

THERMAL ANALYSIS OF POLY(*p*-XYLYLENE) AND POLY($\alpha,\alpha,\alpha',\alpha'$ -TETRAFLUORO-*p*-XYLYLENE)

A. O. Oyewale* and R. A. Aitken**

* Chemistry Department, Ahmadu Bello University, Zaria, Nigeria

**Chemistry Department, St. Andrews University, Fife, Scotland, UK

(Received January 20, 1994; in revised form December 30, 1994)

Abstract

The TG(DTG) and DTA of poly(*p*-xylylene) and poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) are reported. The degradation was performed from ambient temperature to 900°C in both air and nitrogen. Both polymer degrade faster in air than under nitrogen but the fluorinated polymer eventually decomposed at higher temperature in air than in nitrogen atmosphere. The activation energies of the degradation processes is given.

Keywords: activation energy, degradation, differential thermal analysis, poly(α,α' -difluorostilbene), poly(*p*-xylylene), polystilbene, poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene), *p*-xylylene, thermogravimetric analysis, vaporization

Introduction

The *p*-xylylene polymer was first prepared in 1904 [1]. An excellent review on the preparation and properties of the polymer has been written by Szwarc and Errede [2]. When the polymer is heated, no change is observed until about 380°C, when the white opaque polymer film turns into a transparent one without losing its shape [3]. This change has been attributed to an irreversible transformation of the α -form of the polymer to its β -form and may also involve a chemical transformation, namely dehydrogenation of poly(*p*-xylylene) into a linear polystilbene in which each phenyl ring has a quinoid structure [4]. Decomposition of the poly(*p*-xylylene) was reported to take place on melting at about 400°C, with random chain scission to give benzene, toluene, xylenes, *p*-methylstyrene and *p*-ethyltoluene as volatile products [5].

(*p*-Xylylene) polymer prepared by low temperature reactions [4, 6, 7], are often of low molecular weight, higher solubility and therefore degrade at lower temperature than the polymer prepared by pyrolysis and deposited on liquid N₂ cooled surface [7]. This paper reports on a comparative study of the simultaneous TG(DTG) and DTA analysis of poly(*p*-xylylene) and poly($\alpha,\alpha,\alpha',\alpha'$ -

tetrafluoro-*p*-xylylene), prepared by gas phase generation and cooled trap deposition [8] of the corresponding intermediate *p*-xylylene.

Experimental

Materials

The polymers were prepared by gas phase dehalogenation, over solid reagents, of the precursor perhalogenated *p*-xylenes. The intermediate *p*-xylylenes generated are then deposited at liquid nitrogen temperature onto a surface. The polymers were obtained as a thin-film and are insoluble in conventional organic solvents. The polymer materials were characterised by elemental analysis and 500 MHz solid state NMR [8].

TG/DTA analysis

Simultaneous thermal studies was carried out on a Perkin-Elmer 7 series thermal analyser, from ambient temperature to 900°C, in both nitrogen and air atmosphere. The samples were heated at the rate of 10 deg·min⁻¹ in a platinum pan. Decomposition temperature was taken at the peak of the DTA endotherm corresponding to a constant TG plot.

Results and discussion

The *p*-xylylene polymer (I) exhibited remarkable heat stability in nitrogen atmosphere and shows virtually no weight loss until about 490°C (Fig. 1). This

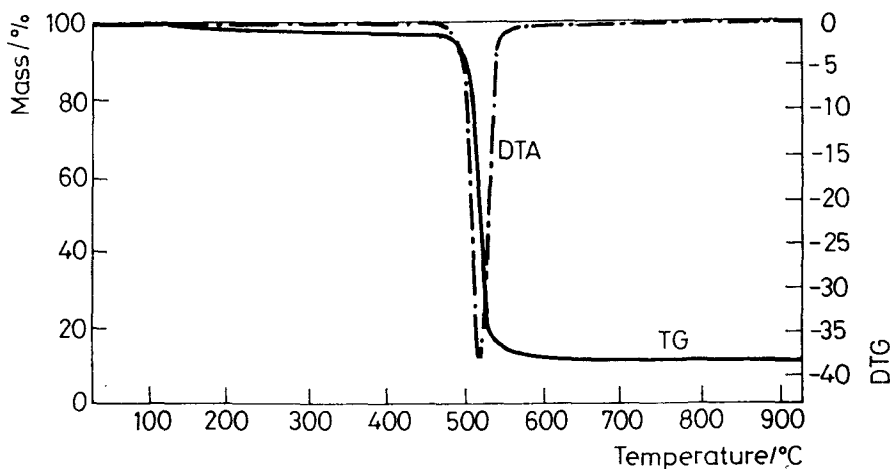
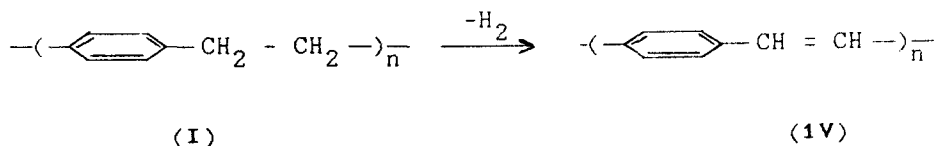


Fig. 1 TG curve of polymer (I) in N₂

was followed by very rapid weight loss (about 90%), with the polymer decomposing at 520°C. After this vigorous reaction, the unidentified decomposition residue remain unchanged up to 900°C. This residue is likely crack-carbon, which is often formed when thermal decomposition is performed in a non-oxidizing atmosphere [9].



In air, polymer (I) was stable to about 280°C (Fig. 2), after which the DTA curve shows an irregular shape between 280–300°C followed by a small endotherm peak at 340°C. The decomposition endotherm peak appear at about 490°C. The TG curve shows that the irregular shape portion and the small endotherm peak on the DTA curve correspond to a total of 20.0% weight loss. This is then followed by a gradual weight loss (about 20%) between 340–473°C, with the polymer finally decomposing in the 487–525°C range, on the TG curve.

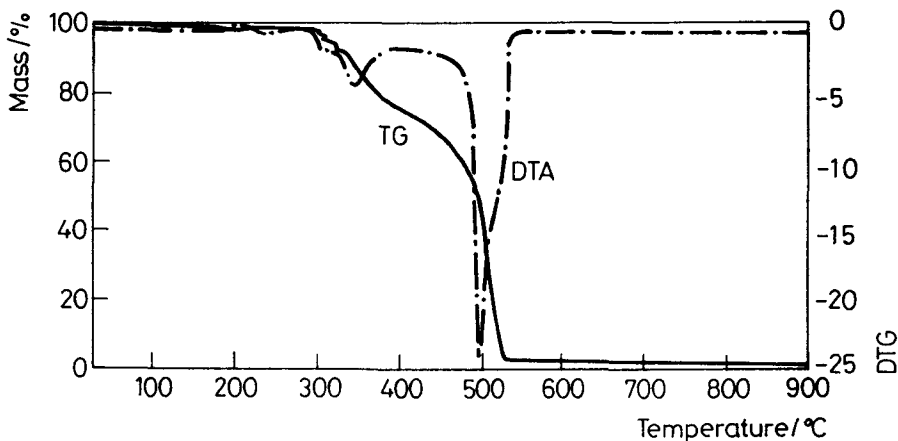


Fig. 2 TG curve of polymer (I) in air

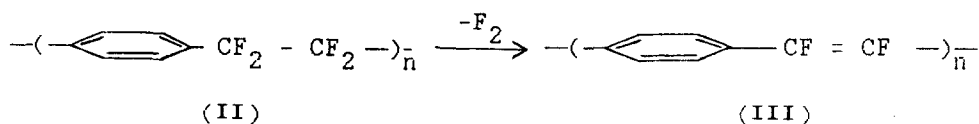
The plots of $\ln(\text{DTG})$ vs. $1/T$ allow determination of the E_a , activation energy value in the Arrhenius equation. In both nitrogen (Fig. 3) and air (Fig. 4) atmosphere, the graphs consist of two straight line segments, the one at low temperature being attributed to polymer rupture and melting, while the high temperatures segment, to decomposition and vaporization. In air, polymer (I) rupture was accompanied by vaporization, as indicated by the endotherm at 340°C on the DTA curve and the corresponding weight loss (20.0%) on the TG curve. The degradation processes of polymer (I), in air occur at a lower tem-

perature than in N₂ atmosphere. This is not uncommon, as degradation is almost always faster in the presence of oxygen [10]; presumably due to the lower activation energy required for the degradation processes in air than in N₂ atmosphere (Table 1).

Table 1 Degradation processes and activation energies

		Temp.-range °C	Process	E_a /J·mol ⁻¹
Polymer (I)	in N ₂	490–505	Melting + rupture	26.6·10 ³
		510–525	Decomp. + vaporization	41.6·10 ³
Polymer (I)	in air	340–473	Melting + rupture	1.25·10 ³
		487–525	Decomp. + vaporization	9.15·10 ³
Polymer (II)	in N ₂	100–440	Defluorination	
		460–530	Melting + rupture	3.24·10 ³
		535–580	Decomp. + vaporization	14.1·10 ³
Polymer (II)	in air	100–440	Defluorination	
		490–568	Melting + rupture	1.50·10 ³
		585–638	Decomp. + vaporization	9.15·10 ³

Polymer (II), poly($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylene) show thermal stability similar to polymer (I). The DTA curve show only a single endotherm, which appear when the polymer decomposed at 570°C, under N₂ atmosphere (Fig. 5). In air, a small endotherm appear at 200°C, similar to the small endotherm observed at 340°C on the TG plot of polymer (I); with the decomposition occurring at 620°C (Fig. 6). On the TG plot, polymer (II) show a 20% weight loss prior to decomposition in both air and N₂ atmosphere. This weight loss corresponds to the elimination of fluorine molecules from the polymer chain. The elimination therefore transforms polymer (II) to poly(α,α' -difluorostilbene) – (III) and the decomposition temperature recorded is actually due to polymer (III). The defluorination process occurs between 100–440°C in both air and N₂ atmosphere.



A similar transformation may occur during the thermal degradation of polymer (I) to give the linear polystilbene (IV); evidence exist in the literature to

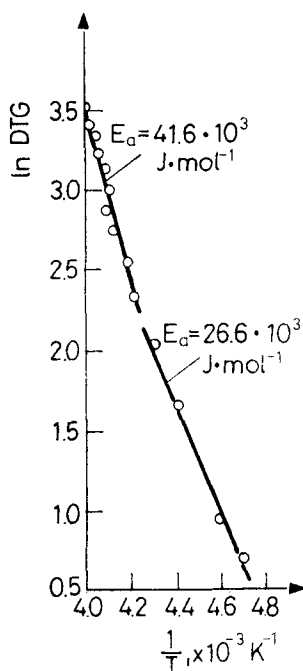


Fig. 3 A plot of $\ln(\text{DTG})$ vs. $1/T$ of polymer (I) in N_2

support such transformation [4]. However due to the small weight loss associated with the elimination of hydrogen molecules (less than 2%) from polymer (I), the weight loss is not clearly evident on the TG curve.

A plot of $\ln(\text{DTG})$ vs. $1/T$ for the degradation process of polymer (II) in N_2 (Fig. 7) and air (Fig. 8), gave straight line graphs which consist of two line segments, similar to the plot for polymer (I). The low temperature segment is attributed to polymer rupture and melting, while the high temperature segment is due to polymer decomposition and vaporization.

In general, the activation energies for the degradation processes (Table 1) is lower in air than in N_2 atmosphere, for both polymers. However, a rather unusual observation is that polymers (II) decomposed at a higher temperature in air than in N_2 atmosphere, despite the fact that oxygen is known to promote degradation [10]. The reason for this deviation is not apparent but may be due to some form of polymer cross-linkage through fluorine atoms, in the presence of oxygen, to give a material of very high thermal stability. This material may also account for the unidentified decomposition residue, corresponding to 45.0% of the initial polymer weight on the TG curve, which was obtained when polymer (II) was degraded in air. The residue did not vaporize, even at 900°C .

In addition, the activation energies estimated for the degradation processes of both polymers, are relatively low when compared to most reactions that pro-

ceed at a reasonable rate (half-life of minutes to hours). The E_a value for such reactions often range from 50–100 kJ [11]. However, the low E_a for the degradation processes of the polymers is not surprising owing to the high temperature nature of the reaction. High temperature is known to lower the E_a value of most reactions, according to the Arrhenius equation.

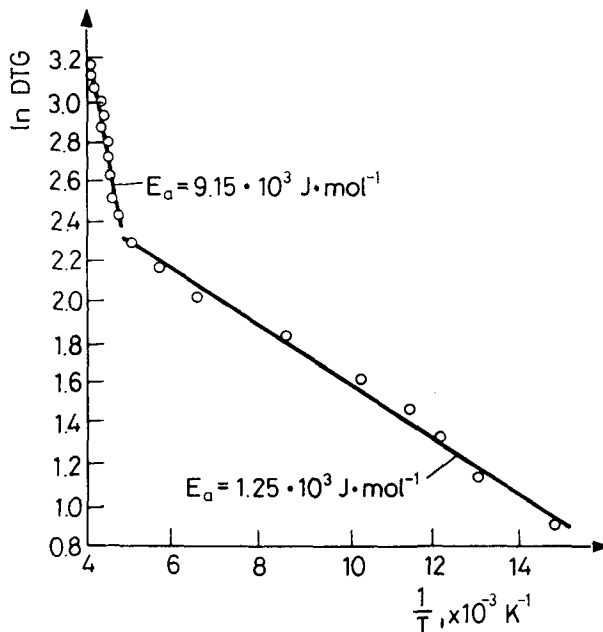


Fig. 4 A plot of $\ln(\text{DTG})$ vs. $1/T$ of polymer (I) in air

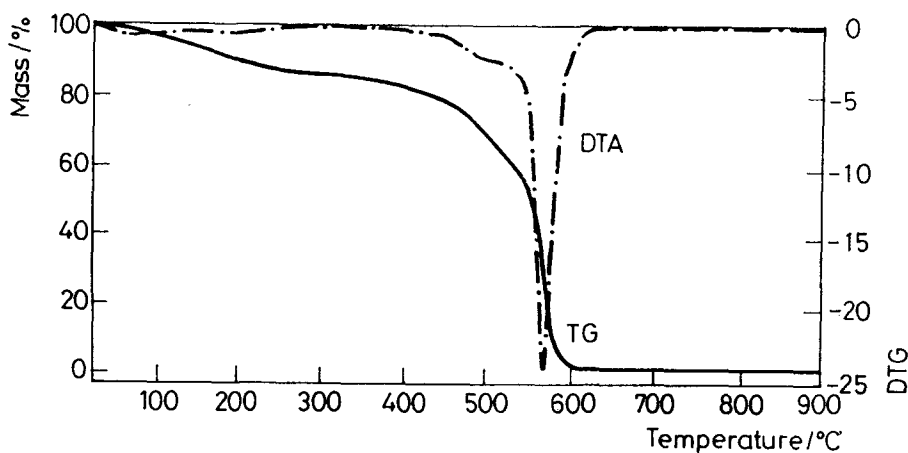


Fig. 5 TG curve of polymer (II) in N_2

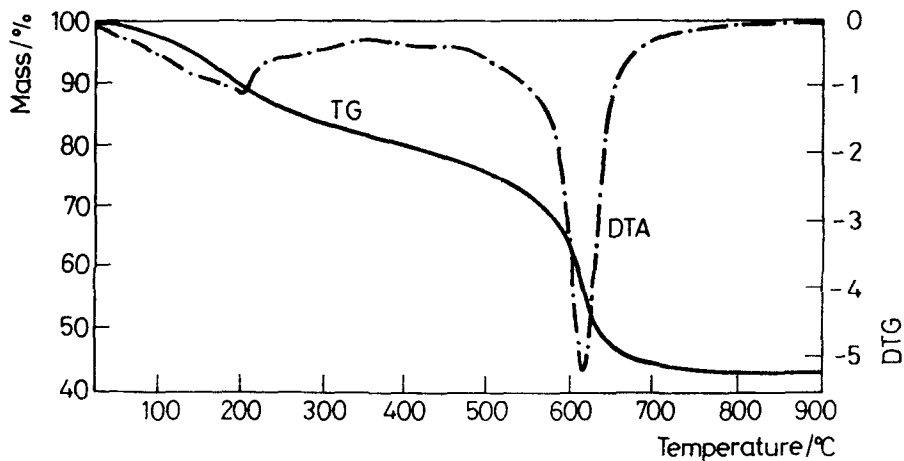


Fig. 6 TG curve of polymer (II) in air

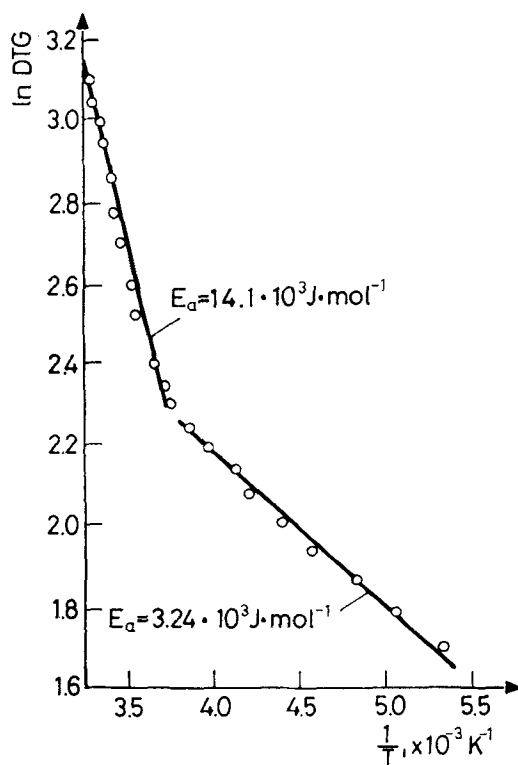


Fig. 7 A plot of $\ln(\text{DTG})$ vs. $1/T$ of polymer (II) in N_2

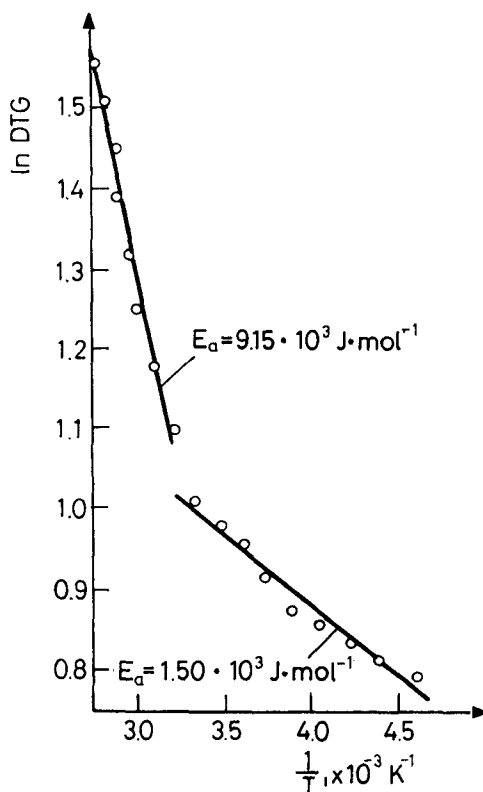


Fig. 8 A plot of $\ln(\text{DTG})$ vs. $1/T$ of polymer (II) in air

Conclusion

The comparative thermal stability of polymer (I) and (II); and by implication polymers (IV) and (III) respectively, can be attributed to the identical bond strength of the C-H ($435.3 \text{ kJ}\cdot\text{mol}^{-1}$) and C-F ($456.3 \text{ kJ}\cdot\text{mol}^{-1}$) bonds [11]. As a reflection of this slight bond energy difference polymer (II) decomposes at a slightly higher temperature than polymer (I). Although the activation energies (Table 1) for the degradation processes is higher for polymer (I) than polymer (II), in N_2 atmosphere; the latter decomposed at a higher temperature than the former. In air, both polymers have identical activation energies, however, polymer (II) still decomposed at a higher temperature than polymer (I).

References

- 1 J. Thiele and H. Balhorn, Ber, Dtsch. Chem. Ges., 37 (1904) 1463.
- 2 M. Szwarc and L. A. Errede, Quart. Rev., 12 (1958) 301.

- 3 M. Szwarc, *Discussions Faraday Soc.*, 2 (1947) 46; *J. Polymer Sci.*, 6 (1951) 319.
- 4 C. J. Brown and A. C. Farthing, *J. Chem. Soc.*, (1953) 3270.
- 5 S. L. Madorsky and S. Strauss, *J. Res. Nat. Bur. Stand.*, 55 (1955) 223.
- 6 H. G. Gilch and W. L. Wheelwright, *J. Polymer Sci.*, 4 (1966) 1337.
- 7 L. A. Auspos, L. A. Hall, J. K. Hubbard, W. Kirk, J. R. Schaeffgen, R. John and S. B. Speck, *J. Polymer Sci.*, 15 (1955) 9.
- 8 A. O. Oyewale, 'Unpublished Ph. D. Thesis', St. Andrews University, Scotland, UK, 1990.
- 9 R. J. Acheson and A. K. Galwey, *J. Chem. Soc.*, (1967) 1174; H. Yokobayashi, K. Nagase and K. Muraishi, *Bull Chem. Soc., Japan*, 45 (1975) 2789.
- 10 N. Grassie and G. Scott, 'Polymer Degradation and Stabilisation', 1st Edn., Cambridge University Press, UK, 1985.
- 11 J. A. Kerr, M. J. Parsonage and A. F. Trotman-Dickenson, 'Handbook of Chemistry and Physics', 55th Edn., CRC Publishing Co., F-213 to F-216 1975.

Zusammenfassung — Es wird die TG(DTG) und DTA von Poly(*p*-xylylen) und von Poly-($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-*p*-xylylen) beschrieben. Der Abbau wurde sowohl in Luft als auch in Stickstoff von Raumtemperatur bis 900°C durchgeführt. Beide Polymere werden in Luft schneller abgebaut als in Stickstoff. Die Aktivierungsenergien der Abbauvorgänge werden gegeben.