Pergamon

0014-3057(93)E0025-L

Eur. Polym. J. Vol. 30, No. 6, pp. 693–699, 1994
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0014-3057/94 $7.00 + 0.00

MASS SPECTRAL ANALYSIS OF POLY(3-AMINOCROTONAMIDE) OBTAINED BY RADIATION INDUCED SOLID STATE POLYMERIZATION

OMAR MELAD, ALI USANMAZ* and JALE HACALOĞLU
Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

(Received 13 July 1993; accepted 29 July 1993)

Abstract—Polymerization of 3-aminocrotonamide has not been reported before. It was polymerized by radiation in the solid-state to obtain a crystalline polymer which has a similar crystal structure to that of the monomer. In this work the structure and mode of monomer addition in the polymer chain were investigated by mass spectroscopy. The data indicated that the addition of monomer molecules takes place by a condensation process with evolution of $2n - 1$ NH_3 molecules for each $2n$ monomer molecules. The highest yield of thermal degradation products was obtained at 246° during the direct pyrolysis of the polymer.

INTRODUCTION

Mass spectrometry has become a powerful tool for the investigation of polymers [1–4]. A wide variety of pyrolysis methods and ionization modes are now available for studies of thermal degradation of macromolecules [5–9]. Among these is direct pyrolysis low energy electron impact mass spectrometry (DP-MS) which is clearly one of the most appropriate techniques, not only for investigation of the products of mechanism of thermal degradation, but also for structural characterization of the polymers [8, 9]. In this method the occurrence of secondary reactions during pyrolysis is reduced considerably as the degradation products are volatilized and removed readily from the hot zone under high vacuum conditions ($< 10^{-7}$ mbar). Consequently, primary thermal decomposition products, fragments of high masses which are often diagnostic for structure of the polymer can be detected.

In this work, DP-MS was applied to investigate the structure of the polymer produced by radiation induced solid state polymerization of 3-aminocrotonamide. In contrast to amide and 3-amino derivatives of acetoacetic acid, 3-aminocrotonamide has not been extensively investigated [10, 11].

EXPERIMENTAL PROCEDURES

3-Aminocrotonamide was a product of Aldrich Chemical Co., Ltd and purified by recrystallization in warm chloroform and dried under vacuum. Monomers were irradiated in ampoules evacuated at 10^{-4}–10^{-5} mbar for 5–6 hr on a high vacuum system, by γ-rays from a Co-60 source having a dose rate of 0.04 Mrad/hr.

Infrared spectra of monomer and polymer were obtained using a Nicolet-510 FTIR spectrophotometer u.v. spectra were recorded on a Hewlett–Packard 8452-A diode array spectrophotometer using methanol as solvent. Elemental analyses were carried out with a Hewlett–Packard HP 185 instrument.

The PY-MS experiments were performed by using the modified direct introduction system of a Balzers QMG 311 quadruple mass spectrometer. Basically a direct pyrolysis probe composed of a stainless steel tube, connected to a copper assemble carrying the copper sample holder was used. The probe was inserted directly inside the mass spectrometer through a valve that allows differential pumping of the inlet line. Further experimental details have been described recently [8, 9]. A personal computer was coupled to the system for control of MS and data acquisition and processing.

RESULTS AND DISCUSSION

The detailed kinetics and mechanism of polymerization are being prepared for publication. The polymerization of the monomer was first expected to take place by an addition reaction through a vinyl group. However, in the FTIR spectrum of the polymer no change in absorbance peaks of a vinyl group compared to that of the monomer was observed. This was also supported by chemical analysis of unsaturated bond percentages in monomer and polymer. The polymer spectra showed C—N—C absorptions indicating formation of this bond which does not exist in monomer. In the u.v. spectrum of the polymer —C═C—CO—NH_2 absorption band at 268 nm disappeared totally and a new band at 302 nm appeared. Elemental analysis gave the percent of N in the polymer as 20.4%. The reduction from the calculated 27.98% in monomer points to loss of nitrogen during irradiation. The mass spectrometric analysis of the gaseous phase above the sample after irradiation indicated formation of NH_3 during the process, thus explaining the decrease in nitrogen percentage in the polymer.

Direct pyrolysis products of the polymer were studied by recording mass spectra as a function of temperature in order to investigate the structure and

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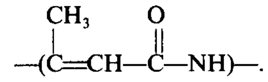
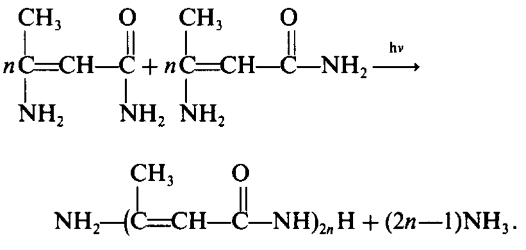
*To whom all correspondence should be addressed.

thermal behaviour of the polymer. The temperature was increased to 150° rapidly and then the sample was heated at a rate of 1°/min. Some spectra had characteristic and intense peaks; the mass spectrum corresponding to maximum product yield at 246° is given in Fig. 2. The base peak was at 28 a.m.u. and the relative intensities of all the peaks at higher masses were <30% of the base peak. Ionization of the thermal decomposition products with energetic electrons causes further fragmentation which in turn results in a considerable decrease in the relative abundances of high mass fragments. In order to diminish dissociation during ionization, analysis of pyrolysis products of the sample were carried out using 20 eV electrons. Maximum product yield was again at 246°. The mass spectrum recorded at this temperature is given in Fig. 3. The base peak was now at 139 a.m.u. Increases in relative intensities of high mass peaks are also apparent. The most characteristic and/or diagnostic peaks produced by ionization of direct pyrolysis products of the polymer with 65 and 20 eV electrons and assigned chemical formulae are collected in Table 1. As fragmentation during ionization was almost completely eliminated by decreasing electron energy, the peaks observed in low energy spectra can be directly related to thermal degradation products. The chemical formula assignments for high mass peaks such as peaks at 289 and 292 a.m.u. can be used to assign the structure of the polymer as:



$$-(\overset{\overset{CH_3}{|}}{C}{=}CH-\overset{\overset{O}{\|}}{C}-NH)-.$$

Then NH_3 formation during radiation induced polymzeriation of the monomer can be explained by the following reaction:



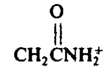
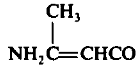
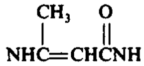
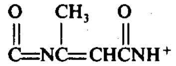
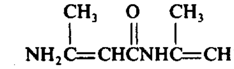
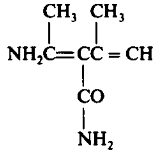
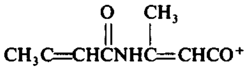
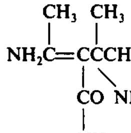
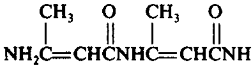
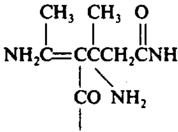
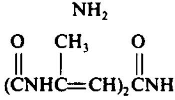
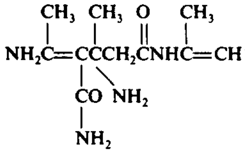
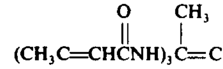
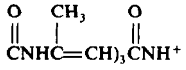
$$n\underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}CH-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{C}}+n\underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}CH-\overset{\overset{O}{\|}}{C}-NH_2\xrightarrow{h\nu}$$

$$NH_2-(\overset{\overset{CH_3}{|}}{C}{=}CH-\overset{\overset{O}{\|}}{C}-NH)_{2n}H+(2n-1)NH_3.$$

It is observed that this structure also explains the presence of C=C and C—N—C vibration peaks in i.r. spectra. Furthermore, the 302 nm band in the u.v. spectrum of the polymer may then be attributed to a bathochromic shift of the 268 nm band of the monomer.

Ion-temperature profiles of some diagnostic fragments are plotted in Fig. 4 for monitoring thermal degradation process. As can be observed from this Figure decomposition started at 180–190° by evolution of low mass fragments such as 17, 28, 30, 43 and 44 a.m.u. fragments. Their production was more dominant at temperatures below 240°. However, main degradation yielding high mass fragments started above 230°. Maximum product formation occurred at 246°. Formation of 30 a.m.u. fragment was maximum at 230° and decreased rapidly above this temperature. 17, 28, 43 and 44 a.m.u. fragments

Table 1. The relative intensities, RI, of the most characteristic and/or intense peak observed in the mass spectra, during pyrolysis of the polymer, recorded using 65 and 20 eV electrons

m/z	RI		
a.m.u.	65 eV	20 eV	Assignment
28	1000	155	CO^+
30	10	151	$CH_2{=}NH_2^+$, H_2CO^+
32	82	35	$NH_2NH_2^+$
43	66	394	$CH_2{=}CHNH_2^+$, $NHCO^+$
44	222	271	NH_2CO^+
58	12	123	 $CH_2\overset{\overset{O}{\|}}{C}NH_2^+$
65	5	215	$CH_3C{=}CHC{=}CH^+$, $NH{=}C{=}CHC{=}CH^+$
84	11	95	 $NH_2\overset{\overset{CH_3}{|}}{C}{=}CHCO^+$
98	27	90	 $NH\overset{\overset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}NH^+$
125	1	53	 $\overset{\overset{O}{\|}}{C}{=}N\overset{\overset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}NH^+$
139	15	1000	 $NH_2\overset{\overset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}{=}CH^+$,  $NH_2\overset{\overset{CH_3}{|}}{C}{=}\underset{\substack{\vert\\ CO\\ \vert\\ NH_2}}{\overset{\overset{CH_3}{|}}{C}}C = CH^+$
151	5	39	 $CH_3C{=}CH\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}{=}CHCO^+$
156	4	320	 $NH_2\overset{\overset{CH_3}{|}}{C}{=}\underset{\substack{\vert\ \diagdown\\ CO\ NH_2\\ \vert\\ NH_2}}{\overset{\overset{CH_3}{|}}{C}}CCH_2^+$
183	9	9	 $NH_2\overset{\overset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}NH_2^+$
200	1	51	 $NH_2\overset{\overset{CH_3}{|}}{C}{=}\underset{\substack{\vert\ \diagdown\\ CO\ NH_2\\ \vert\\ NH_2}}{\overset{\overset{CH_3}{|}}{C}}CCH_2\overset{\overset{O}{\|}}{C}NH_2^+$
210	136	615	 $(\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}{=}CH)_2\overset{\overset{O}{\|}}{C}NH_2^+$
238	—	12	 $NH_2\overset{\overset{CH_3}{|}}{C}{=}\underset{\substack{\vert\ \diagdown\\ CO\ NH_2\\ \vert\\ NH_2}}{\overset{\overset{CH_3}{|}}{C}}CCH_2\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}{=}CH^+$
289	—	14	 $(CH_3C{=}CH\overset{\overset{O}{\|}}{C}NH)_3\overset{\overset{CH_3}{|}}{C}{=}CH^+$
292	—	12	 $\overset{\overset{O}{\|}}{C}NH\overset{\overset{CH_3}{|}}{C}{=}CH)_3\overset{\overset{O}{\|}}{C}NH^+$

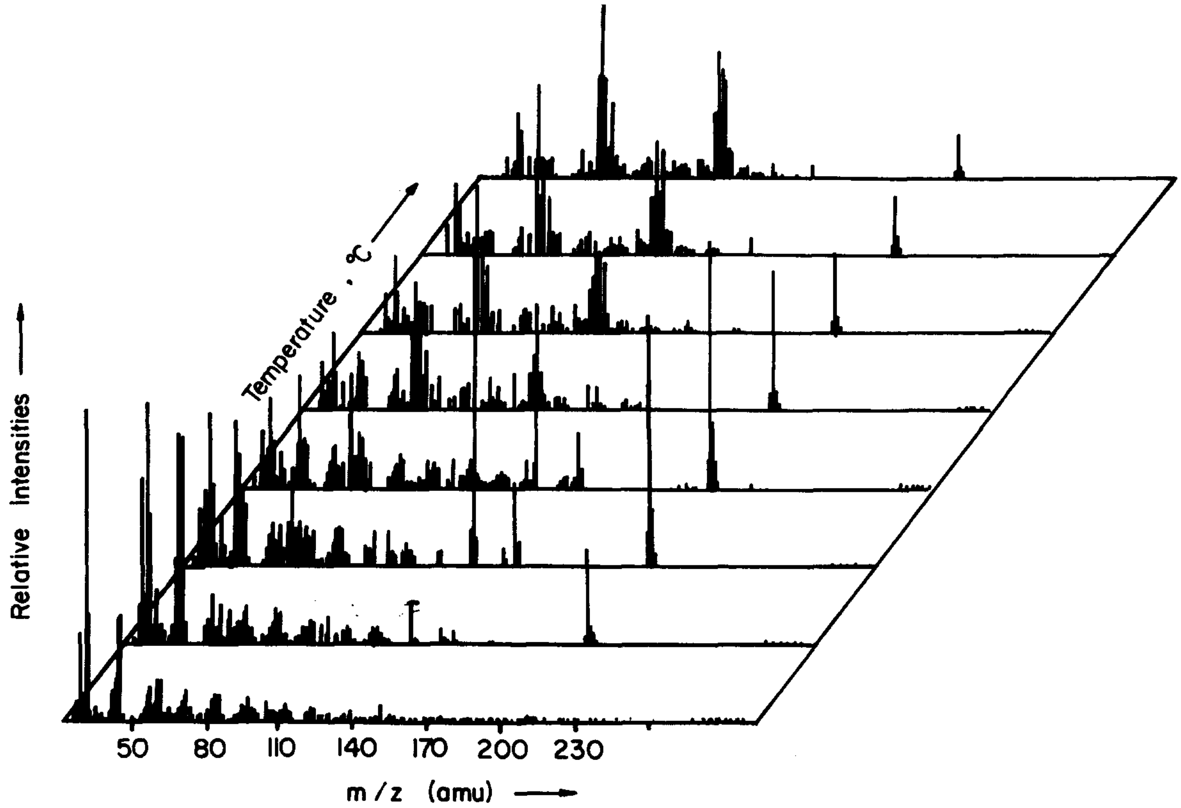


Fig. 1. Mass spectra recorded during pyrolysis of the polymer.

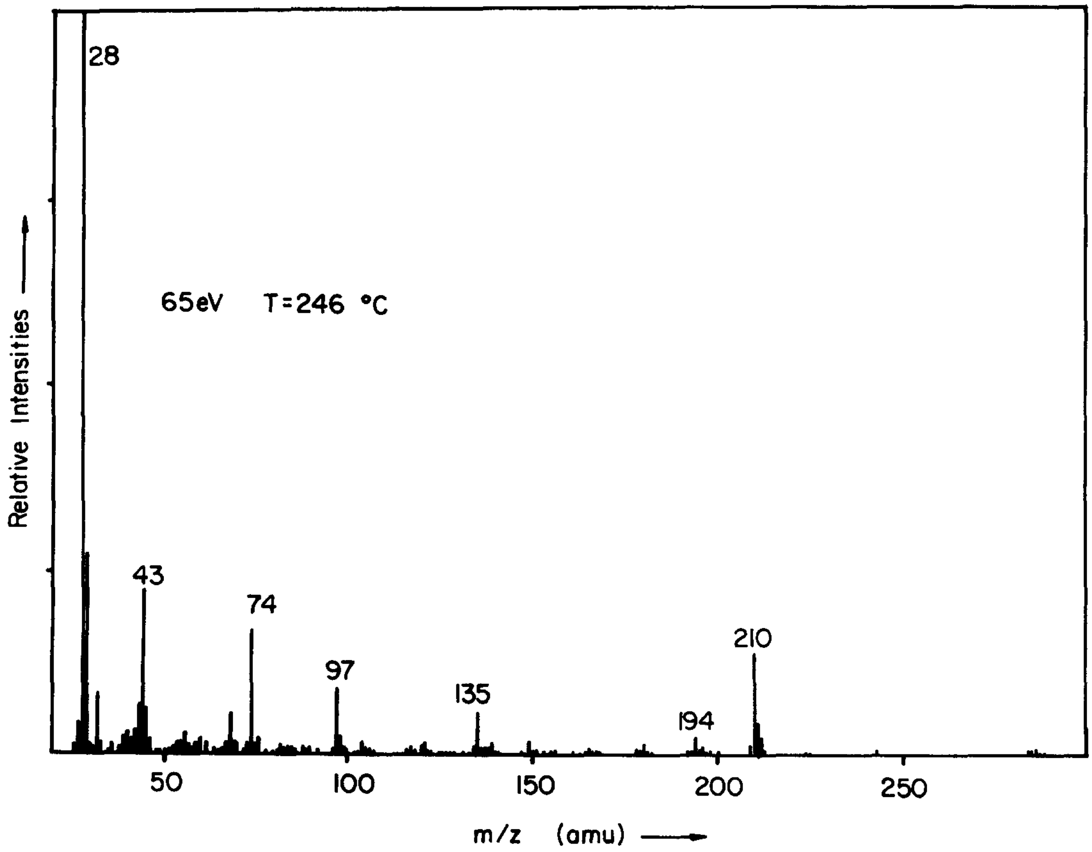


Fig. 2. Mass spectrum recorded during pyrolysis of the polymer at 246° using 65 eV electrons.

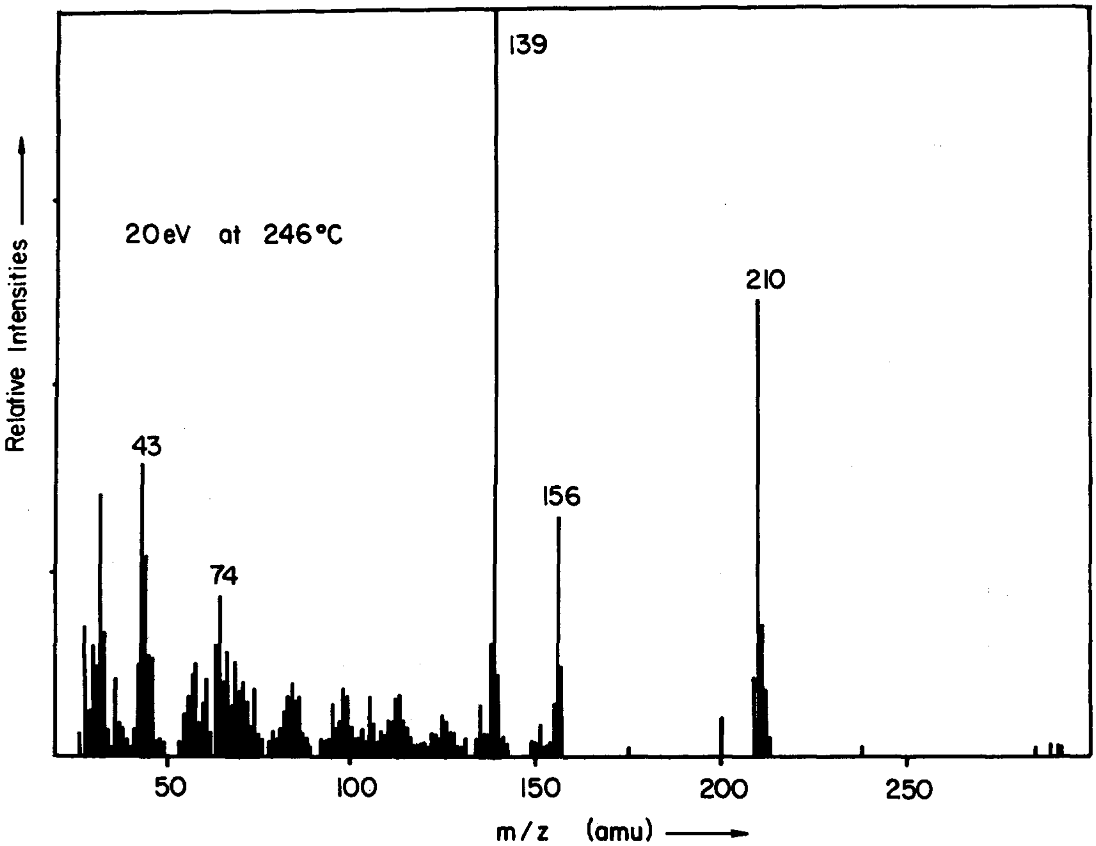
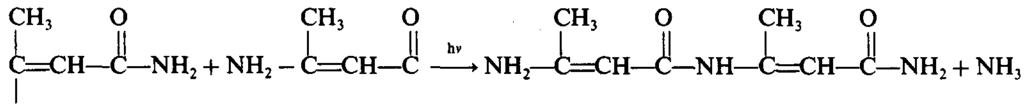


Fig. 3. Mass spectrum recorded during pyrolysis of the polymer at 246° using 20 eV electrons.

also showed relatively high yields at 230°. Thus, it can be concluded that decomposition started by evolution of low mass volatile fragments such as NH_3, CO, H_2CO and NH_2CO.

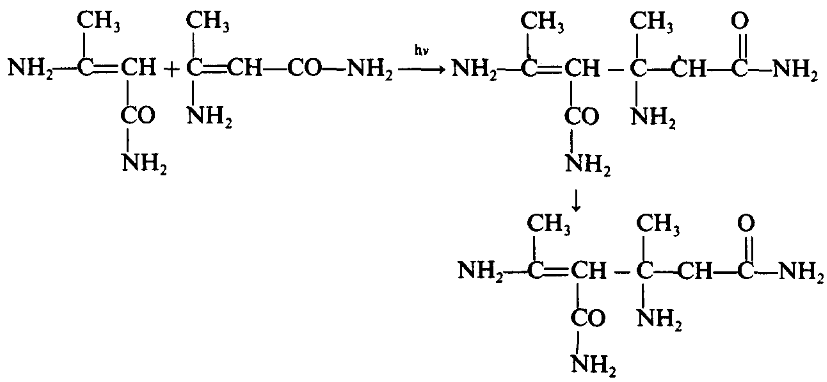
The ion-temperature profiles of fragments at 30, 139, 156 and 200 a.m.u. showed a second but weaker maximum around 210°. Presence of high mass fragments at low temperature values may be attributed to presence of oligomers absorbed on the polymer. Existence of peaks at 183 and 200 a.m.u. may be related to two different dimers produced by two different mechanisms;



$$\underset{NH_2}{\overset{CH_3}{C}}=CH-\overset{\overset{O}{\|}}{C}-NH_2+NH_2-\overset{CH_3}{C}=CH-\overset{\overset{O}{\|}}{C}\xrightarrow{h\nu}NH_2-\overset{CH_3}{C}=CH-\overset{\overset{O}{\|}}{C}-NH-\overset{CH_3}{C}=CH-\overset{\overset{O}{\|}}{C}-NH_2+NH_3$$

183 a.m.u.

and



$$NH_2-\overset{CH_3}{C}=\underset{\underset{NH_2}{|}}{\underset{CO}{CH}}+\underset{NH_2}{\overset{CH_3}{C}}=CH-CO-NH_2\xrightarrow{h\nu}NH_2-\overset{CH_3}{C}=\underset{\underset{NH_2}{|}}{\underset{CO}{CH}}-\underset{NH_2}{\overset{CH_3}{C}}-\dot{C}H-\overset{\overset{O}{\|}}{C}-NH_2$$

$$\downarrow$$

$$NH_2-\overset{CH_3}{C}=\underset{\underset{NH_2}{|}}{\underset{CO}{CH}}-\underset{NH_2}{\overset{CH_3}{C}}-CH-\overset{\overset{O}{\|}}{C}-NH_2$$

200 a.m.u.

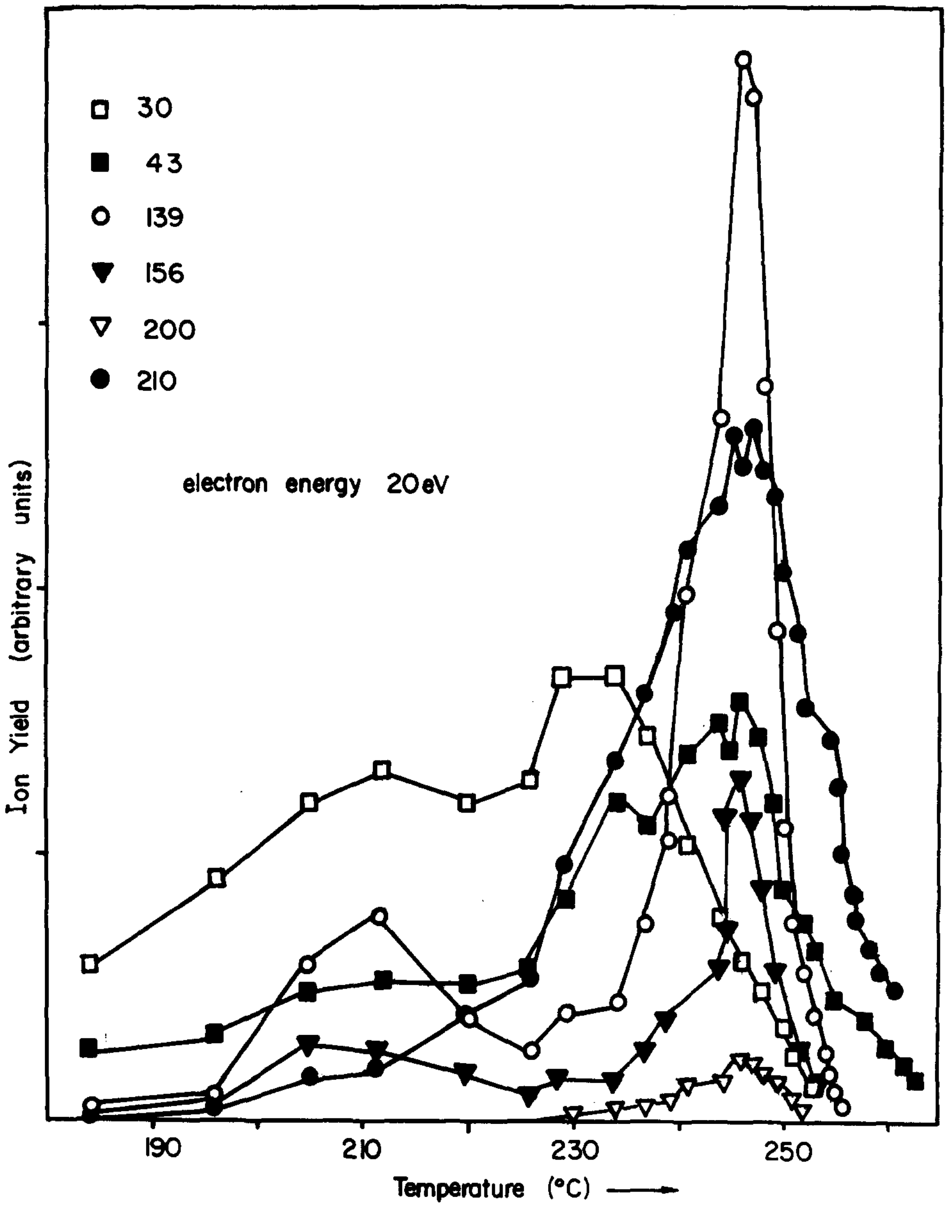
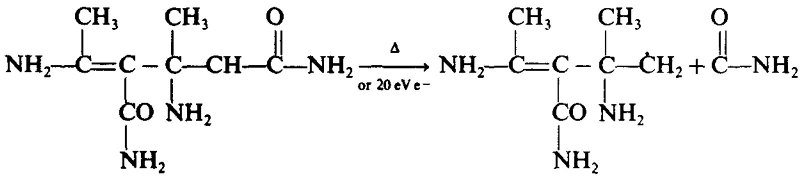


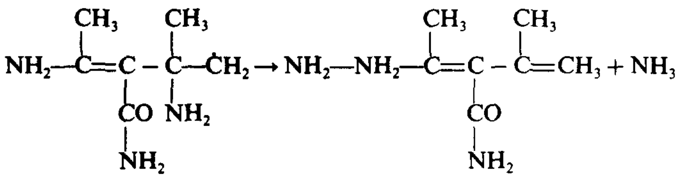
Fig. 4. Ion-temperature profiles of some diagnostic fragments observed during the pyrolysis of the polymer.

Then the formation of 156 and 139 a.m.u. fragments may be related to degradation of 200 a.m.u. dimer according to the following reactions;



$$NH_2-\underset{\underset{NH_2}{|}}{\underset{|}{\underset{CO}{|}}}\!\!\overset{CH_3}{\overset{|}{C}}=C-\underset{\underset{NH_2}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{or 20 eV e}^-]{\Delta} NH_2-\underset{\underset{NH_2}{|}}{\underset{|}{\underset{CO}{|}}}\!\!\overset{CH_3}{\overset{|}{C}}=C-\underset{\underset{NH_2}{|}}{\overset{CH_3}{\overset{|}{C}}}-\dot{C}H_2+\overset{O}{\overset{\|}{C}}-NH_2$$

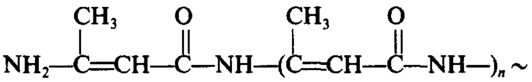
156 a.m.u.



$$NH_2-\underset{\underset{NH_2}{|}}{\underset{|}{\underset{CO}{|}}}\!\!\overset{CH_3}{\overset{|}{C}}=C-\underset{\underset{NH_2}{|}}{\overset{CH_3}{\overset{|}{C}}}-\dot{C}H_2\rightarrow NH_2-NH_2-\overset{CH_3}{\overset{|}{C}}=\underset{\underset{NH_2}{|}}{\underset{|}{\underset{CO}{|}}}\!\!C-\overset{CH_3}{\overset{|}{C}}=CH_3+NH_3$$

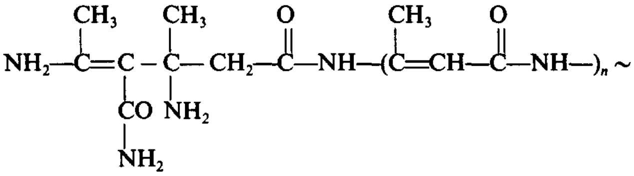
139 a.m.u.

However, the trends in ion-temperature profiles may be also associated with the presence of different end groups affecting thermal stability. It has been found that end groups affect the thermal stability and decomposition products [12, 13]. Extensive studies on thermal decomposition of polystyrenes showed that the production of volatile material occurs almost exclusively at chain ends and polystyrenes with different end groups exhibit different stabilities. A close study of the mass data indicated that different end groups were generated during the radiation induced polymerization of 3-aminocrotonamide such as



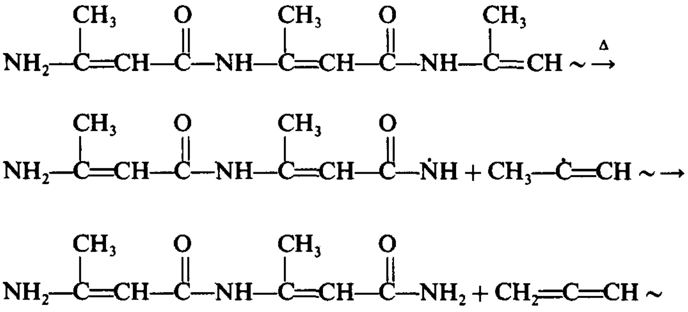
$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-}(\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-})_n\sim}$$

and



$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}\underset{\substack{|\\CO\\|\\NH_2}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\NH_2}}{C}}{-}CH_2{-}\overset{\substack{O\\\|}}{C}{-}NH{-}(\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-})_n\sim}$$

The formation of dimers at higher temperatures can be explained by random scissions of the main chain followed by intermolecular H-transfer:

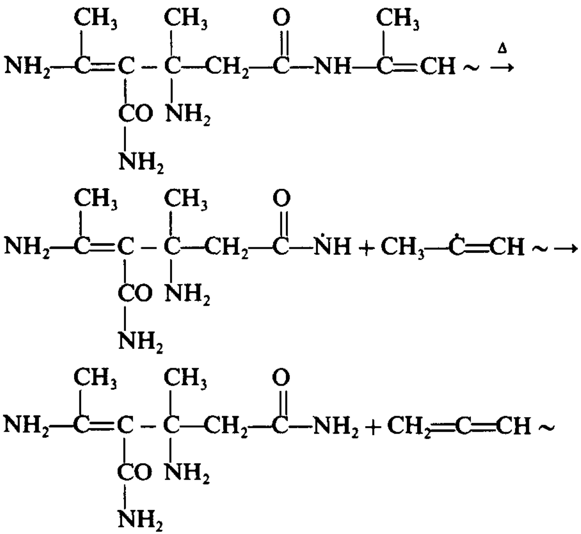


$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-}\overset{\substack{CH_3\\|}}{C}{=}CH\sim}\xrightarrow{\Delta}$$

$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}\dot{N}H+CH_3{-}\dot{C}{=}CH\sim}\longrightarrow$$

$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH{-}\overset{\substack{CH_3\\|}}{C}{=}CH{-}\overset{\substack{O\\\|}}{C}{-}NH_2+CH_2{=}C{=}CH\sim}$$

183 a.m.u.



$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}\underset{\substack{|\\CO\\|\\NH_2}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\NH_2}}{C}}{-}CH_2{-}\overset{\substack{O\\\|}}{C}{-}NH{-}\overset{\substack{CH_3\\|}}{C}{=}CH\sim}\xrightarrow{\Delta}$$

$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}\underset{\substack{|\\CO\\|\\NH_2}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\NH_2}}{C}}{-}CH_2{-}\overset{\substack{O\\\|}}{C}{-}\dot{N}H+CH_3{-}\dot{C}{=}CH\sim}\longrightarrow$$

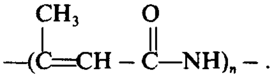
$$\mathrm{NH_2{-}\overset{\substack{CH_3\\|}}{C}{=}\underset{\substack{|\\CO\\|\\NH_2}}{C}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\NH_2}}{C}}{-}CH_2{-}\overset{\substack{O\\\|}}{C}{-}NH_2+CH_2{=}C{=}CH\sim}$$

200 a.m.u.

Thus, it seems possible to say that thermal degradation took place at lower temperatures with evolution of volatile products. The main degradation process at temperatures above 230° occurred through a mechanism involving free radicals produced by random chain scissions. Intermolecular H-transfer reactions also took place to some extent.

CONCLUSION

Polymerization of 3-amonocrotonamide by radiation induced solid state polymerization occurred by a condensation process with evolution of $(2n - 1)$ NH_3 molecules for each $2n$ monomer molecules. The repeating unit of the polymer was determined to be



$$-(\overset{CH_3}{\overset{|}{C}}{=}CH-\overset{O}{\overset{\|}{C}}-NH)_n-.$$

The presence of two different end groups affecting thermal stability was detected. The thermal decomposition took place at low temperatures with evolution of volatile products. However, main degradation occurred above 230°, with the highest yield at 246°, by random chain scissions followed by intermolecular H-transfer reactions.

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