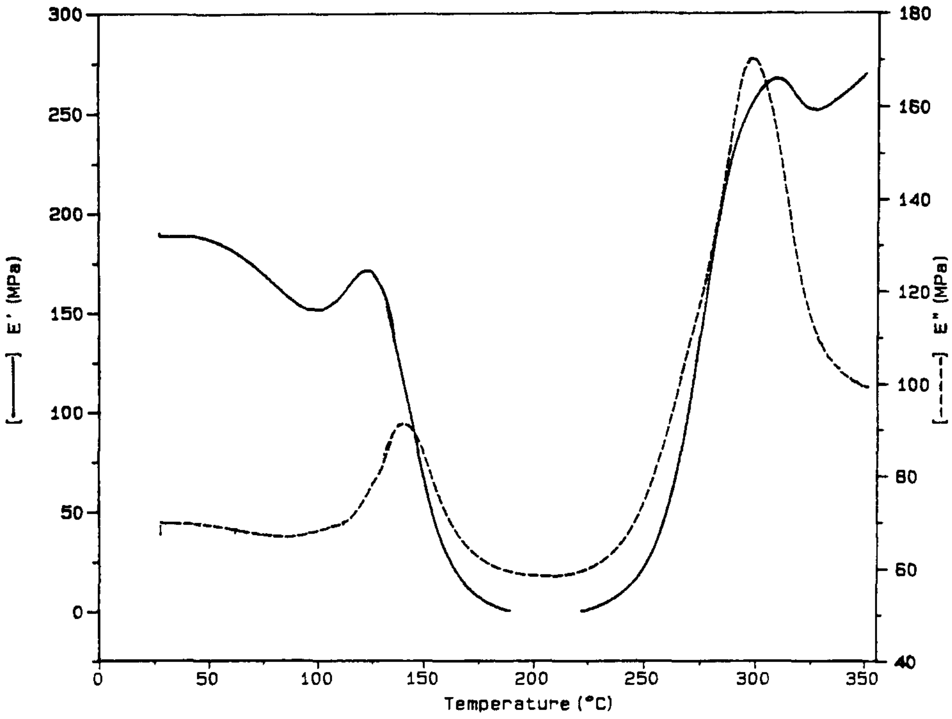

Figure 3 D.m.a. of the emeraldine base film of polyaniline containing ~16% of NMP solvent. Thickness of the film: 0.07 ± 0.03 mm; dynamic loading at a fixed frequency of 1 Hz

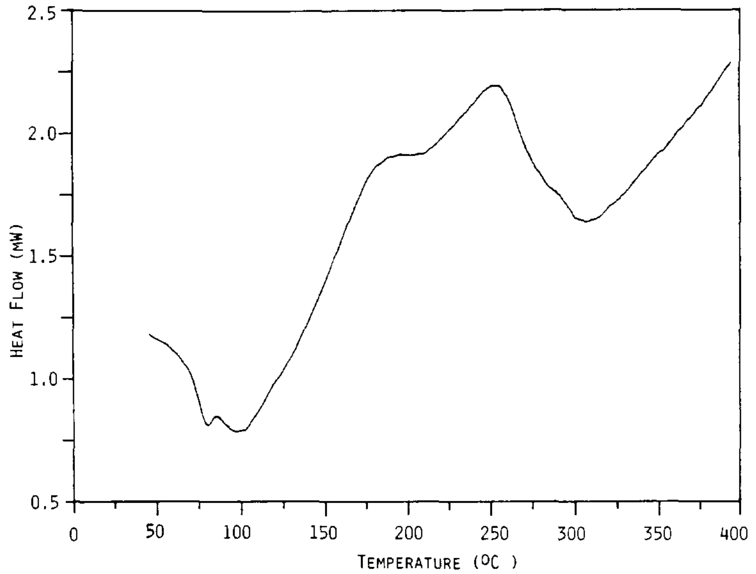

Figure 4 D.s.c. thermogram of the emeraldine base film of polyaniline containing ~16% of NMP solvent

NMP-containing EB films (*Figure 3*), the glass transition takes place in the temperature region from ~125 to 170°C as indicated by drastic changes in both E' and E''. In this narrow temperature range, E' decreased by several orders of magnitude to the values of ~0.1–1 MPa, as expected for a typical glass transition. The T_g of the polymer was ~140°C as measured by the maximum in the E'' curve and by the point of inflection of E' (*Figure 3*).

A similar glass transition was also observed in d.s.c. thermograms. A typical d.s.c. thermogram of the NMP-containing EB film is shown in *Figure 4*. There appeared to be two endotherms in the region around 100°C followed by two exothermic processes which reach their peaks at ~180 and 250°C, respectively. Based on the t.g.a. results (*Figure 2b*), the small amount of moisture contained in the film evaporate at temperatures above ~50°C, which also contributes in part to the endotherms in this temperature region in the d.s.c. measurement (*Figure 4*). Therefore, additional procedures were employed for the d.s.c. measurements of the glass transition of the film to eliminate the interference from the moisture evaporation process. Thus, the film was kept isothermal at 90°C for 15 min in the d.s.c. cell and then cooled to ambient temperature before the measurement of the d.s.c. thermograms at a heating rate of 20°C min^{-1}. *Figure 5* gives the thermograms of a sample recorded after annealing at 90°C for 15 min. A sharp endothermic peak was observed for the first scan

(*Figure 5a*). Normally, a glass transition appears as a sudden change in slope in the d.s.c. curve but sometimes it appears as an endothermic peak[18]. The endotherm observed in *Figure 5a* is attributed to the glass transition of the EB film. Furthermore, when the same sample was subjected to the second heating programme, the d.s.c. curve (*Figure 5b*) clearly shows a normal (step-like) glass transition; and the exothermic increase in the curve at the temperatures after the transition is due to the subsequent exothermic processes (*Figure 4*). The T_g of the EB film is therefore determined to be ~105°C measured from the points of inflection in both the first and the second curves (*Figures 5a* and *b*, respectively). The discrepancy in the T_g values measured by d.m.a. and d.s.c. is believed to arise mainly from the content of NMP solvent in the film and will be discussed later.

The introduction of a small molecular weight plasticizer into a polymer has been established to significantly reduce the T_g of the polymer[19]. Thus, in this case the NMP solvent molecules can act as plasticizers in the NMP-containing EB films resulting in a shift of the glass transition to lower temperatures. Effects of the content of NMP in the EB films on T_g were further studied by thermal annealing experiments. Thus, the NMP-containing EB films were annealed at 100°C for 1 and 3 h or at 150°C for 1 h in nitrogen to remove part of the NMP ($M_w = 99.13$) solvent present in the films. The thermal analyses were then performed on these annealed EB films. The contents of NMP after the thermal treatments were determined by t.g.a. from the weight loss at 270°C. The reduction of the NMP content upon annealing is also indicated by a decrease in the intensity of the i.r. absorption band at 1671 cm^{-1} for C=O stretching in NMP. As shown in *Table 1*, the NMP content in the films decreases after the thermal treatments. The plots of E' *versus* temperature obtained from d.m.a. are given in *Figure 6* for the annealed EB films. The T_g increases with increase in the annealing temperature and time. The d.s.c. results showed a similar trend as demonstrated in *Table 1*. For the film annealed at 275°C for 1 h, the d.m.a. scan shows no transition up to ~400°C at which temperature the sample broke down. The above data clearly demonstrate the relationship between the content of NMP and T_g for the EB films and the function of NMP as the plasticizer. The value of T_g for the NMP-free EB films should therefore be expected to be even higher. *Figure 7* shows a d.m.a. scan of the NMP-free EB film (sample size 0.95 × 13.5 × 0.03 mm). There are two significant changes in E' at the onset temperatures of ~50 and ~190°C, respectively. The second change in E' is attributed to the glass transition of the polymer. The T_g was estimated to be

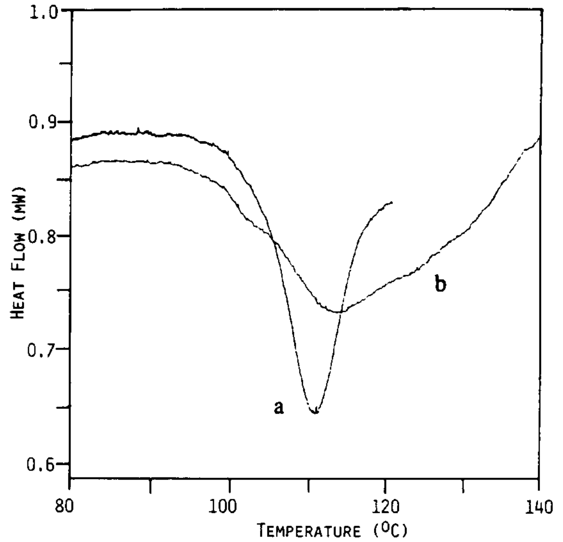

Figure 5 D.s.c. thermograms of the emeraldine base films of polyaniline. (a) The sample was preheated to and kept isothermal at 90°C for 15 min prior to the d.s.c. scan; (b) the second d.s.c. scan on the same sample

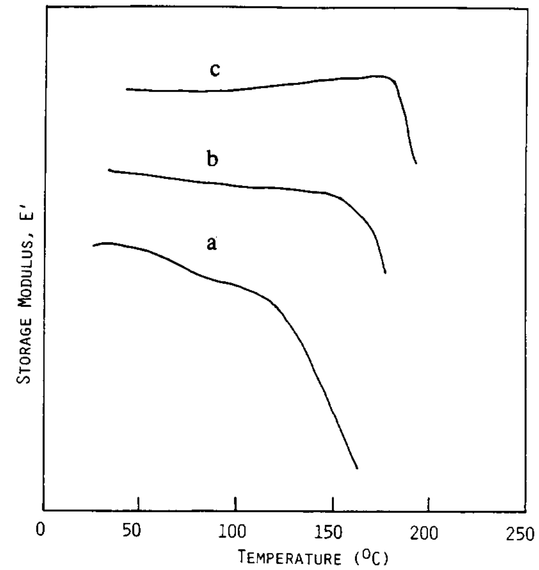

Figure 6 Plots of E' *versus* temperature from d.m.a. scans on the NMP-containing EB films of polyaniline after annealing at (a) 100°C for 1 h, (b) 100°C for 3 h and (c) 150°C for 1 h

Table 1 Effects of the NMP content on the T_g of the EB films of polyaniline

Film of polyaniline in base form	Annealing conditions		T_g (°C)		NMP content (wt% by t.g.a.)
	Temperature (°C)	Time (h)	D.m.a.[a]	D.s.c.[b]	
Containing NMP	–	–	140	105	16
	100	1	170	125	11
	100	3	180	140	9
	150	1	190	150	7
Upon removal of NMP	–	–	220	–	<0.5

[a] The values of T_g were determined from the point of inflection in the E' curves

[b] The samples containing NMP were annealed at 90°C for 15 min before recording the d.s.c. thermograms. The T_g for the polymer film after removal of NMP could not be accurately determined by d.s.c. because of the interference of the exotherm at ~250°C

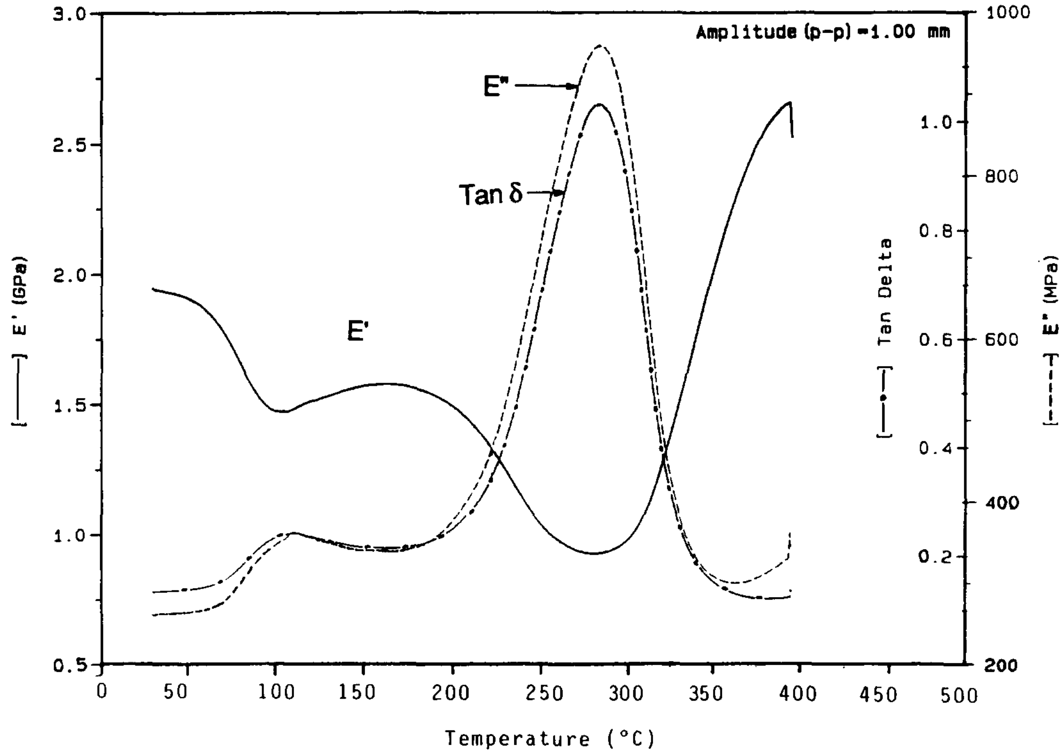

Figure 7 D.m.a. of the NMP-free EB film. Thickness of the film: 0.03 mm

~220°C from the point of inflection in the E'-temperature curve. The nature of the first drop in E' starting at ~50°C which was also observed in the d.m.a. of the NMP-containing EB films (*Figure 3*) is not understood as yet. Since the thermally annealed films showed less drop in E' in the temperature range of ~50–100°C (*Figure 6*), this drop might be due to the evaporation of the small amount of moisture and/or to some local motions of the polymer chain segments similar to the β transitions observed for many common polymers (e.g. polymethacrylates[20]). The glass transition for the NMP-free EB films cannot be observed clearly in the d.s.c. thermograms because of the interference of the broad exotherm at ~250°C (*Figure 3*).

As discussed above, the value of T_g of an EB film is very sensitive to the content of NMP in the film which in turn is affected by the annealing temperature and time. *Figure 8* shows a plot of the T_g determined by d.m.a. against the original content of NMP in the EB films. The T_g appears to be proportional to the NMP content. The slope of the plot is ~5°C %$^{-1}$ which represents the sensitivity of T_g towards the change in the NMP content. Therefore, a difference in the programmed heating rates for the thermal analysis techniques d.s.c. and d.m.a. should be expected to result in quite different contents of NMP in the polymer samples and different T_g values as a consequence, even though the samples originally contained the same amount of NMP. In the d.s.c. experiments, a high heating rate (20°C min^{-1}) was used in order to obtain a well-defined glass transition[20], whereas in the d.m.a. experiments, a relatively lower heating rate of 5°C min^{-1} was employed, which was generally recommended by the manufacturer of the instrument as the up-limit heating rate for reproducible results. The evaporation of NMP begins at ~80°C (*Figure 2a*). With a higher heating rate as in the case of d.s.c., the content of NMP at the temperatures around the T_g should be closer to that present in the original film, while with a lower heating rate as in d.m.a., more NMP will be evaporated, resulting in a higher T_g. Therefore, the discrepancy between the values of T_g measured by d.s.c. and by d.m.a. (*Table 1*) should mainly result from the different heating rates in these two techniques. In addition, there are other factors (e.g. heating rate) which will affect the T_g because the glass transition is not a primary thermodynamic phase transition[17,20]. The value of T_g of a polymer measured with a dynamic technique such as d.m.a. (1 Hz applied in our experiments) is usually higher than that measured by d.s.c.[17]. This could also contribute to the discrepancy in the values of T_g observed for the EB films.

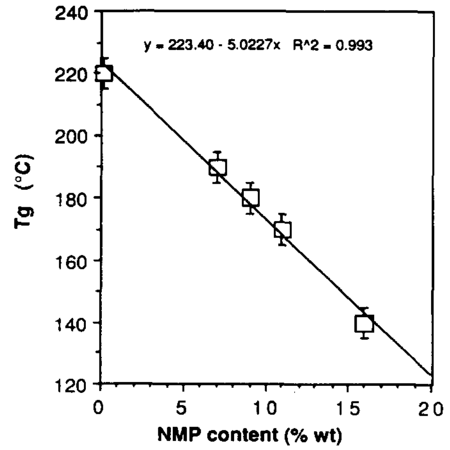

Figure 8 Effect of the content of NMP solvent on the T_g of the EB films determined by d.m.a.

As shown in *Figure 3*, the d.m.a. scan of the NMP-containing EB film shows a plateau in E' after the glass transition and in the temperature range of

~170–250°C. The moduli, E' and E'', indicate that the polymer is in a viscoelastic rubbery state in this range where the segmental diffusional motions are very rapid. Therefore, it should be possible to process the EB films still further in this temperature range (e.g. by uni- and/or bi-axial orientation, etc.) to improve the mechanical, electronic and other properties of the polymer[21]. Since the removal of the NMP solvent results in an increase in the T_g and, therefore, leads to the higher processing temperatures, the presence of NMP in the EB films is actually advantageous. As the temperature further increases (*Figure 3*), E' increases drastically and reaches a maximum at ~310°C. This process, which appears to correspond to the d.s.c. exotherm at ~250°C (*Figure 4*), is attributed to crosslinking of the polymer chains[9]. For the EB films free of NMP, the E' increases almost immediately after the glass transition, which results in a narrower temperature range suitable for the further processing.

It should be noted that there are two distinguishable broad exothermic peaks at ~180 and 250°C in the d.s.c. thermogram of the NMP-containing EB film (*Figure 4*). When the NMP solvent was partially removed by thermal annealing (e.g. at 150°C for 1 h), the exotherm at ~250°C remained intact while that at ~180°C almost disappeared (*Figure 9*). The d.s.c. thermogram of the film which has already been heated once to 300°C does not give any thermal process in the region of ~25–300°C. No major weight loss was observed in the t.g.a. thermogram at ~250°C. Therefore, the exotherm at ~250°C is attributed to crosslinking of the polymer chains. This assignment is further supported by the results of cyclic voltammetry and *FT*i.r. spectroscopy of the polymer. After a thermal annealing at high temperature, e.g. ~200°C, for 1 h in nitrogen, the polymer has a poor solubility in NMP; and the cyclic voltammogram of the polymer shows a significant increase in the current of the middle peaks which are indicative of crosslinking structure in polyaniline[22]. The intensity of i.r. absorption bands around 957 cm^{-1} corresponding to multisubstitution (e.g. 1,2,4-) on the benzene ring[15] is also increased because of the crosslinking.

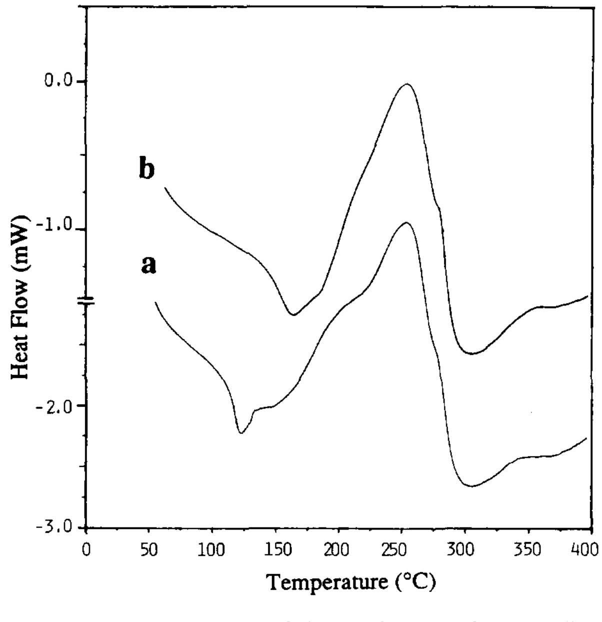

Figure 9 D.s.c. thermogram of the EB film (a) after annealing at 100°C for 10 min and (b) after annealing at 150°C for 1 h

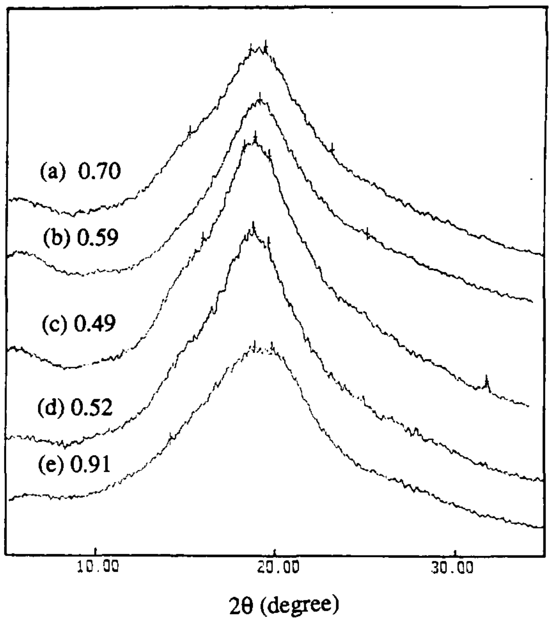

Figure 10 Wide-angle X-ray diffraction spectra of the EB film after annealing at (a) 40°C for 24 h, (b) 100°C for 1 h, (c) 150°C for 1 h, (d) 200°C for 1 h and (e) 280°C for 30 min. The numbers on the spectra represent the ratios of half-width to height of the diffraction peak

A series of X-ray diffraction experiments was carried out in an effort to interpret the d.s.c. exotherm at ~180°C. *Figure 10* shows wide-angle X-ray diffraction patterns of a polyaniline film annealed under various conditions in nitrogen. In general, no distinctive crystal structure is observed in this material. The amorphous peak appears at a 2θ of ~19.2°. The polymer heated at 40°C for 24 h gives essentially the same diffraction pattern (*Figure 10a*) as that before heating. There are several reports[4–6] on the X-ray diffraction of partially crystalline polyaniline in which crystalline diffraction peaks overlap with an amorphous peak also at a 2θ of ~19.5°. In a study of conducting polymer morphology, Warren and co-workers[23] found that the ratio of half-width to height (HW/H) of the X-ray diffraction peak reflects order in the polymer backbone. The smaller the value of HW/H, the higher the order[23]. Therefore, the values of HW/H for the EB film annealed under various conditions were determined as depicted in *Figure 10*. The value of HW/H first decreases with the annealing temperature and reaches a minimum at ~150°C (*Figure 10c*), then increases again as the temperature further increases. This observation indicates that the EB film imparts the highest order upon annealing at ~150°C. Noteworthy is that in a study of partially crystalline polyaniline in powder form, Wang and co-workers[4] also observed a maximum in crystallinity when the polymer was annealed at 150°C. Therefore, we suggest that at temperatures above T_g, the polyaniline chains reorganize into a more ordered or partially crystalline structures, which is responsible for the minimum in the HW/H value and for the d.s.c. exotherm at ~180°C.

Figure 4 demonstrates that the onset temperature of the broad exotherm at ~180°C is in the vicinity of, or overlaps with, the T_g of the NMP-containing EB film. Since the rigidity of a polymer will generally be increased as the polymer chains become more ordered or partially

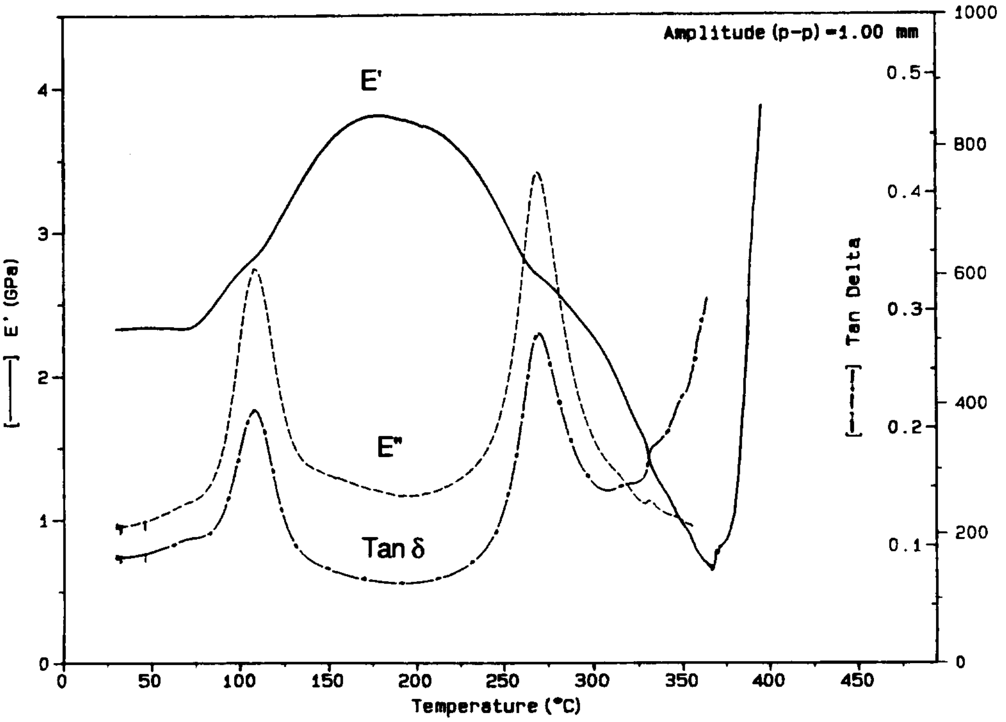

Figure 11 D.m.a. of the EB film after doping with 1 M HCl. Thickness of the film: 0.04 mm

crystallized[20], changes in the mechanical properties of the EB films in the glass transition region may appear to be less drastic than expected for a typical polymer. The *E'* of a typical polymer should drop three to four orders of magnitude in the glass transition region. In many cases, the *E'* of the EB films only decreases by a factor of 10 or less (*Figure 7*). This is likely due to the increased ordering or partial crystallization of the polymer chains. Crosslinking is also known to increase the rigidity of a polymer[21]. The T_g of the NMP-free EB film (~220°C) overlaps with the crosslinking exotherm at ~250°C, resulting in a less drastic decrease in the *E'* of the film and a broader transition region (*Figure 7*). Further studies of the EB film by increasing the frequency of dynamic loading are in progress to characterize the glass transition of polyaniline.

Electrical conductivities of the EB films are $<10^{-8}$ $S\,cm^{-1}$ regardless of their NMP content. When doped with 1 M HCl, the films show a metallic copper-like colour in the surface reflectance and moderately high conductivities in the order of magnitude of $10\,S\,cm^{-1}$. *Figure 11* shows a typical d.m.a. scan of the HCl-doped polyaniline film (0.95 × 13.0 × 0.04 mm). The *E'* of the film increases in the range of ~80–170°C. It has been found from the t.g.a. studies of HCl-doped polyaniline[9] that the HCl dopant and a small amount of moisture are evaporated in this temperature range. The dopant and moisture might also function as small molecule plasticizers and their removal should therefore be responsible for the increase in *E'*. After the evaporation of the HCl dopant, the *E'* decreases significantly in the temperature ranges of ~220–360°C. Both *E''* and tan *δ* showed maxima at ~275°C which should represent the T_g for the polymer. The broadening of the transition temperature range is attributed to the crosslinking of polyaniline[9]. When the temperature is further increased after the glass transition, the *E'* increases sharply, because of the crosslinking of the polymer, followed by breakdown of the film at ~400°C. Further studies of the thermal transitions of the doped polyaniline films is in progress in our laboratories.

CONCLUSIONS

We have observed and characterized the glass transition of NMP-solution-cast films of the EB of polyaniline. The T_g of the EB films is strongly dependent on the content of residual NMP solvent in the films. For the films containing ~16–0% of residual NMP solvent, the T_g was determined to be ~105–220°C, respectively, by d.m.a. and d.s.c. methods. The NMP solvent functions as a plasticizer which significantly reduces the T_g of the EB film. Depending on the NMP content, the EB films have an *E'* value in the range of ~200 MPa–2 GPa at temperatures below T_g. In the glass transition region, the films become much more flexible and *E'* decreases significantly to a value as low as ~0.1 MPa. The temperature range for the EB film in the rubbery state increases as the content of NMP in the film increases. When the temperature is further increased, the EB film becomes stiffer again and *E'* increases sharply to a value of ~270 MPa–5 GPa, because of the ordering/partial crystallization and crosslinking of the polymer chains. The polymer films break down at ~400°C.

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