THERMAL ANALYSIS OF ELECTROACTIVE POLYMERS BASED ON ANILINE AND ITS DERIVATIVES
A comparative study

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The thermal characteristics of polyaniline (PANI), poly(*o*-aminobenzoic acid) (POABAC) and poly(*o*-aminobenzyl alcohol) (POABOL) are determined and compared by thermogravimetry (TG) and differential scanning calorimetry (DSC). The higher thermal stability of POABOL is attributed to heat-induced condensation between the polymer chains. The DSC results suggest both intra- and inter-molecular interaction in the form of hydrogen bonding due to the substituent group in POABAC and POABOL. These interactions, however, occur mainly in the doped from and is greatly reduced when the dopant is expelled from the system at higher temperatures.

Keywords: conducting polymers, DSC, heat-induced condensation reaction, hydrogen-bonding, intramolecular and inter-molecular interaction, polyaniline, poly(*o*-aminobenzoic acid), poly(*o*-aminobenzyl alcohol), TG.

Introduction

Electrically conducting organic polymers are a novel class of synthetic metals that combine the chemical and mechanical attributes of polymers with the electronic properties of metals and semiconductors. They breach the traditional view of mutual exclusion between plastics and electrical conductivity, and their development has spurred intense interdisciplinary research in the last fifteen years [1–4].

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A wide variety of polyenes, polyaromatics and polyheterocycles have been investigated in the search for conducting polymers. Among those attracting considerable interest are polyacetylene [5], polythiophene [6], polypyrrole [7] and polyaniline (PANI) [8]. Polyaniline offers several advantages over the other conducting polymers: straightforward synthesis; ease of transformation between conducting and insulating forms; and thermal stability.

Initially the commercial exploitation of polyaniline has been hampered by its intractable nature, as it is normally produced as an insoluble powder chemically [9], or as a thin brittle film electrochemically [10]. A number of attempts to improve the solubility have been reported by the use of substituted aniline [11–13] or the post sulphonation of PANI [14] which provided a more soluble PANI with a conductivity of about 0.1 S cm^{-1}.

Recently the thermal stability of PANI has been reported by a number of workers [15–19]. The degradation can be roughly divided into three major steps: the loss of moisture and free HCl and unreacted monomer; the elimination of dopant; and the destruction of the skeletal backbone at increasing temperatures. While the loss of dopant is mainly responsible for the drop in conductivity at high temperatures, Kulkarni [20] suggested that for polyaniline tosylate, oxidation and possible structural rearrangement may also play an important part. Hagiwara *et al.* [15] reported that the deterioration of conductivity in air was based on the chemical change involving the elimination of hydrochloric acid of the amino group and the simultaneous chlorination of the aromatic ring.

We like to report in this communication a comparison of the thermal behavior of polyaniline (PANI), poly(*o*-aminobenzoic acid) (POABAC) and poly(*o*-aminobenzyl alcohol) (POABOL) based on TG and DSC. The results have been rationalized based on the effect of the –COOH and –CH2OH substituents on the polymer stability.

Experimental

Chamicals

Aniline (Aldrich) was distilled and stored under nitrogen in the dark prior to polymerization. Anthranilic acid (Aldrich) was recrystallized from H2O; mp. 145°–147°C. *o*-aminobenzyl alcohol (Aldrich), sodium persulphate (Na2S2O8) and HCl (BDH) were used without further purification.

Preparation of PANI

A 50 ml solution of Na2S2O8 (3.8 g; 16 mmol) was added dropwise with constant stirring to a 100 ml solution containing fresh aniline (1.5 ml; 16 mmol) and

about 1.0 *M* of HCl to maintain a *pH* of about 1.0. Polymerization was carried out at room temperature for 24 h, after which the powder obtained was filtered, washed with a small amount of HCl and dried in a desiccator.

Preparation of poly(o-aminobenzoic acid)

The procedure is similar to above except for a longer polymerization time of about 48 h.

Preparation of poly(o-aminobenzyl alcohol)

The procedure is similar to that of polyaniline except that the polymerization was carried out at 0°–5°C, to avoid oxidation of the pendent –CH_2OH group. Polymerization at ambient temperature ($\approx$30°C) afforded mainly POABAC.

Conductivity measurement

The polymers were pressed into disk-shaped pellets 7 mm in diameter. The conductivities were measured using a four-in-line-probe with 1 mm spacings. The two outer probes were connected to a Keithley model 228 constant voltage/current source. The inner two probes were connected to a Keithley model 195A digital multimeter for voltage measurement.

Thermogravimetry

The samples in powder form (10–20 mg) were analyzed using the Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer. A heating rate of 10°C was employed unless otherwise stated. The runs were conducted from room temperature to 700°C. Air flow over samples were maintained at 75 ml·min^{-1}.

Differential scanning calorimetry

A DSC 2910 module was used in conjunction with the Du Pont 2100 Thermal Analyst system. The analyses were conducted from room temperature to 350°C at a heating rate of 10 deg·min^{-1}. Powdered samples of approximately 10 mg each were used. An air flow rate of 75 ml·min^{-1} was used.

Results and discussion

The stoichiometries and the conductivities of the polymers are summarized in Table 1. The TG curves for the polymers are shown in Fig. 1 and the results are summarized in Table 2. A comparison indicates that in general the thermal degradation of the polymers can be divided into three main weight loss steps, in good agreement with those previously reported [16, 17]. The first weight loss from room temperature to ca. 180°C is due primarily to the expulsion of absorbed water together with some free acid and unreacted monomer from the polymer matrix. The second weight loss from 190° to 320°C has been attributed to the loss of acid dopant. The third weight loss from 350° to 700°C is caused by the oxidative thermal breakdown of the polymer backbone. More specifically, the second weight loss step for both POABAC and POABOL is greater than that of PANI. This is due to the loss of CO_2 from POABAC and the decomposition or rearrangement of CH_2OH from POABOL respectively. It is interesting to note that the temperature for the maximum rate of weight loss in the final degradation step for

Table 1 Stoichiometries and conductivities of PANI, POABAC and POABOL

Polymer	Atomic ratios found (Atomic ratios expected)	Conductivity / $S \cdot cm^{-1}$
PANI	$C_{6.19}H_{6.06}N_{1.00}Cl_{0.47}S_{0.04}$ $(C_{6.00}H_{5.00}N_{1.00}Cl_{0.50}S_{0.00})$	3.0×10^{0}
POABAC	$C_{6.90}H_{5.10}N_{1.00}Cl_{0.28}S_{0.12}$ $(C_{7.00}H_{5.00}N_{1.00}Cl_{0.50}S_{0.00})$	3.0×10^{-8}
POABOL	$C_{7.75}H_{8.94}N_{1.00}Cl_{0.47}S_{0.07}$ $(C_{7.00}H_{7.00}N_{1.00}Cl_{0.50}S_{0.00})$	1.4×10^{-3}

Table 2 Summary of TG results

Polymer	1st weight loss step	2nd weight loss step	3rd weight loss step	Main degradation temperature / °C
PANI	30°–142°C (10%)	142°–297°C (9.1%)	365°–630°C (71.2%)	514
POABAC	30°–142°C (7.6%)	142°–316°C (18.2%)	372°–610°C (65.2%)	489
POABOL	30°–180°C (12.9%)	180°–326°C (15.2%)	439°–700°C (60.6%)	600

POABOL is about 100°C higher than the other two polymers. The enhanced thermal stability of POABOL may be rationalized by the proposed mechanism shown in Fig. 2. Adjacent $-CH_2OH$ units undergo a heat-induced condensation, expelling water and forming ether or methylene cross-linkages, which stabilize the polymer against thermal decomposition. Close examination of the first weight loss step for POABOL suggests that the high 15.8% loss may have included the H_2O from the condensation.
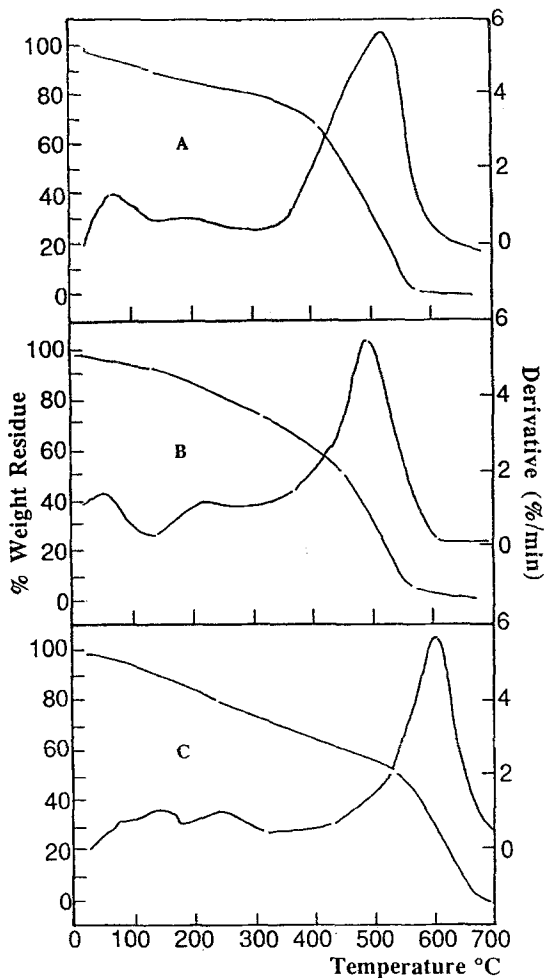

Fig. 1 TG curves of PANI (A); POABAC (B) and POABOL (C)

The DSC curves are shown in Fig. 3 and the results are summarized in Table 3. The endothermic enthalpy change (192.3 J·g^{-1}) for PANI between 100° to 250°C is attributable to the energy required to expel the dopant. The glass tran-

sition temperature (T_g) reported for PANI film [21] at about 140°C was not observed as it may have been masked by the other overlapping enthalpic changes in the polymer. For POABAC, we have attributed the two exotherms at 105° and
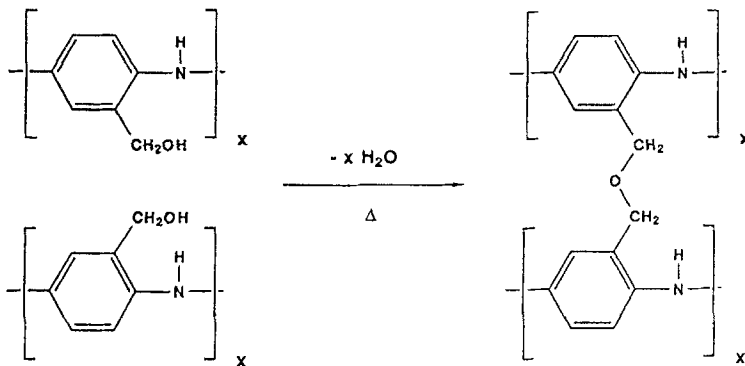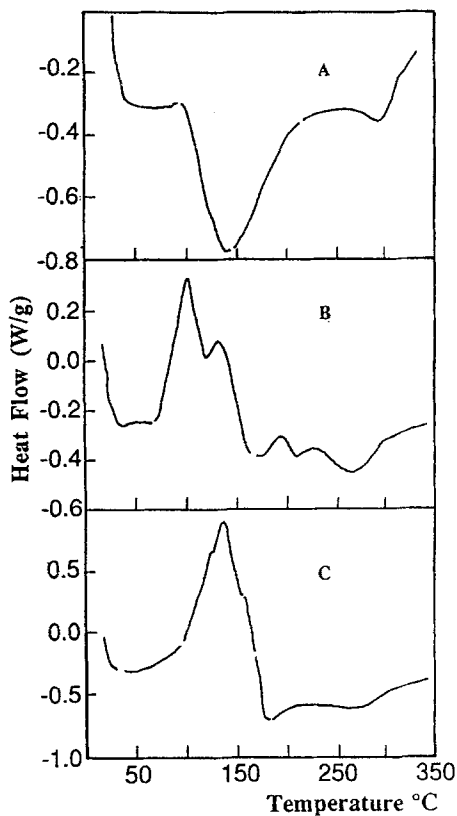

Fig. 2 Proposed condensation mechanism in POABOL

Fig. 3 DSC curves of PANI (A); POABAC (B) and POABOL (C)

Table 3 Summary of DSC results

Polymer	1 st Transition peak	2 nd Transition peak
PANI	94° –212°C (endo)	270° –312°C (endo)
	141°C (peak temp.)	293°C (peak temp.)
POABAC	64° –165°C (exo)	235° –293°C (endo)
	100°; 132° C (peak temp.)	263°C (peak temp.)
POABOL	64° –180°C (exo)	237° –304°C (endo)
	135°C (peak temp.)	274°C (peak temp.)

132°C respectively to intra- and inter-molecular hydrogen bonding made possible by the –COOH substituent as shown in Fig. 4. The degree of hydrogen-bonding is particularly pronounced in the doped polaronic form as the hydrogen of the amine group is made more positive. In the case of POABOL, the thermal behavior is complicated by the possibility of the formation of ether or methylene linkages mentioned earlier. The large exothermic peak at 135°C is likely to be a composite of a number of events: The exothermic inter- and intra-molecular hydrogen-bonding also possible in POABOL as shown in Fig. 5; the energy required to expel the H_2O; and the possible evolution of energy due to new ether bond formation. More work is needed to resolve the different processes to determine the temperature at which they occur and the nature of the competing overlapping transitions. An en-
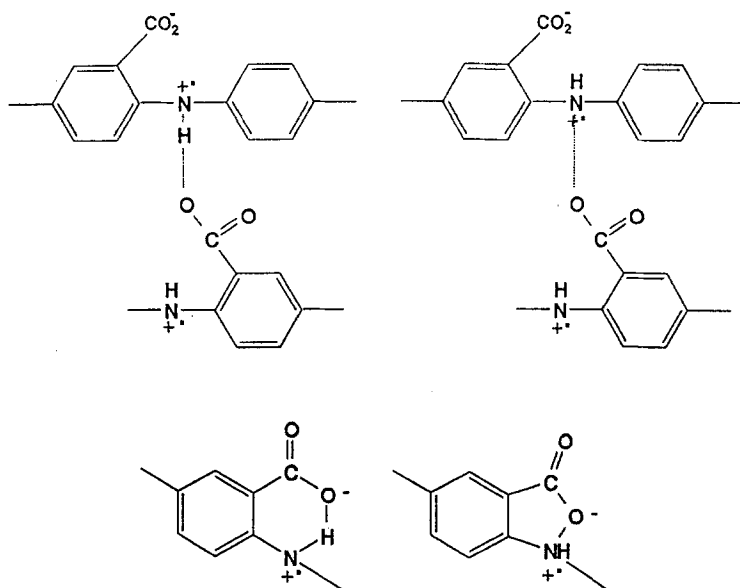
Fig. 4 Proposed inter- and intra-molecular interaction in POABAC

dothermic drift can be observed for all polymers around 235° to 310°C. This can be attributed to morphological changes within the polymer matrix although no visual changes were detected under the hot-stage microscope.
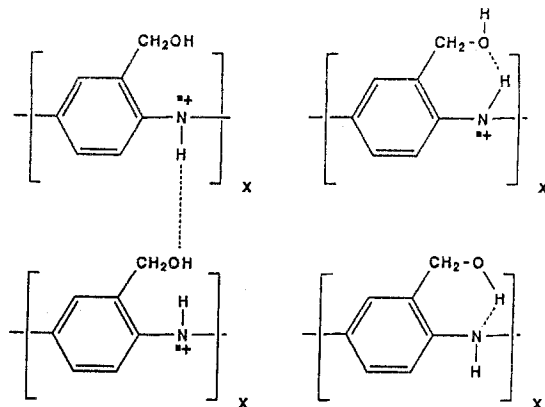

Fig. 5 Proposed inter- and intra-molecular interaction in POABOL

Usually the association between polymer chains due to hydrogen-bonds means a higher thermal stability, as more energy is required to overcome the secondary forces in operation. This, however, is not observed in POABAC which has a very similar overall thermal stability to PANI. This implies that the interaction between chains due to hydrogen-bonding is greatly diminished after the expulsion of the dopant at an earlier temperature between 140° to 320°C. The covalent ether linkages in POABOL, however, are not affected by the loss of dopant, remaining effective in stabilizing the polymers against thermal oxidative degradation.

Conclusions

We have compared the thermal properties of doped polyaniline, poly(o-amonobenzoic acid) and poly(o-aminobenzyl alcohol) by TG and DSC. Intra- and inter-molecular interactions in the form of hydrogen bonds have been proposed to explain the DSC exothermic peaks observed for the two substituted aniline polymers. Paradoxically, TG results indicate that such secondary association between polymer chains has no apparent effect on the overall stability at temperatures beyond the removal of the dopant. We propose that the hydrogen bonding occurs mainly in the doped state, whose effect is greatly reduced when the dopant is completely expelled at about 250°C.

In the case of POABOL, the superior thermal stability to PANI and POABAC can be attributed to the possible heat-induced condensation of the benzyl alcohol groups to form the ether or methylene linkage. This covalent linkage, unlike the secondary H-bonding mentioned above, remains effective at high temperatures.

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Zusammenfassung — Es wurden die thermischen Eigenschaften von Polyanilin (PANI), Poly(o-aminobenzoylsäure) (POABAC) und Poly(o-aminobenzylalkohol) (POABOL) ermittelt und mittels TG und DSC miteinander verglichen. Die höhere Thermostabilität von POABOL wird der wärmeinduzierten Kondensationsreaktion zwischen den Polymerketten zugeschrieben. Die DSC-Resultate weisen auf sowohl intra- als auch intermolekulare Wechselwirkungen in Form von Wasserstoffbrückenbindungen infolge der Substituenten in POABAC und POABOL hin. Diese Wechselwirkungen treten hauptsächlich in der dotierten Form auf und werden in großem Maße reduziert, wenn die Dotierungsmittel bei höheren Temperaturen ausgetrieben werden.