Thermal analysis of conducting polymers. Part II. Thermal characterization of electroactive copolymers from aniline and anthranilic acid

H.S.O. Chan, S.C. Ng and W.S. Sim

Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge, Singapore 0511 (Singapore)

(Received 16 July 1991)

Abstract

Conducting homopolymers and soluble copolymers of aniline (AN) and anthranilic acid (AA) have been synthesized and doped with hydrochloric acid (HCl). DSC results indicate strong intra- and intermolecular hydrogen bonding (H bonding) in the case of polyanthranilic acid (PAA) and the copolymer. Paradoxically, TG studies show that the overall high-temperature thermal stability which usually increases as a result of such secondary forces, is almost the same for PAA, the copolymer CP11 (AN/AA:1/1) and polyaniline (PAN), which is incapable of forming H bonds. This implies that the H bonding occurs only in the doped form and is greatly reduced when the HCl dopant is expelled at about 250°C.

INTRODUCTION

Polyaniline, which was discovered in the late nineteenth century [1], has recently aroused much interest because of its easy protonation reversibility and excellent redox recyclibility. The polymer can be used as an electrode material [2–4], in microelectronics [5,6] and as an electrochromic device [7]. Future possibilities may include its use in radiation shielding and recordable optical discs [8].

The commercial usefulness of PAN has been limited by its intractable nature, especially in the doped form which is normally produced chemically as an insoluble powder [9] or electrically as an in situ fragile thin film on the electrode [10]. In an attempt to improve solubility, many substituted anilines have been studied [11–15]. In general, the increase in solubility is achieved at the expense of conductivity. Recently the post sulphonation of PAN base yielded a soluble PAN with conductivity in the region of 10^{-1} S cm^{-1} [16]. An alternative approach to the solubility problem involves the

---

Correspondence to: H.S.O. Chan, Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge, Singapore 0511, Singapore.

fabrication of PAN into tougher films either in the homogeneous form or as composites. This can be done by polymerization on a porous support [17], blending with conventional polymers [18,19] and Languiv Blodgett (LB) thin films of polymers containing heterocyclic rings [20].

Thermal techniques such as TG and DSC have recently been widely used to study the thermal behavior of polyanilines [21–23]. The results reported are in good agreement in terms of the temperature at which loss of dopant occurs, the overall degradation pattern of the backbone polymer in air and nitrogen, and the volatilization of trapped solvent and water. We would like to report in this communication the TG and DSC results on conducting homopolymers and novel soluble copolymers prepared from aniline and anthranilic acid.

EXPERIMENTAL

Chemicals

The aniline and anthranilic acid were purchased from Aldrich Chemical Co. Inc. The $Na_2S_2O_8$ and HCl were obtained from B.D.H. The aniline was distilled and stored under nitrogen in the dark prior to polymerization. Anthranilic acid was recrystallized from H_2O, m.p. 145–147°C.

Preparation of polyaniline

A 50 ml solution of $Na_2S_2O_8$(3.8 g, 16 mmol) was slowly added, dropwise with constant stirring to a 100 ml solution containing fresh aniline (1.5 ml, 16 mmol) and about 1.0 M HCl to maintain a pH of about 0.1. Polymerization was carried out at room temperature for about 24 h, after which the polymer powder obtained was filtered, washed with a small amount of HCl and dried in a desiccator.

Preparation of polyanthranilic acid

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

Preparation of copolymers

A 50 ml solution of $Na_2S_2O_8$ (3.8 g, 16 mmol) was added dropwise, with constant stirring to a 100 ml solution containing aniline (0.75 g, 8 mmol), anthranilic acid (1.1 g, 8 mmol) and HCl to maintain a pH of about 0.1. The polymerization was carried out for approximately 48 h. The polymer powder formed was filtered off and dried in a desiccator. The coding for the different copolymers prepared based on different feed ratios of the

TABLE 1

Conductivities and yields of homopolymers and copolymers

Code	Monomer feed (ratio)	Yield (%)	Conductivity (S cm^{-1})
PAN	(1:0 AN/AA)	57.4	7.7×10^0
CP21	(2:1 AN/AA)	50.1	4.0×10^0
CP11	(1:1 AN/AA)	39.2	6.5×10^{-3}
CP12	(1:2 AN/AA)	32.1	2.2×10^{-5}
PAA	(0:1 AN/AA)	7.8	2.7×10^{-8}

co-monomers and the homopolymers, and their conductivities are given in Table 1 for ease of reference. Their general structure is given in Fig. 1.

Conductivity measurement

The homopolymers and copolymers were pressed into disk-shaped pellets 12.7 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 2100 Thermal Analyst system with a TGA 2950 thermogravimetric analyzer. A heating rate of 10°C min^{-1} was used unless otherwise stated and the runs were conducted from room temperature to 700°C. A dynamic air flow rate of 75 cm^3 min^{-1} was selected.

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 tempera-
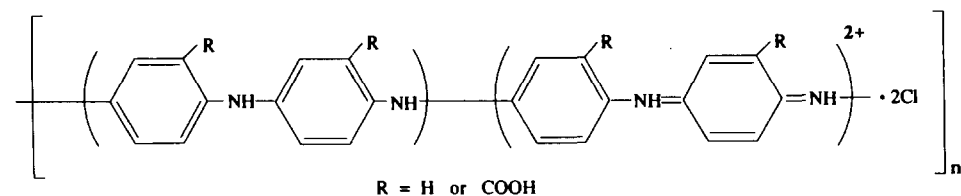

R = H or COOH

Fig. 1. General structure of copolymer.

ture to 350°C at a heating rate of 10°C min^{-1}. Samples of approximately 10 mg each were used.

RESULTS AND DISCUSSION

The TG curves for PAN–HCl, PAA–HCl and CP11–HCl (which is representative of the copolymers) are given in Figs. 2A, 2B and 2C respectively. It can be seen that the three polymers behave similarly, which is expected because the polymers are not very different in structure. Moreover, the weight loss pattern is in good agreement with previous reports on polyaniline [21–23]. The first weight loss at around 30–100°C can be attributed to the volatilization of solvent or surface HCl. The second small step between 175 and 280°C is due to the loss of the dopant HCl, and in the case of the CP11 and PAA, the co-evolution of CO_2 (12–15% compared to 8% in PAN). The major step with the maximum rate of decomposition at around 530°C indicates the breakdown of the polyaniline backbone. The present TG results suggest that the use of the copolymers offers no advantage in terms of thermal stability over polyaniline.
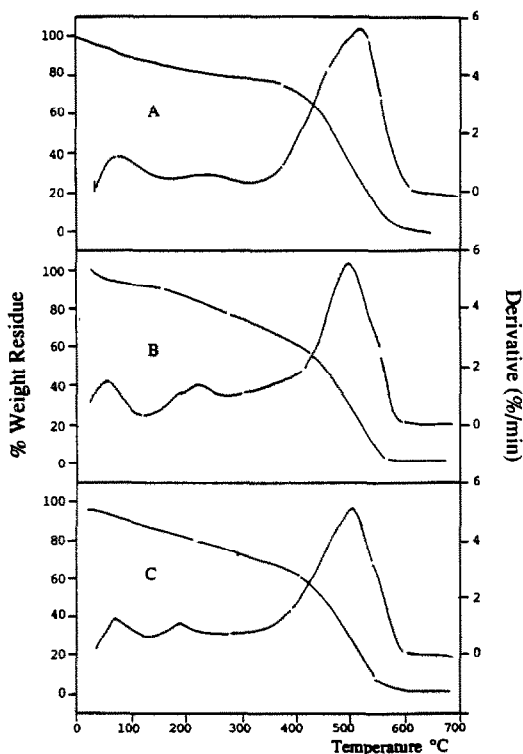

Fig. 2. TG curves of: A, PAN–HCl; B, PAA–HCl; and C, CP11–HCl.
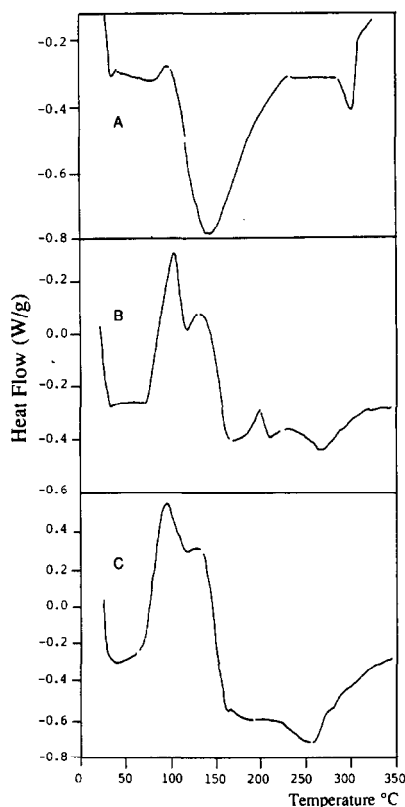
Fig. 3. DSC curves of: A, PAN–HCl; B, PAA–HCl; and C, CP11–HCl.

The DSC curves for PAN–HCl, PAA–HCl and CP11–HCl are shown in Figs. 3A, 3B and 3C respectively. The large endothermic peak for PAN–HCl between 180 and 260°C correlates with the loss of HCl dopant in the TG study and the enthalpy of this process is 192.3 J g^{-1}. The glass transition temperature (T_g) reported for polyaniline film [24] at about 140°C was not observed because it may have been masked by other overlapping enthalpic changes in the polymer. Moreover, a different sample form was used in this work. For the copolymer CP11 and homopolymer PAA, we have attributed the two exotherms at 95°C and 136°C to intra- and intermolecular hydrogen bonding inherent in the polymer structure as shown in Fig. 4. The degree of hydrogen bonding is particularly pronounced in the doped form because the hydrogens attached to the protonated amine or imine nitrogen atoms are made more electropositive. Maximum hydrogen bonding is achieved, especially in the case of intermolecular interaction, when the polymer chains have acquired enough energy to orientate and align themselves above the glass transition temperature at which segmental rotation through the C–C single bond is possible. This gives an indirect measure of the T_g which is in the region of 130–140°C, close to that
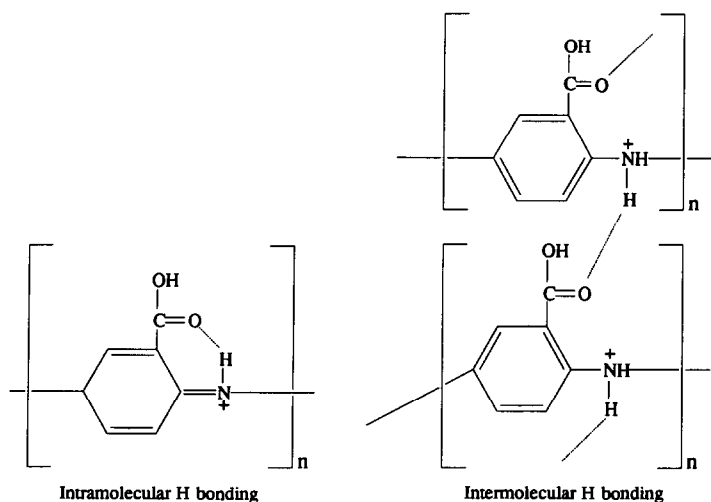
Fig. 4. Mechanism of H bondings found in PAA–HCl and CP11–HCl.

reported previously [24]. The endothermic drift between 250 and 300°C in Figs. 3A–3C can be attributed to morphological changes within the polymer matrix. Examination under a microscope up to 300°C did not show any flow behavior.

Usually the association between molecules or polymer chains through the formation of hydrogen bonds is responsible for higher thermal stability, because more energy is required to overcome the hydrogen bonds formed prior to the decomposition of the polymer backbone. This, however, is not observed in the present study as indicated by the very similar TG curves obtained for the homopolymers and copolymer. This implies that in the undoped state after the expulsion of the HCl dopant, the interaction between chains due to hydrogen bonding is diminished to the extent that it has no influence on the subsequent thermal behavior of the polymer.

CONCLUSION

We have synthesized polyanthranilic acid and copolymers based on aniline and anthranilic acid. The increase in solubility of the copolymers is achieved at the expense of conductivity. DSC results suggest strong intra- and intermolecular H bonding in both the doped PAA and copolymer CP11. Interestingly, the overall stability of the polymers studied at higher temperatures is apparently independent of the H bonding. This suggests that after the expulsion of the HCl dopant, the strong inter-chain interactions due to H bondings are greatly reduced and they no longer exert a stabilizing influence on the decomposition of the polymer.

REFERENCES

1 A.G. Green and A.E. Woodhead, J. Chem. Soc., 97 (1910) 2388.
2 A.G. MacDiarmid, J. Chiang, M. Halpern, W.S. Wu, N.L.D. Somasiri, and S.I. Yaniger, Mol. Cryst. Liq. Cryst., 121 (1985) 375.
3 N. Oyama and T. Ohsaka, Synth. Met., 18 (1987) 375.
4 C.M. Carlin, L.J. Kepley and A.J. Bard, J. Electrochem. Soc., 132 (1985) 353.
5 E.P. Lofton, J.W. Thackeray and M.S. Wrighton, J. Phys. Chem., 90 (1986) 6080.
6 S. Chao and M.S. Wrighton, J. Am. Chem. Soc., 109 (1987) 6627.
7 A. Kitani, J. Yano and K. Sasaki, J. Electroanal. Chem., 209 (1986) 227.
8 E. Edelson, Popular Science, June (1990) 90.
9 S.P. Armes and J.F. Miller, Synth. Met., 22 (1988) 385.
10 W.S. Huang, B.D. Humphery and A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. 1, 82 (1986) 2385.
11 T. Osaka, T. Okajimi and N. Oyama, J. Electroanal. Chem., 200 (1986) 159; 215 (1987) 181.
12 P. Snauwaert, R. Lazzaroni, J. Riga and J.J. Verbist, Synth. Met., 21 (1987) 181.
13 S.K. Manohar, A.G. MacDiarmid, K. Kromack, J.M. Ginder and A.J. Epstein, Synth. Met., 29 (1989) E349.
14 E.M. Genies, J.F. Penneau and M. Lapkowski, New J. Chem., 12 (1988) 765.
15 P. Snauwaert, R. Lazzaroni, J. Riga and J.J. Verbist, Synth. Met., 18 (1987) 335.
16 J. Yue and A.J. Epstein, J. Am. Chem. Soc., 112 (1990) 2800.
17 R.B. Bjorklund and I. Lundstrom, J. Electron. Mater., 13 (1984) 211.
18 B. Wessling and H. Volk, Mol. Cryst. Liq. Cryst., 160 (1988) 205.
19 H.S.O. Chan, P.K.H. Ho, K.L. Tan and B.T.G. Tan, Synth. Met., 35 (1990) 333.
20 K. Hong and M.F. Rubner, Thin Solid Films 160 (1988) 369.
21 Y. Wei and K.F. Hsueh, J. Polym. Sci. Part A, 27 (1989) 4351.
22 T. Hagiwara, M. Yamaura and K. Iwata, Synth. Met., 25 (1988) 243.
23 H.S.O. Chan, M.Y.B. Teo, E. Khor and C.N. Lim, J. Therm. Anal., 35 (1989) 765.
24 Y. Wei, G.W. Jang and K.F. Hsueh, Polym. Mater. Sci. Eng., 61 (1989) 916.