Thermochimica Acta, 132 (1988) 245–251
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDY OF THERMAL STABILITIES OF POLYETHYLENEOXIDES (MOLECULAR WEIGHT RANGE, $\bar{Mn}$ = 200–4000)

DHOAIB AL-SAMMERRAI and NEDHAL NIDAWY

Petroleum Research Centre, P.O. Box 10039, Jadiriyah, Baghdad (Iraq)

KHALIL AL-YASEEN

Board of Scientific Research, Mesbah, Baghdad (Iraq)

(Received 15 January 1988)

ABSTRACT

Differential scanning calorimetric and thermogravimetric analyses of polyethyleneoxides of molecular weights ranging between 200 and 4000 were carried out under different atmospheres. Information was obtained about their thermal stability and their thermal decomposition patterns. The polyethyleneoxides with low molecular weights (< 1000) exhibited explosive behaviour under the oxidizing conditions of oxygen gas.

INTRODUCTION

Controlled oxidation of ethylene oxide under alkali conditions yields a range of polymers which have molecular weights up to 20 000. They are viscous liquids or waxes depending on the degree of polymerization [1].

Low molecular weight polyethyleneoxides are an interesting class of products which have wide application as lubricants, vehicles, binders, intermediates, solvents, carriers, cosmetics, etc. [2,3].

Thermoanalytical techniques, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG) have been used extensively in recent years for studying the thermal behaviour and decomposition patterns of many polyene-type polymeric products under different atmospheric conditions [4–7].

Since polyethyleneoxides are subjected to high temperatures especially during blending or in service, it is appropriate to investigate their thermal behaviour and thermal degradation in different atmospheres using thermoanalytical techniques.

0040-6031/88/$03.50

EXPERIMENTAL

Differential scanning calorimetry (DSC), thermogravimetric (TG) and differential thermogravimetric (DTG) measurements were carried out on a HERAEUS TA 500 thermal analyser.

In the DSC measurements, samples weighing 10–15 mg were heated at a rate of 10 °C $\min^{-1}$ in an aluminium crucible under a static atmosphere of nitrogen or air. The reference cell was filled with pure, dry aluminium oxide powder.

TG and DTG curves were recorded simultaneously by placing a sample weighing 10–15 mg in a platinum crucible and heating at a rate of 20 °C $\min^{-1}$ under a flowing atmosphere of nitrogen or oxygen gas. Gas flow rates were 6 l h^{-1}.

The number average molecular weights ($M\bar{n}$) of polyethyleneoxide samples were characterized using an AKNAUR vapour pressure osmometer equipped with variable temperature thermostats and probes. Double distilled water was used as solvent and benzil ($C_{14}H_{10}O_2$) as standard. All $M\bar{n}$ measurements were made at 310 K. Table 1 shows $M\bar{n}$ values for different polyethyleneoxides measured by the vapour pressure osmometer.

All thermal and molecular weight determinations were performed in duplicate.

Fresh polyethyleneoxide samples were manufactured at BASF, F.R.G.

RESULTS AND DISCUSSION

Typical DSC curves recorded between 0 °C and 350 °C for polyethyleneoxides under static nitrogen and air atmospheres are shown in Figs. 1 and 2, respectively.

Under both atmospheres a sharp endothermic peak attributed to the melting of the polymers was recorded and its position moved up the

TABLE 1

Molecular weights of polyethyleneoxides studied

Sample	Molecular weight, $M\bar{n}$
A	200
B	400
C	1000
D	1500
E	2000
F	4000

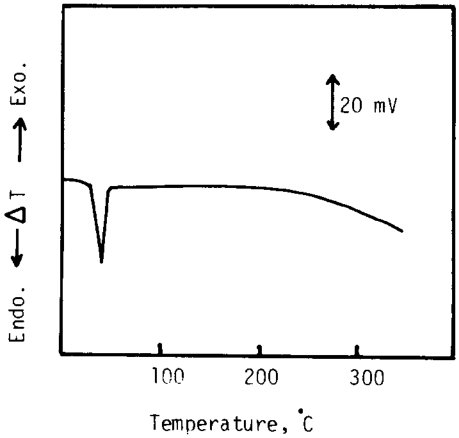

Fig. 1. Typical DSC curves of the polyethyleneoxides performed in static nitrogen atmosphere.

temperature scale with an increase in molecular weight. A good correlation was exhibited between the onset temperature of the melting endotherms and the corresponding literature melting points as shown in Table 2.

This was followed under a nitrogen atmosphere by another endothermic offset which was attributed mainly to the start of volatilization of the polyethyleneoxides. The onset temperatures of this transition are displayed in Table 3. It is clear from this table that the onset temperatures increased with an increase in molecular weight of the polymers.

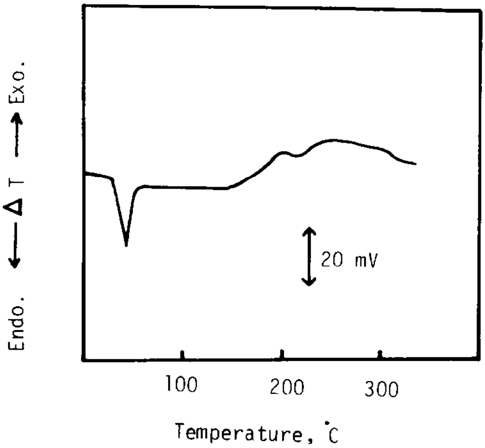

Fig. 2. Typical DSC curves of the polyethyleneoxides performed in static air atmosphere.

TABLE 2

Onset temperatures of the melting transition of polyethyleneoxides and some of their corresponding literature melting points

Sample	Melting onset temp. (°C) [a]	Literature m.p. (°C) [b]
A	–	–
B	8.0	4–8
C	36.5	37–40
D	45	43–46
E	50	–
F	53.5	53–56

[a] From DSC traces. [b] From ref. 3.

However, under an air atmosphere an exothermic system starting at about 160 °C was recorded which was attributed to the start of the overwhelming oxidative degradation in addition to volatilization of the polymers. This onset temperature (~ 160 °C) is lower than that recorded for the corresponding polyethylenes [4]. This behaviour could be attributed to the fact that the polymers containing oxygen bridges in the main chain are more susceptible to degradation than those having a backbone of mainly carbon atoms.

The typical features of the TG and DTG curves of the polyethyleneoxides studies, performed in an atmosphere of nitrogen or oxygen gas between room temperature and 650 °C, are displayed in Fig. 3.

Under the inert atmosphere of nitrogen gas the polyethyleneoxides underwent volatilization which proceeded with a well-defined single transition indicating a maximum weight loss between 200 and 300 °C for the lower molecular weight polymers ($\overline{Mn} = 200$ and 400), and between 400 and 500 °C for the higher molecular weight polymers ($\overline{Mn} > 1000$). This is displayed in Table 4 which shows the percentage weight loss at 100 °C intervals. These data were extracted from the TG curves and no residual matter remained at the end of the temperature programme. The initial temperatures of the transition (T_i), the maximum temperatures of the

TABLE 3

The onset temperatures of volatilization of the polyethyleneoxides recorded from the DSC trace under nitrogen gas

Sample	Onset temperature (°C)
A	155
B	210
C	225
D	260
E	340
F	–

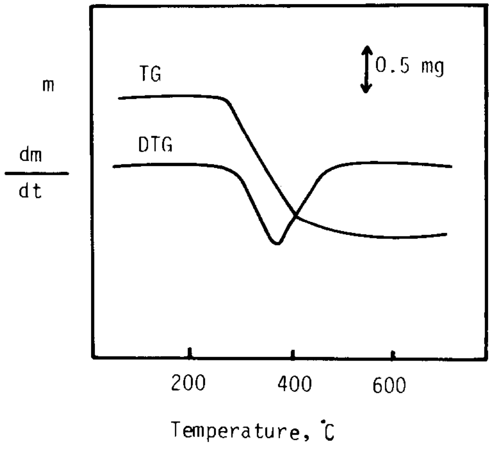

Fig. 3. Representative TG and DTG curves of the polyethyleneoxides performed in dynamic nitrogen and oxygen atmospheres.

transition (T_m) and the final temperatures of the transition (T_f) of the weight loss volatilization step, which were recorded from the DTG curves in nitrogen gas, are displayed in Table 5. The initial temperatures of the transition (T_i) recorded from the DTG curves correlate well with the onset temperatures of the transition recorded in the corresponding DSC trace under nitrogen atmosphere (see Table 3). It is also worth noting that the temperatures of the transition recorded from the DTG trace increased with an increase in the molecular weight of the polyethyleneoxides.

The polyethyleneoxides under oxygen gas underwent degradative volatilization which proceeded with a well-defined single transition indicating a maximum weight loss between 200 and 300 °C for all the polymers with the exception of those having molecular weights less than 1000, which exploded soon after the heating programme started. The percentage weight losses recorded at 100 °C intervals are displayed in Table 4. No residual matter remained at the end of the temperature programme.

The temperatures of the transition (T_i, T_m and T_f), which were recorded from the DTG curves in oxygen gas, are displayed in Table 5. These temperatures of transition increased with an increase in $\overline{Mn}$ values of the polyethyleneoxides. However, owing to their explosive nature, the polymer with the lowest molecular weight (200) showed no initial temperature of transition, while the polymer with a molecular weight of 400 showed no maximum temperature of transition. These two polymers did not behave explosively in the DSC measurements, because of the lower concentrations of oxygen gas present in the static air atmosphere. It is also worth noting that the initial temperatures of transition (T_i) of the polyethyleneoxides (excluding PEO $\overline{Mn} = 200$) are lower in value than the corresponding T_i values recorded under nitrogen gas.

TABLE 4

The percentage weight loss at 100 ° C intervals for the polyethyleneoxides recorded from the TG curves in nitrogen and oxygen atmospheres

Temperature range (° C)	N_2 gas						O_2 gas					
	A	B	C	D	E	F	A	B	C	D	E	F
100–200	40.0	0	0	0	0	0	–	1.8	2.0	0	0	0
200–300	50.5	69.0	25.0	5.7	0	0	–	–	97.5	98.0	97.5	96.5
300–400	7.5	27.0	68.5	31.4	30.0	15.8	–	–	0.5	2.0	2.0	3.0
400–500	2.0	4.0	6.5	62.9	70.0	83.9	–	–	0	0	0.5	0.5
500–600	0	0	0	0	0	0.3	–	–	0	0	0	0

TABLE 5

Onset temperatures of transition of polyethyleneoxides recorded from DTG curves in nitrogen and oxygen atmospheres

Sample	N_2 gas			O_2 gas		
	T_i	T_m	T_f	T_i	T_m	T_f
A	150	255	440	Explodes	–	–
B	200	320	450	175	Explodes	–
C	225	400	475	190	260	370
D	250	440	500	200	280	400
E	345	450	510	205	285	425
F	350	455	550	210	290	440

T_i, initial temperature of transition (°C); T_m, maximum temperature of transition (°C); T_f, final temperature of transition (°C).

The explosive behaviour of some of the polyethyleneoxides and the decrease in the T_i values under oxygen can be attributed to the fragile oxygen-containing backbone which.is more susceptible to breakdown under the severer oxidizing conditions.

ACKNOWLEDGMENT

We express our thanks to Dr. M. Al-Jarrah for providing us with the fresh polyethyleneoxide samples.

REFERENCES

1 C.A. Finch, Polyethyleneoxides, John Wiley, London, 1973.
2 J.A. Brydson, Plastic Materials, 4th edn., Butterworth Scientific, London, 1982.
3 N.M. Bikales (Ed.), Encyclopedia of Polymer Science and Technology, Vol. 6, Wiley, New York, 1967, p. 103.
4 I. Gömory, J. Therm. Anal., 11 (1977) 327.
5 J. Chiu, Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem., 14 (1973) 846.
6 D. Al-Sammerrai, Polym. Deg. Stab., 15 (1986) 183.
7 D. Al-Sammerrai, J. Appl. Polym. Sci., 31 (1986) 1.