CHARACTERIZATION OF DEGRADATION PRODUCTS OF POLYETHYLENE OXIDE BY PYROLYSIS MASS SPECTROMETRY

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Abstract—The techniques of direct and indirect (evolved gas analysis) pyrolysis MS are used to characterize the thermal degradation products of polyethylene oxide. Using direct pyrolysis MS technique the main degradation process is determined to be due to C—O and C—C scissions yielding fragments characteristic of the polymer. Evolved gas analysis indicates formation of small molecular stable compounds such as $C_2H_5OC_2H_5$, CH_3CHO, CO_2, CO and C_2H_4.

INTRODUCTION

Polyethylene oxide, PEO, is a tough ductile highly crystalline thermoplastic and is readily soluble in water. It is finding increasing commercial use [1, 2] in the form of disposable laundary bags, packaging for agricultural seeding, hazardous dyes and detergents, chromatographic stationary phases and wet-track adhesives. It is also used as a conducting medium in light weight energy density batteries [3]. Although, chemical and physical characteristics of PEO have been extensively studied, only few reports about thermal [1, 4, 5] or thermo-oxidative [6, 7] stability and degradation appeared in the literature.

Thermal degradation of polymers have been studied with different techniques; differential scanning calorimetry [5, 6], thermo gravimetric method [1, 4], thermal volatilization analysis [8], dynamic mechanical thermal analysis [2], pyrolysis, evolved gas analysis [9–13] by i.r., MS or GC. However most of the commonly used thermal analysis methods can not give any information about the chemical nature of the degradation products. Recently pyrolysis products of several polymers by i.r. and MS have been studied in our laboratory [9–11]. Now, we report results obtained by a more direct pyrolysis technique applied to analyze thermal degradation products of PEO.

EXPERIMENTAL PROCEDURES

Standard PEO homopolymer with M_w of 9×10^5 and 4×10^6 g·mol^{-1} were obtained from Aldrich chemical company. In direct pyrolysis experiments, 20 μl 1% (w/v) PEO–ethyl alcohol solution was placed inside the sample holder and the solvent was evaporated to dryness at room temperature. In direct pyrolysis (evolved gas analysis) experiments 10 mg samples were used.

For direct pyrolysis experiments, a probe (Fig. 1) that can be inserted directly inside the mass spectrometer through a

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valve that allows differential pumping of the probe inlet line was designed. It is basically composed of a stainless steel tube connected to a copper assemble carrying the copper sample holder. A heater is placed inside the stainless steel tube, and a thermocouple is connected to measure temperature.

The system used for evolved gas analysis was similar to the one described in our previous studies [9, 10]. Simply it consists of an oven, a pyrex reactor chamber and a needle valve which is connected to the mass spectrometer.

Duplicate runs indicated high reproducibility of the techniques used. The mass spectrometer was Balzers QMG 311 quadrupole mass spectrometer conected to a personal computer for the control of the MS, data acquisition and analysis.

RESULTS AND DISCUSSION

Direct pyrolysis analysis

Thermal degradation products of PEO ($M_w = 9 \times 10^5$ g·mol^{-1}) were studied by recording mass spectra as a function of temperature. The temperature was increased to 120° rapidly and then the sample was heated at a rate of 15°/min until the temperature reached 210°. Finally the rate of heating was decreased to 1°/min and kept constant.

The peak of 45 a.m.u. was the first that appeared at 140° and increased slowly until it reached a maximum of 222°. Then it nearly disappeared around 230°. At 235° it again showed up together with the peaks related to dimer ($m/z = 89$ a.m.u.), trimer ($m/z = 133$ a.m.u.), tetramer ($m/z = 177$ a.m.u.), pentamer ($m/z = 221$ a.m.u.) and hexamer ($m/z = 265$ a.m.u.). Ion yields increased rapidly and reached their maximum values at 248° and disappeared totally at 254°. Thus, it can be concluded that the degradation of the polymer mainly occurred at 235–255° range. The main peaks observed in the mass spectra represent $CH_3CH_2O(CH_2CH_2O)_n^+$, $CH_3CH_2O(CH_2CH_2O)_nCH_2^+$ and $CH_3CH_2O(CH_2CH_2O)_nCH_2CH_2^+$ fragments where $n = 0$–6. Relatively weaker peaks due to hydrogen losses from
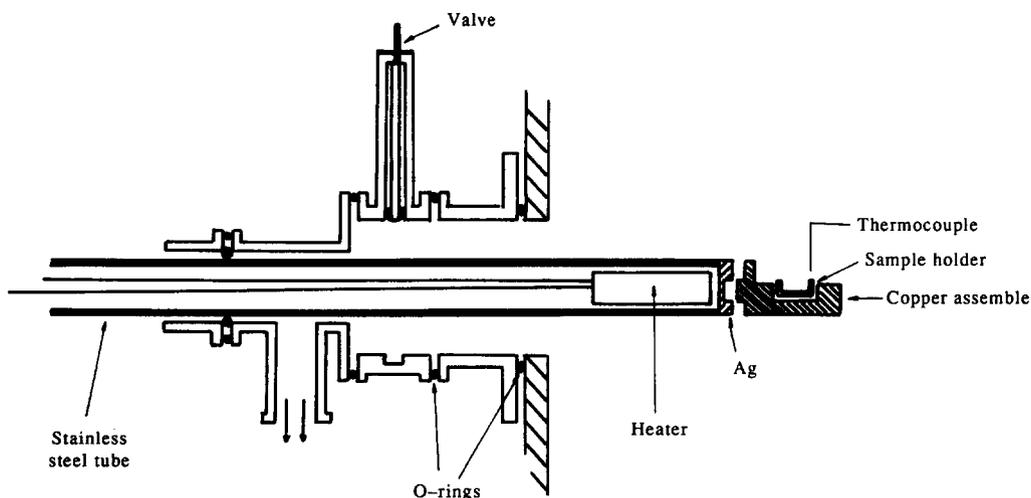
Fig. 1. Pyrolysis probe.

these main fragments were also present. The base peak was the monomer peak at 45 a.m.u., $CH_3CH_2O^+$, throughout the experiment at any temperature. Relative intensities of the main peaks decreased as the chainlength increased. Variation of intensities of peaks related to monomer, dimer, trimer and tetramer as a function of temperature are given in Fig. 2. In general stability of a radical fragment decreases with chain length. The experimental observations are in accordance with this fact. However, one should also consider the fragmentation of the degradation products in the ion source of the mass spectrometer. Ionization of the thermal decomposition products with energetic electrons will cause further fragmentation which in turn results in considerable increase in the relative abundances of the low mass ions.

$$\text{\textasciitilde\textasciitilde\textasciitilde}CH_3CH_2O(CH_2CH_2O)_nCH_2CH_2O\text{\textasciitilde\textasciitilde\textasciitilde}$$

$$\xrightarrow{\Delta} CH_3CH_2O(CH_2CH_2O)_n^\bullet$$

$$CH_3CH_2O(CH_2CH_2O)_n^\bullet + e^-$$

$$\rightarrow CH_3CH_2O(CH_2CH_2O)_m^+$$

where $n > m$

In order to investigate the extent of fragmentation in the mass spectrometer, analysis of pyrolysis products of the same sample were carried out at different electron energies; 65, 50, 40, 30 and 20 eV. In all these experiments degradation occurred at the same temperature range (235–255°) revealing the high reproducibility of the pyrolysis technique used. In Fig. 3, mass spectra recorded at 248°, corresponding to maximum product yield temperature, using 65, 50, 40, 30 and 20 eV electrons are plotted. It can be observed from the figure that relative intensities of the higher mass peaks increased noticeably as the electron energy decreased. The base peak shifted to mass 89 a.m.u. (dimer) and relative intensities of higher mass fragments increased compared to the monomer peak. A three fold increase in case of dimer and tetramer and about a four fold increase in case of trimer and pentamer were observed (Table 1). Identical

increases in relative intensities of the peaks related to $CH_3CH_2O(CH_2CH_2O)_nCH_2^+$ and $CH_3CH_2O-(CH_2CH_2O)_nCH_2CH_2^+$ ions were also detected.

The variation of intensities of peaks related to monomer, dimer, trimer and tetramer as a function of temperature recorded at 20 eV are shown in Fig. 4. A very similar trend in degradation of the polymer as a function of temperature can be observed from the figure. But notice also the differences in the relative intensities. Although the relative intensity of the peak at 45 a.m.u. decreased above 230°, it considerably
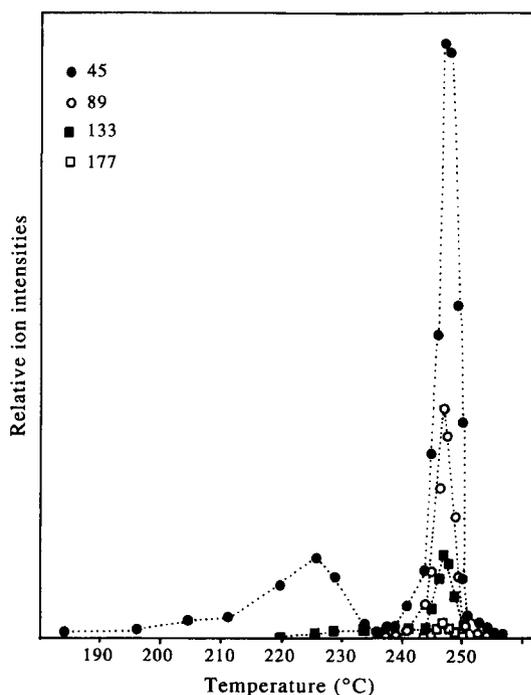
Fig. 2. Variation of intensities of peaks at 45, 89, 133, 177 a.m.u. as a function of temperature at ionization energy of 65 eV.
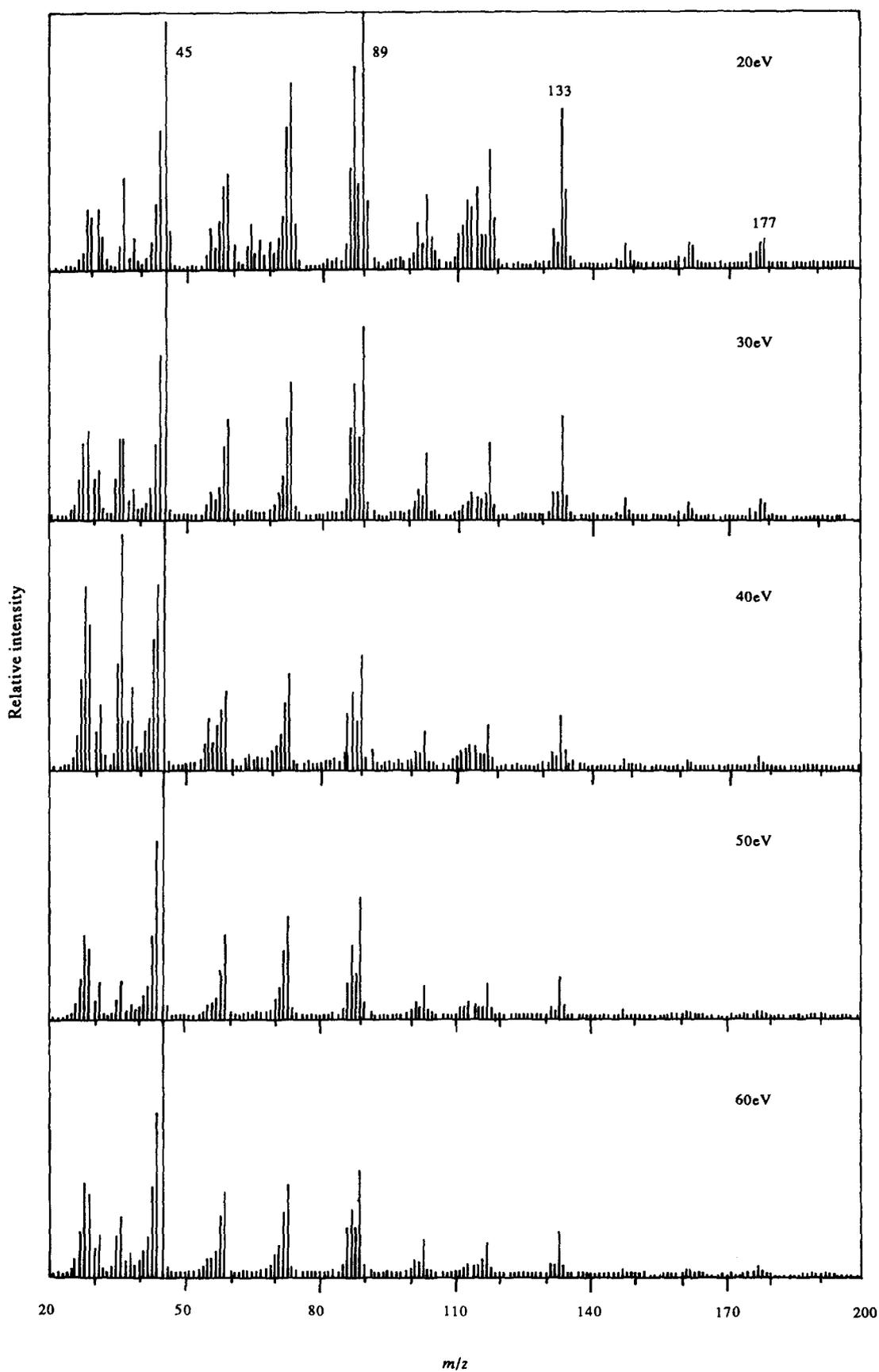
Fig. 3. Mass spectra of pyrolysis products of PEO at 248° at various electron energies.

Table 1. Relative intensities of $CH_3CH_2O(CH_2CH_2O)_n^+$, $CH_3H_2O(CH_2CH_2O)_nCH_2^+$ and $CH_3CH_2O(CH_2CH_2O)_nCH_2CH_2^+$ ions at various electron energies at 248°

Peak	Relative intensity					
			Electron energy			
(a.m.u.)	65 eV	50 eV	40 eV	30 eV	20 eV	Assignment
45	1000	1000	1000	1000	950	$CH_3CH_2O^+$
59	305	330	273	351	364	$CH_3CH_2OCH_2^+$
73	340	390	350	527	709	$CH_3CH_2 OCH_2CH_2^+$
89	383	473	464	755	1000	$CH_3CH_2OCH_2CH_2O^+$
103	112	130	118	221	294	$CH_3CH_2OCH_2CH_2OCH_2^+$
117	117	147	150	284	446	$CH_3CH_2 OCH_2CH_2OCH_2CH_2^+$
133	140	180	189	383	607	$CH_3CH_2O(CH_2CH_2O)_2^+$
147	24	28	27	60	84	$CH_3CH_2O(CH_2CH_2O)_2CH_2^+$
161	17	21	23	50	79	$CH_3CH_2O(CH_2CH_2O)_2CH_2CH_2^+$
177	24	29	33	67	84	$CH_3CH_2O(CH_2CH_2O)_3^+$
191	2	2	4	4	6	$CH_3CH_2O(CH_2CH_2O)_3CH_2^+$
205	1	2	2	4	5	$CH_3CH_2O(CH_2CH_2O)_3CH_2CH_2^+$
221	2	2	3	4	7	$CH_3CH_2O(CH_2CH_2O)_4^+$
235	1	1	1	1	1	$CH_3CH_2O(CH_2CH_2O)_4CH_2^+$
249	1	1	1	1	2	$CH_3CH_2O(CH_2CH_2O)_4CH_2CH_2^+$
265	1	1	1	1	1	$CH_3CH_2O(CH_2CH_2O)_5^+$
279	1	1	1	1	1	$CH_3CH_2O(CH_2CH_2O)_5CH_2^+$

increased at the low energy range. No other peak above 45 a.m.u. was detected at this temperature range. It has been known the PEO is susceptible to marked free radical oxidative attack during storage at ambient temperatures [2] and to formation of many oxygenated products. Thus peak at 45 a.m.u. observed at low temperature range may be attributed to an oxidative degradation product of PEO absorbed on the polymer. Furthermore it may be concluded that degradation of the polymer does not start below 220°. Sudden increase in the total ion current above 230° indicated that thermal decomposition of the polymer had started. All the peaks observed showed a very similar trend in 225–255° range.
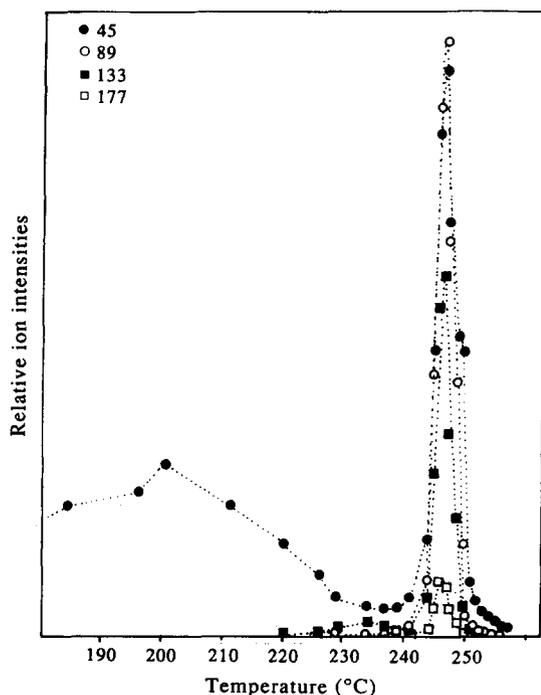
Fig. 4. Variation of intensities of peaks at 45, 89, 133 and 177 a.m.u. as a function of temperature at ionization energy of 20 eV.

These results indicate that decomposition of the polymer is possible at any point along the chain.

$$CH_3CH_2O\text{\large$\sim$}CH_2CH_2\text{---}\!\!\overset{\text{I}}{\underset{}{\text{O}}}\!\!\text{---}\!\!\overset{\text{II}}{\underset{}{\text{CH}_2}}\!\!\text{---}\!\!\overset{\text{III}}{\underset{}{\text{CH}_2}}O\text{\large$\sim$}$$
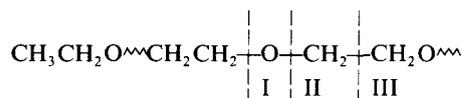
It has been postulated that degradation of pure PEO should initiate by random C—O and C—C scissions and that the radicals formed may depolymerize evolving volatile components such as ethylene, formaldehyde and acetaldehyde [1]. Thus the peaks observed in the spectrum at low ionization energies (20 eV) are directly related to thermal decomposition products. It is also noted that, the relative intensities of the main ions decreased in the order of

$$CH_3CH_2O(CH_2CH_2O)_n^+$$
$$> CH_3CH_2O(CH_2CH_2O)_{n-1}CH_2CH_2^+$$
$$> CH_3CH_2O(CH_2CH_2O)_{n-1}CH_2^+ .$$
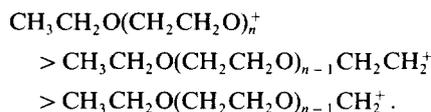
It has been shown that polymers containing oxygen in the main chain tend to degragate more readily than those containing only carbon atoms in their backbone [6, 14]. This is expected on the bases of carbon–oxygen and carbon–carbon bond energies. Thus it can be concluded that cleavages of the polymer chain next to the oxygen atom at I and II positions are more significant during thermal degradation of PEO.

Experiments were repeated using 4×10^6 g · mol^{-1} PEO samples. The very identical results obtained indicated that the technique used, although not sensitive to molecular weight of the polymer under investigation, at least in this molecular weight range, gives reproducible results.

Evolved gas analysis

In evolved gas analysis, peaks due to pyrolysis products started to appear after the oven temperature reached 200°. Total ion yield continuously increased and reached its maximum value at 280°. The mass spectrum recorded at this temperature is given in Fig. 5. No ion above 100 a.m.u. was observed at any time during the experiment at any temperature. Thus it
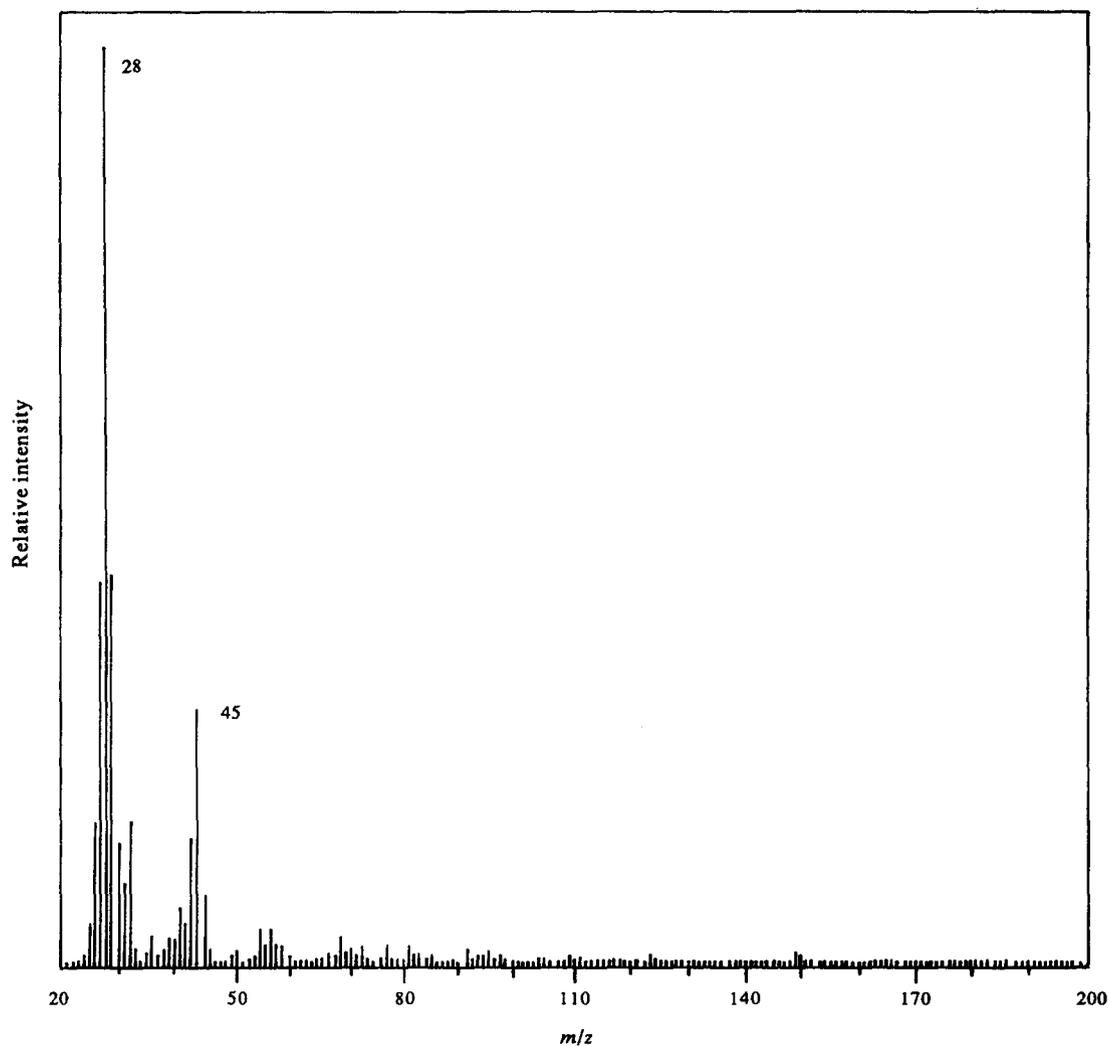
Fig. 5. Mass spectrum of indirect pyrolysis products of PEO at 280°.

can be concluded that only stable, volatile low-molecular weight products could reach the ion source under the experimental conditions. The base peak was at 28 a.m.u. throughout the experiment. Strong peaks at 31, 44, 45, 55, 59, 73, 81 and 96 a.m.u. were detected. Variation of intensities of the peaks as a function of temperature indicated that peaks at 96, 81 and 55 a.m.u. and 73, 59, 45 and 31 a.m.u. were inter-related.

Peaks at 96, 81 and 55 a.m.u. may be attributed to an unsaturated cyclohexanone that would give rise to these peaks by the following mechanism [15]:
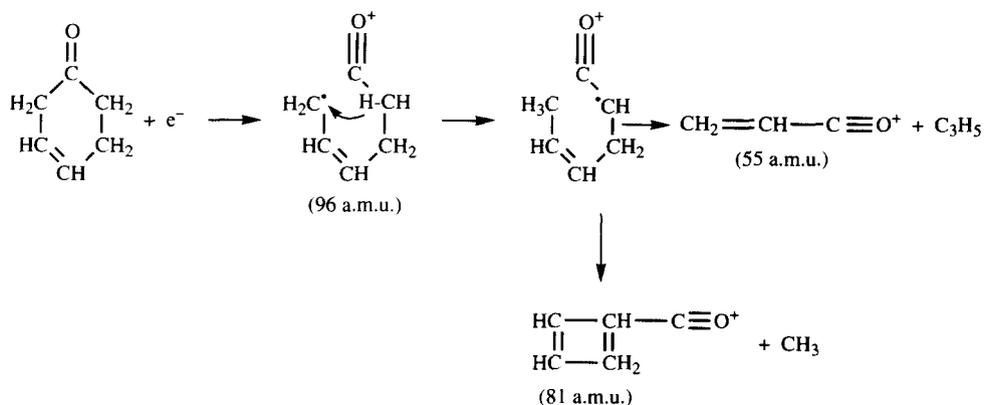
The presence of peaks at 31, 45, 59 and 73 a.m.u. can be related to $CH_3CH_2OCH_2CH_3$ molecule which will yield $CH_3CH_2OCH_2CH_2^+$, $CH_3CH_2OCH_2^+$, $CH_3CH_2O^+$ and CH_2O^+ ions at the observed m/z values. However the trends in ion yields of peaks at 59, 45 and 31 as a function of temperature indicate that these peaks should be also due to another stable molecule, most probably $CH_3CH_2OCH_3$.

Low mass peaks at 44, 31 and 28 a.m.u. can be also directly assigned to CH_3CHO and CO_2, CH_2O, CO and C_2H_4 respectively with the use of literature data [1].

CONCLUSION

The direct pyrolysis technique used gives diagnostic data related to the polymer sample under investigation. Degradation of PEO occurred at the temperature range 235–255° by both C—O and C—C scission, products due to C—O cleavages being more abundant. Peaks related to degradation products upto six monomer units were detected. The main degradation products are $CH_3CH_2O(CH_2CH_2O)_n$-$CH_2CH_2^+$, $CH_3CH_2O(CH_2CH_2O)_nCH_2^+$ and $CH_3CH_2O(CH_2CH_2O)_n^+$ where $n = 0$–6. However with the use of evolved gas analysis technique by mass spectrometry, an indirect pyrolysis method, only low molecular weight volatile products such as CO_2, CH_2O, CH_3CHO and $(CH_3CH_2)_2O$ could be identified. A large variety of molecules might be produced in the reactor during pyrolysis. These thermally stable components may not even be directly related to the sample under study. Thus the spectra obtained are much complicated but less characteristic compared to those recorded in the case of direct pyrolysis. Therefore the direct pyrolysis MS technique should be preferential especially for structural analysis whereas indirect pyrolysis can be applied to investigate stable degradation products of a polymer sample.

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