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Degradation of Poly(2-hydroxyethyl methacrylate) Obtained by Radiation in Aqueous Solution

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The degradation of poly(hydroxyethyl methacrylate), PHEMA obtained by γ-radiation induced polymerization of HEMA in aqueous solution, was studied. The polymer was a gel type and insoluble in common organic solvents. The DSC thermogram of the polymer gave a Tg value at 88.2°C and an endothermic peak showed further polymerization or crosslinking at 110–160°C. The degradation observed in TGA was a depolymerization type. However, the FT-IR of TGA fragments showed no monomer, which was degraded further. The degradation of monomer was studied by the GC-MS method. Similar results were also observed.

Keywords: PHEMA, γ-radiation, degradation, TGA-FTIR, mass spectroscopy

1 Introduction

Hydroxyethyl methacrylate, HEMA polymerizes by different methods such as free radical (1–2), anionic (3–4) and controlled/living polymerization (5–8). Poly(hydroxyethyl methacrylate), PHEMA is a biomaterial used as a homopolymer or a copolymer (9). Despite the wide usage of PHEMA as a biomaterial, some undesired irritating compounds were observed during bio-application. Stol et al.(10) investigated some model compounds assumed to be potential irritants (i.e., HEMA monomer and decomposition products of the polymerization catalysts) and their toxic effects *in vivo*. Results of the intradermal irritation tests revealed that at low concentrations of HEMA and sodium benzoate (up to 1%) only a little irritation was recorded, while at higher levels (5% or more) a significant adverse reaction was detected. Hence, determination of decomposition or degradation products of PHEMA during processing conditions is very vital information, because such products may have toxic effects on living tissues. So, the thermal degradation of PHEMA (11–12) reported to give monomer and some other pyrolysis products such as ethylene glycol dimethacrylate (EGDMA), methacrylic acid and acetaldehyde. Chandrasekhar and White (13) reported that GC/MS and pyrolysis-GC/FT-IR analyses of PHEMA at 500°C revealed that significant quantities of ethylene glycol and ethyleneglycol dimethacrylate were formed along with some ethenol and methacrylic acid. They also showed by TG-MS analyses that ethylene glycol and methacrylic acid were produced at a temperature range of 350–450°C. According to Teijon et al. (14) when the side chain of the polymer is hydrophilic, the formation of cyclic anhydrides is prevented. However, Demirelli et al. (15) suggested some products namely 1, 3-dioxolane and anhydride rings, vinyl methacrylate 2-isopropenyloxyethyl methacrylate and ethyleneoxy methacrylate were also produced after degradation. They found from cold ring fractions (CRFs), the formation of monomer as the main fraction in thermal degradation at 25–400 °C is due to a depolymerization reaction. The side products arising from ester decomposition were a six-membered glutaric anhydride type ring and oxolane type ring. The thermal properties of PHEMA were investigated with DSC and TGA by Çaykara et al. (16) The glass transition temperature (Tg) of PHEMA was found as 87°C. It was observed that the weight loss of PHEMA began at about 322°C and reached a maximum at 361°C. The TG curve of PHEMA indicated one degradation stage which was reflected as a single peak in the DTG curve. Initial degradation temperature of PHEMA showed that the degradation was due to random chain scission. No more work has been reported in recent years for the degradation products.

In this work, HEMA was polymerized in water by a radiation technique under reduced pressure. The presence

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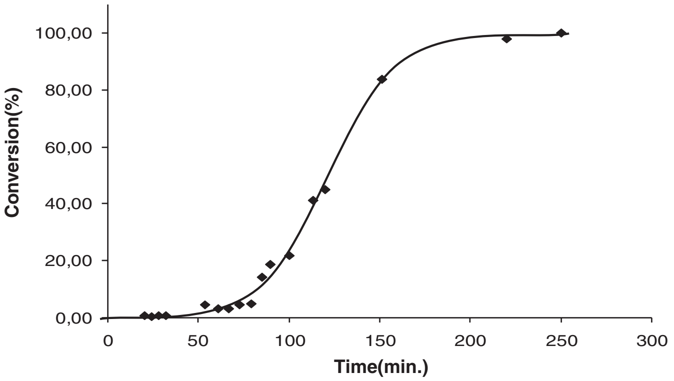


Fig. 1. Conversion–time graph for γ-irradiated PHEMA.

of water was thought to prevent interamolecular hydrogen bonding. This will stabilze radical fragments and prevent side reactions such as side group cyclization and crosslinking. Polymers obtained at different percent conversions were characterized by FT-IR and DSC. The thermal degradation was carried out by TGA-FTIR and electron impact MS methods. This enabled the observation of radical fragments before any recombinations to give different compounds as reported in the literature. The degradation of monomer, which is not reported in the literature, was studied by the GC-MS method.

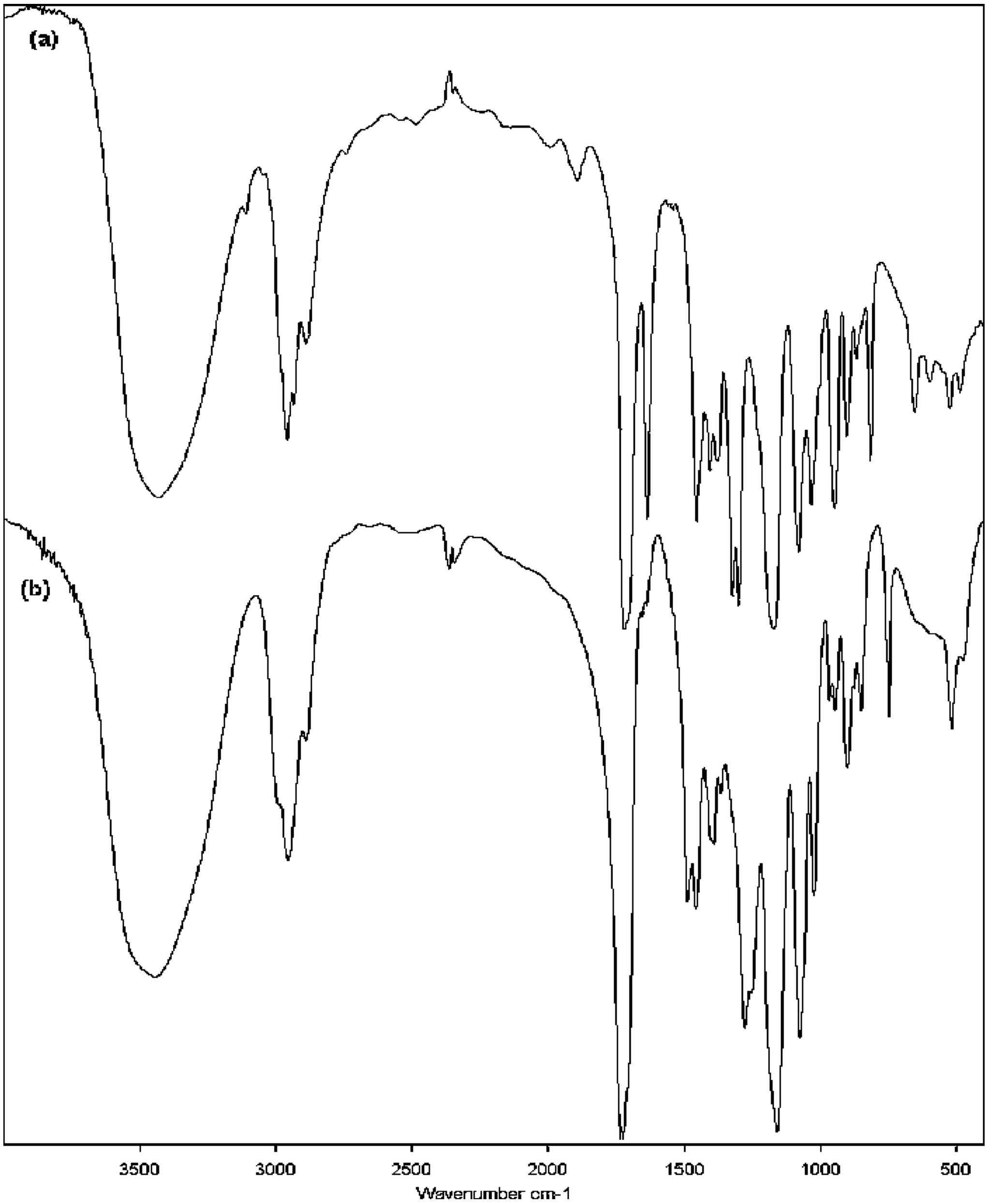


Fig. 2. FT-IR spectrum of (a) HEMA and (b) polymer of HEMA.

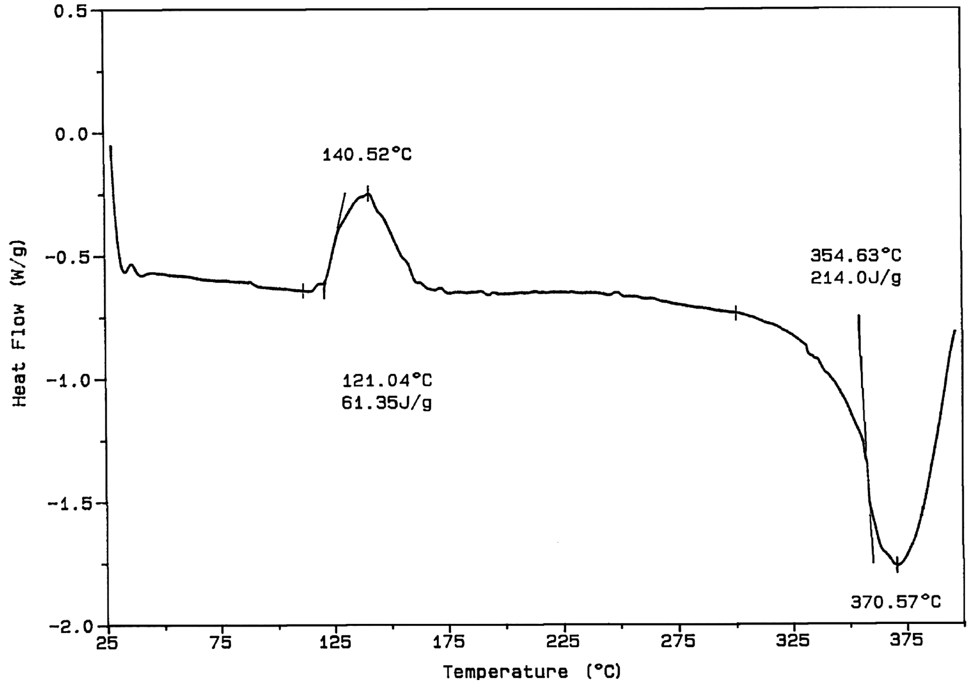


Fig. 3. DSC thermogram of PHEMA.

2 Experimental

Hydroxyethyl methacrylate, HEMA, (ACROS, 98%, USA) was distilled under vacuum. About 5 mL of 40%(v/v) aqueous solution of HEMA was placed in polymerization tubes and evacuated on a high vacuum system at 10^{-5} – 10^{-6} mm-Hg for about 5 h, then sealed by flame. The tubes were then irradiated in a ^{60} Co–γ source with a dose rate

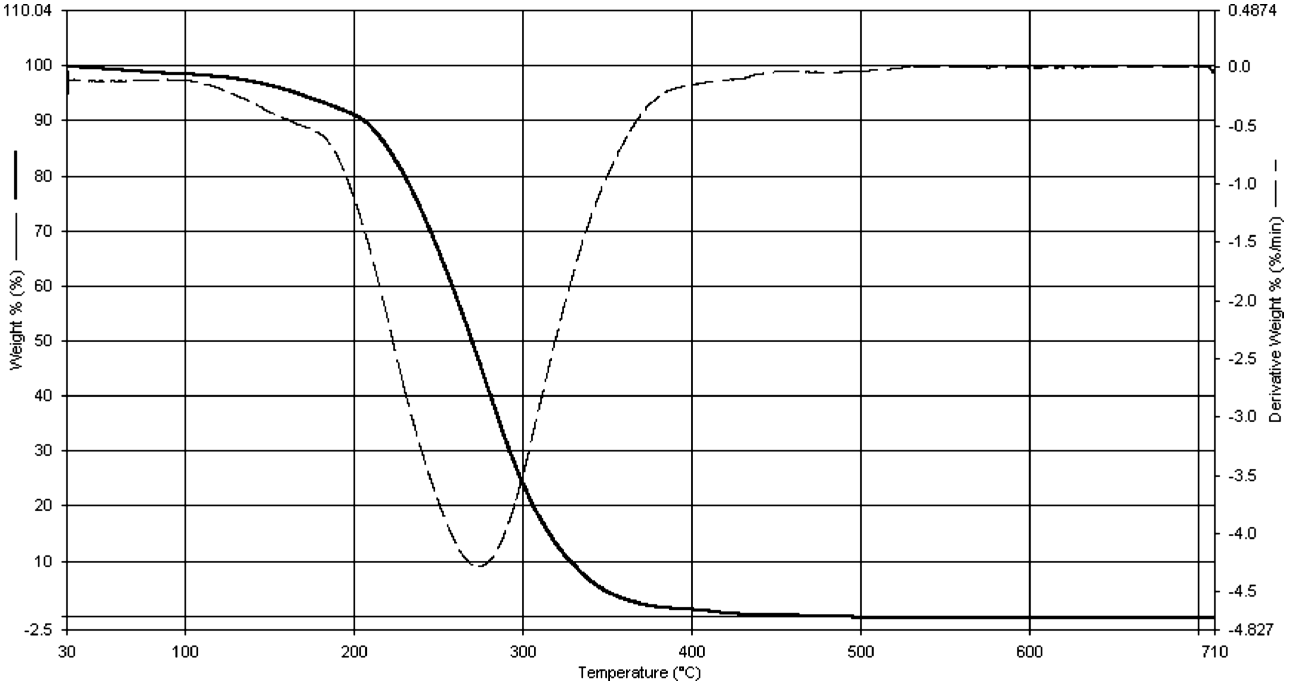


Fig. 4. GC-MS spectrum of HEMA.

of 1.987 kGy/day at 25°C. After the desired irradiation period, tubes were broken open and the unpolymerized monomer was extracted with diethyl ether. Percent conversion was calculated gravimetrically.

The DSC thermogram of PHEMA was taken on a Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S. All the measurements were done under N_2(g) atmosphere in a temperature range of 25°C to 400°C with 10°C/min heating rate.

The monomer degradation was carried out by a GC 2000 Trace Series, which was determined on a phenomenex Zebron ZB-5 capillary column (ThermoQuest Finnigan, Automass). $T_1 = 50^\circ C$ $t = 5$ min., with 5°C/min heating rate $T_2 = 300^\circ C$ $t = 5$ min., $T_3 = 300^\circ C$ $t = 5$ min. Right inlet temperature = 250°C and constant pressure was applied (P = 250 kPa).

The direct insertion probe pyrolysis mass spectrometry used for the thermal analyses consists of a 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system. Polymer samples (0.01 mg) were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of 10°C/min and the scan rate was 2 scans/s.

TGA *in situ* FT-IR thermogram was taken on Perkin-Elmer Pyris 1 TGA and Spectrum 1 FT-IR Spectrometer under N_2(g) atmosphere and polymer was heated from 35°C to 720°C with a heating rate of 5°C/min.

3 Results and Discussion

3.1 Polymerization of HEMA

The time-conversion plot for radiation induced polymerization of HEMA at 25°C is given in Figure 1. The kinetic curve showed an autoacceleration character with a short induction period. The polymer obtained was brittle, transparent and insoluble in common organic solvents.

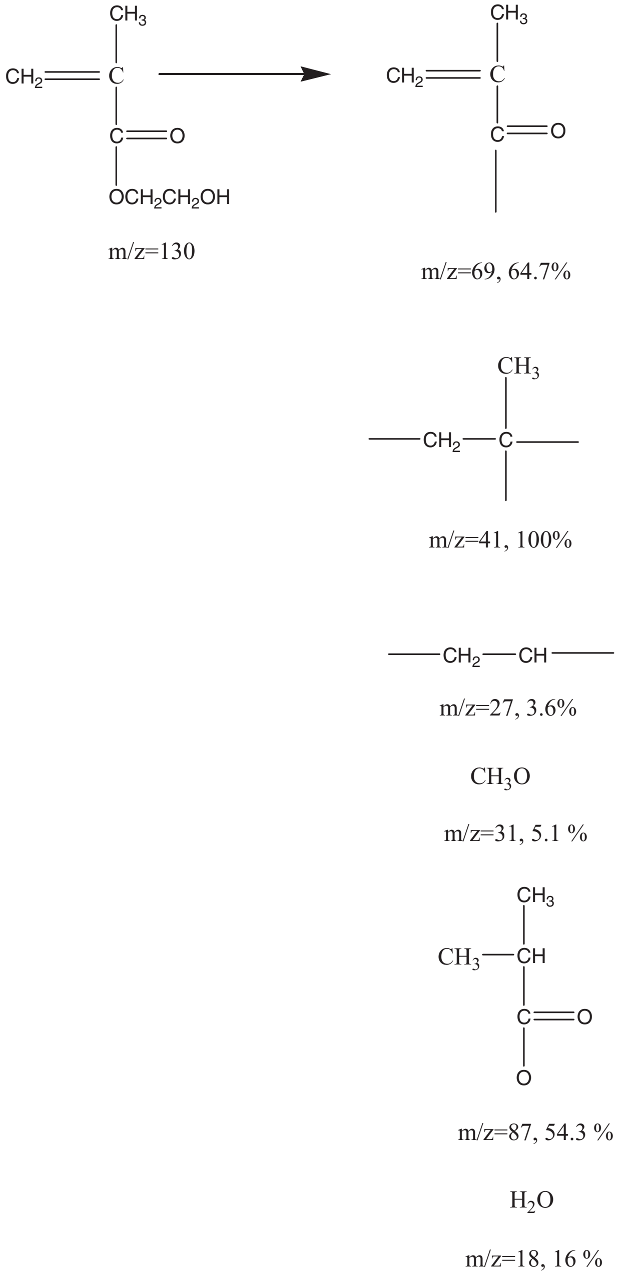
The FT-IR spectra of HEMA and PHEMA are given in Figure 2. In the spectrum of monomer (Fig. 2a) the –OH peak is broad in the range of 3300–3700 cm^{-1} indicating hydrogen bonding. It was also retained in the spectrum of polymer (Fig. 2b). However, the shoulder at 3100 cm^{-1}; peaks at 1637, 933 and 816 cm^{-1} corresponding to the –C=C– in the spectrum of monomer are not present in the polymer spectrum. The –C=O (1719 cm^{-1}), -C-O-C- (1321–1032 cm^{-1}), $-CH_2$ (1404–1379 cm^{-1}) are present in both spectrum. Thus, polymerization proceeds via the opening of double bonds and there is no side chain cyclyzation that might give anhydride or lactons during the polymerization.

3.2 DSC Analysis

The DSC thermogram of PHEMA is given in Figure 3. The detailed analysis of thethermogram by a program showed that the Tg value is 88.2°C and peaks at 110–160 (maximize at 140°C) correspond to further polymerization which was not observed in the second run thermogram. The polymerization peak has the enthalpy of $\Delta H = -61.3$ J/g.

3.3 Thermal Degradation of PHEMA

The GC-MS results of the monomer, HEMA is shown in Figure 4. Monomer degradation is maximum at about 175°C. The main fragments at 175°C are given in Figure 4b. The fragmentation is shown in Scheme 1. The monomer



Sch. 1. GS-MS Fragmentation of monomer.

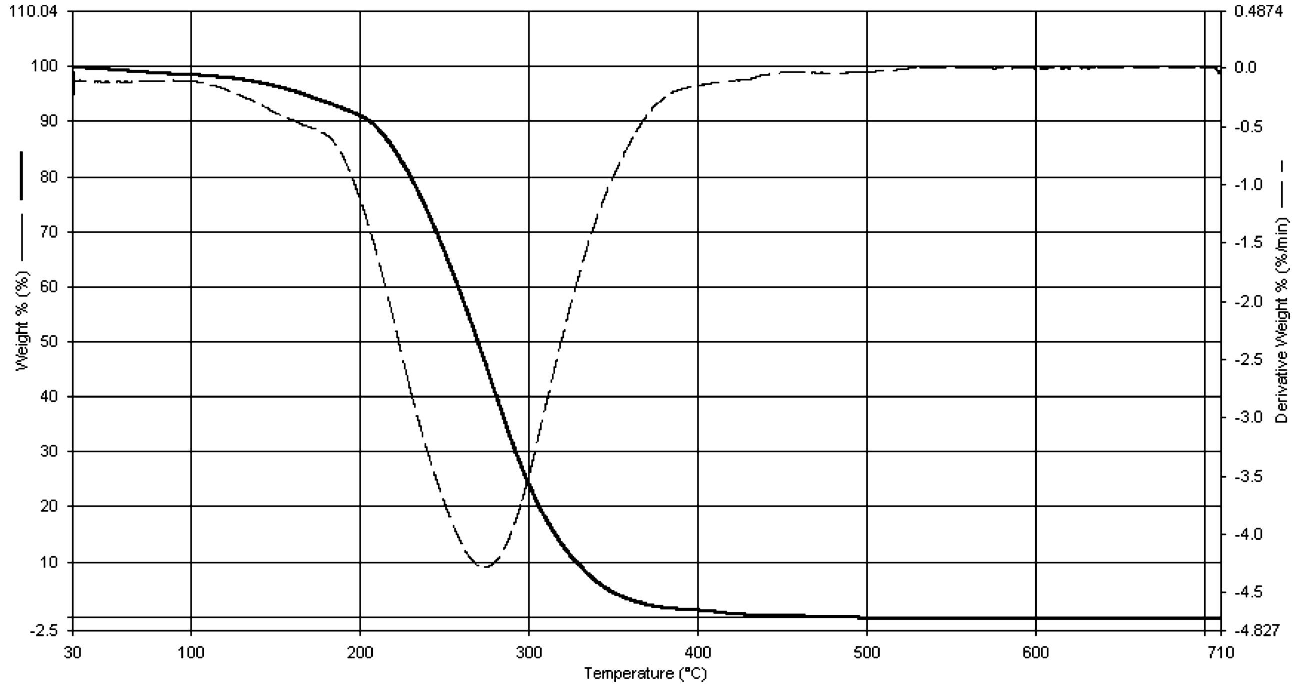


Fig. 5. TGA Thermogram of γ-irradiated PHEMA.

is not observed in the spectrum. Therefore, the monomer is not stable and gives fragments, which are also observed in the mass spectrum of polymer. The main fragments are $CH_2 = C(CH_3)CO$, $CH_2 = C(CH_3)$- and $(CH_3)_2CHCO_2$.

The thermal degradation of PHEMA was investigated by TGA-FTIR and electron impact (70 eV) Mass Spectroscopy methods. The thermal stability of PHEMA was characterized by means of TGA from 35°C to 700°C in N_2 atmosphere as shown in Figure 5. The TGA thermogram showed depolymerization type degradation and derivative weight loss is a broad peak with a maximum at about 275°C. The activation energy of degradation was calculated according to Broido method (17) as 73,06 kJ/mol, which is smaller then the reported activation energy (15).

The polymer was degraded completely at about 483°C. The evolved gas from degradation was recorded continuously by FT-IR spectra. The FT-IR spectra of degraded fragments at 197°C to 431°C are given in Figure 6. The FT-IR spectra for degradation from 125 to 293°C correspond to that of the monomer, which have been depolymerized or in oligomers. However, the broad and strong peak of –OH in monomer FT-IR spectrum (Fig. 2a) was not observed in these spectra. Therefore, there should be linkage type degradation in the early stage of degradation to remove $HOCH_2CH_2$- groups. The noisy peaks at 3800–3700 cm^{-1}, ~2400 cm^{-1}, 1400–1800 cm^{-1} as transmitted correspond to H_2O and CO_2 backgrounds. The degradation is completed at 483°C; thus, the TGA degradation of PHEMA is different than that of PMMA, which is a depolymerization type.

In order to understand the thermal degradation better, the pyrolysis of the polymer sample under vacuum at different temperature were also carried out. The FT-IR spectra of samples after pyrolysis were recorded and shown in Figure 7. The spectra at different temperature are identical to that of the polymer (Fig. 2b), therefore, there is no side group cyclyzation (lactons and/or anhydrides) during the thermal degradation. The degradation is linkage and depolymerization with a combination of monomer fragmentation. The FT-IR spectra (b) at 400°C is that of condensed fragments of degraded polymer. It corresponds to a polymer with a cleavage of $-CH_2CH_2OH$ or $-CH_2OH$ groups that leaves no –OH groups as observed for the fragmented product (Fig. 6).

3.4 Mass Spectral Analysis

The mass thermogram of PHEMA is given in Figure 8. The fragmentation in the thermogram showed four stages at about (a) 30–50°C, (b) 250–350°C, (c) 350–470°C and (d) 470–520°C. The results are tabulated in Table 1. The fragments in the first two stages correspond to that of the monomer degradation; this is mostly affected by electron impact rather than temperature. The degradation fragments in the first stage are the same as the fragments obtained from GC-MS of monomer (Fig. 4 and Sch. 1). Unlike other acrylates, if there is a functional group in

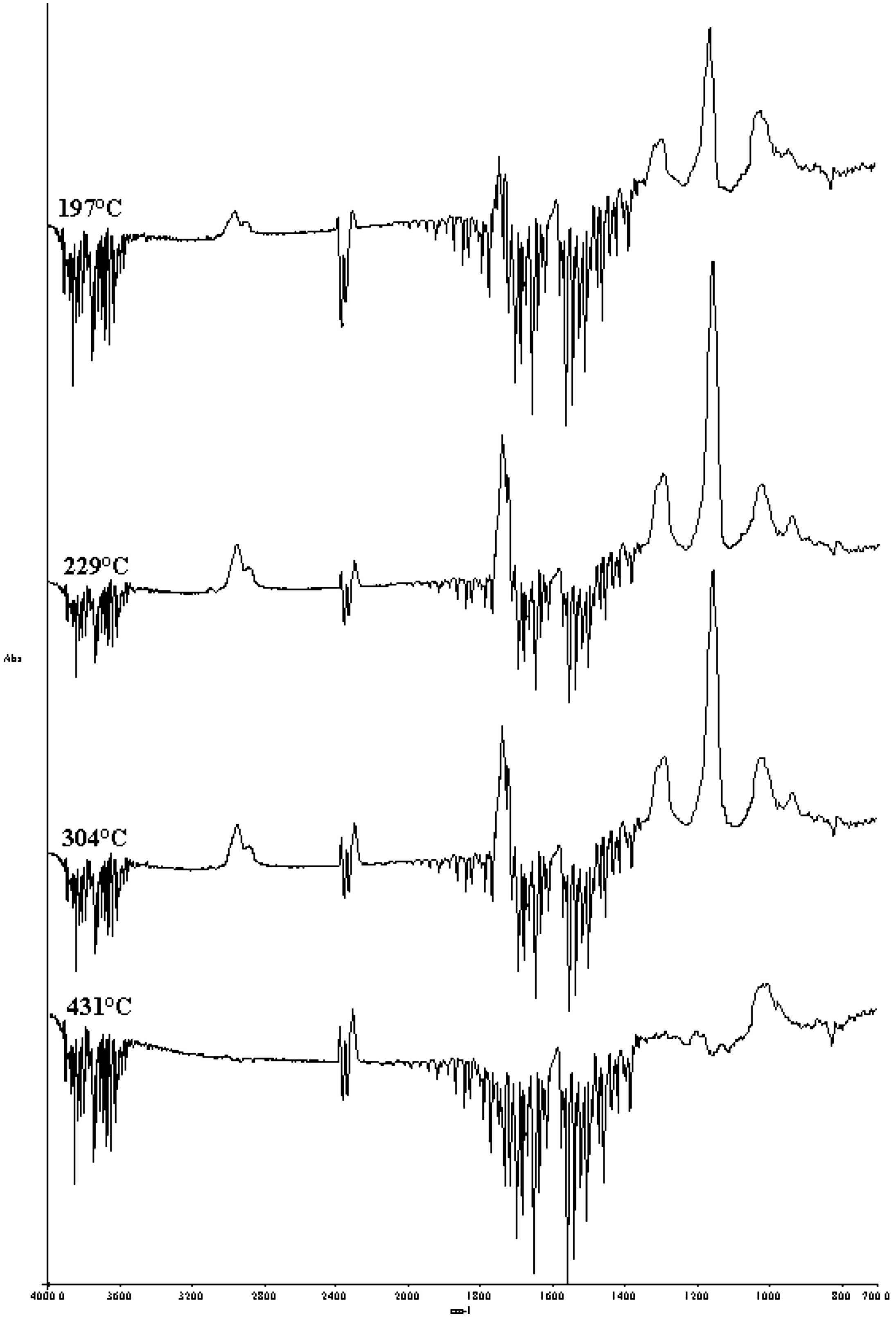


Fig. 6. FT-IR spectrum of decomposition gases from TGA analysis.

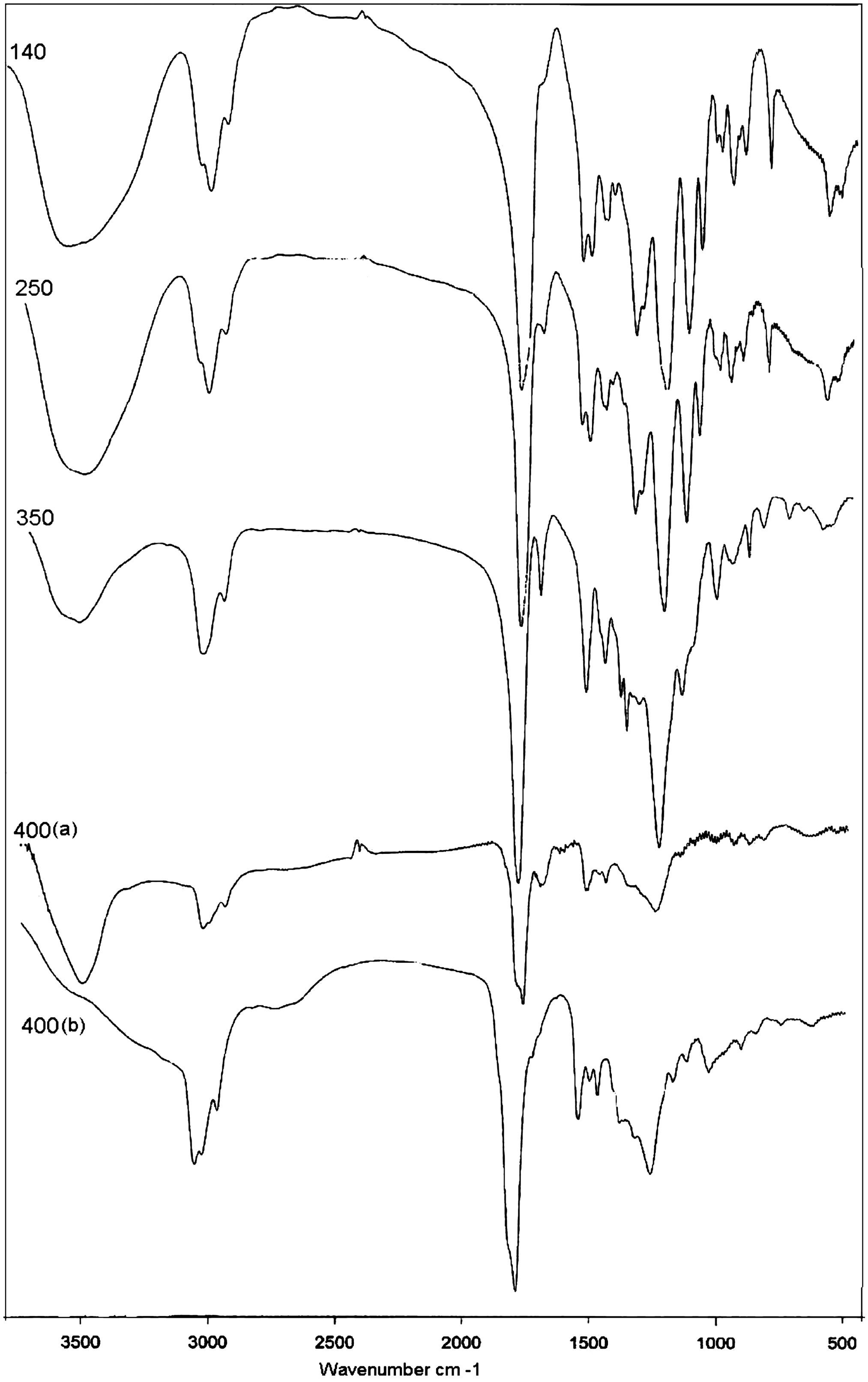


Fig. 7. FT-IR spectra of PHEMA after pyrolysis at different temperatures.

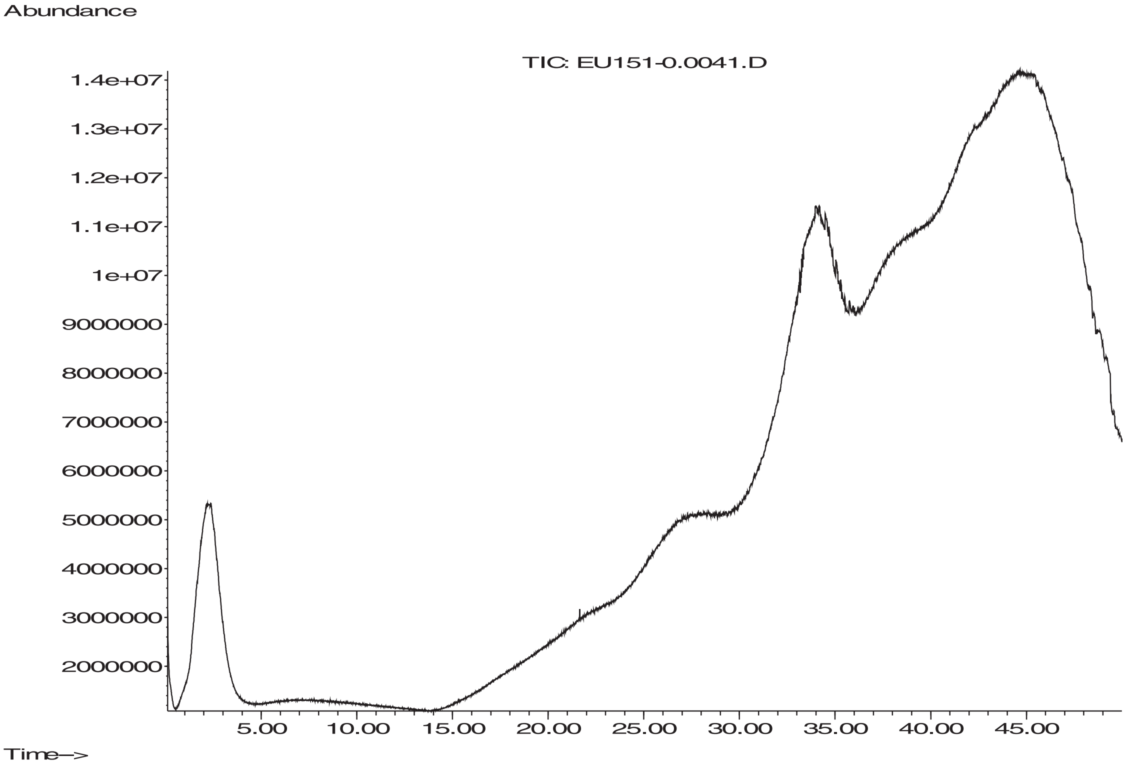


Fig. 8. Mass thermogram of PHEMA.

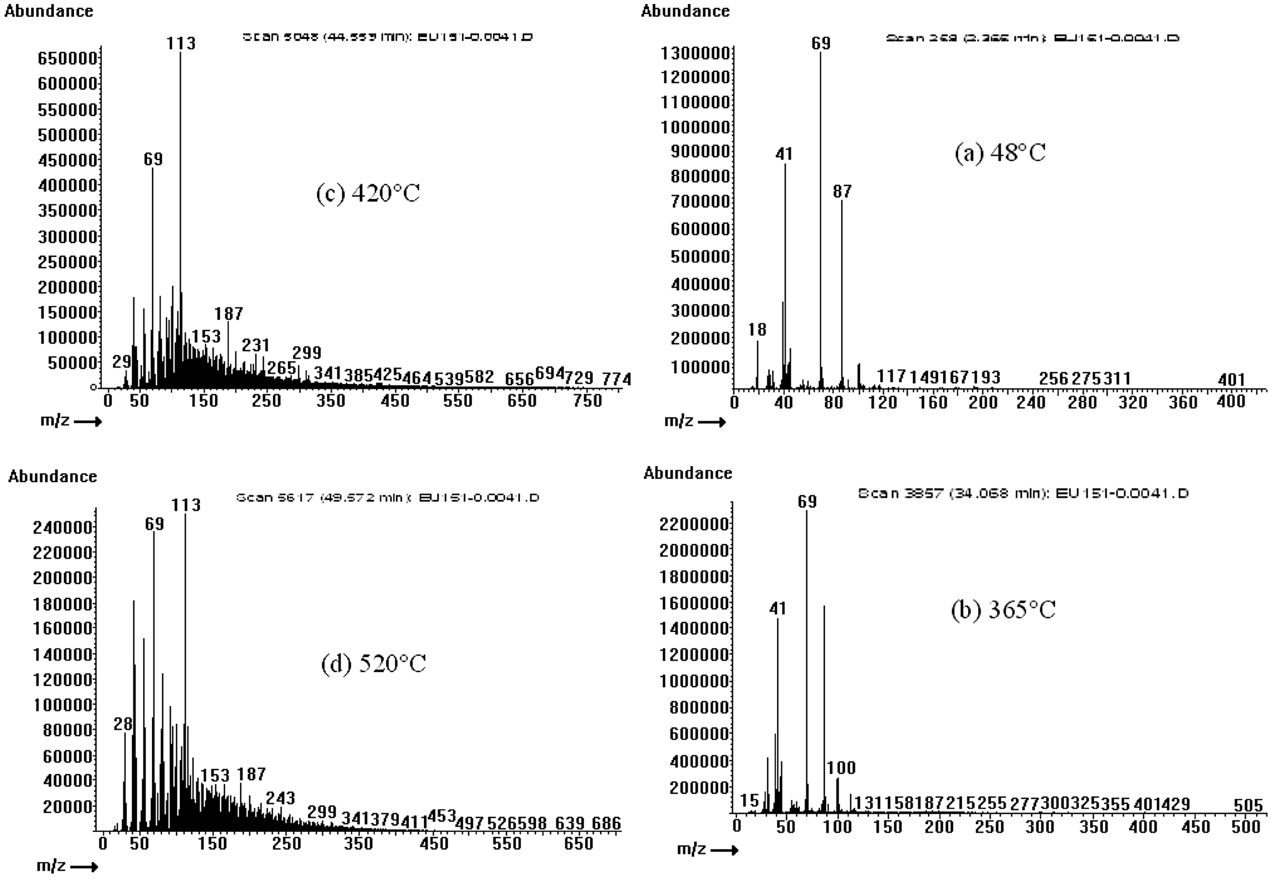


Fig. 9. Fragments of PHEMA obtained at (a)48°C, (b)365°C (c) 420°C and (d) 520°C.

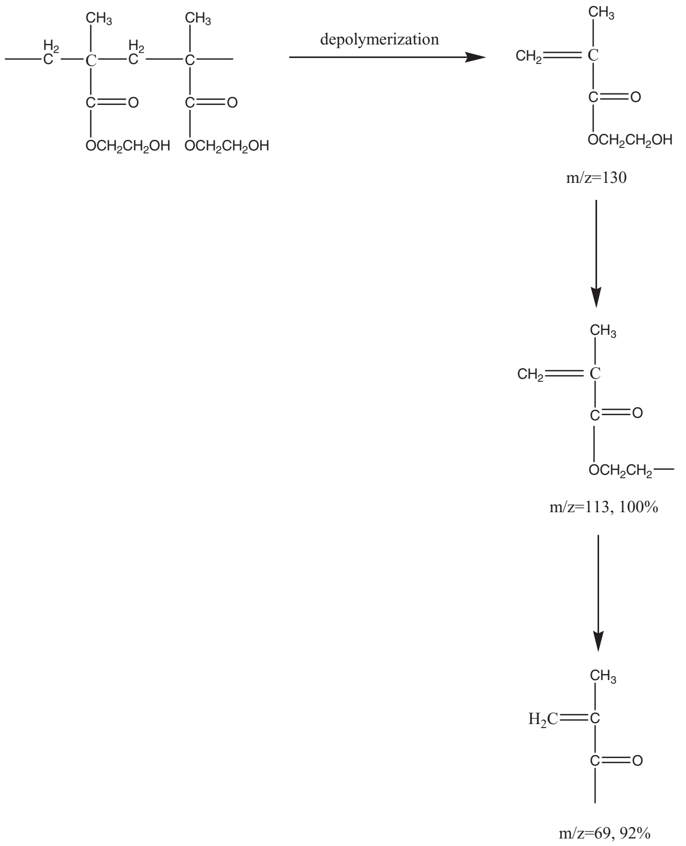
Table 1. Mass spectral fragments at different stage of degradation

	2.216 (48°C)		*34.068 (365°C)*		*44.507 (470°C)*		*49.519 (520°C)*	
m/z	I/I_0	*Fragments*	I/I_0	*Fragments*	I/I_0	*Fragments*	I/I_0	*Fragments*
15	0.59	CH_3	0.69	CH_3	0.25	CH_3	1.76	CH_3
17	3.63	OH	0.07	OH	0.03	OH	0.58	OH
18	16.34	H_2O	0.25	H_2O	0.13	H_2O	2.35	H_2O
27	3.64	C_2H_3	3.44	C_2H_3	3.27	C_2H_3	14.96	C_2H_3
28	5.74	CO,C_2H_4	2.24	CO,C_2H_4	3.61	CO,C_2H_4	29.57	CO,C_2H_4
29	3.88	C_2H_5	6.76	C_2H_5	5.36	C_2H_5	24.98	C_2H_5
31	5.14	CH_3O	17.82	CH_3O	2.08	CH_3O	8.53	CH_3O
41	64.67	C_3H_5	62.14	C_3H_5	26.01	C_3H_5	69.87	C_3H_5
43	6.54	C_3H_7,C_2H_3O	11.45	C_3H_7,C_2H_3O	12.01	C_3H_7,C_2H_3O	38.90	C_3H_7,C_2H_3O
44	7.82	C_2H_4O,CO_2	12.54	C_2H_4O,CO_2	11.84	C_2H_4O,CO_2	51.21	C_2H_4O,CO_2
45	11.52	C_2H_5O	16.28	C_2H_5O	7.89	C_2H_5O	22.21	C_2H_5O
53	1.05	C_4H_5	1.54	C_4H_5	6.74	C_4H_5	16.17	C_4H_5
55	2.54	C_3H_3O	3.86	C_3H_3O	22.44	C_3H_3O	58.52	C_3H_3O
61	0.43	$C_2H_5O_2$	1.32	$C_2H_5O_2$	0.41	$C_2H_5O_2$	0.92	$C_2H_5O_2$
69	100.00	C_4H_5O	100.00	C_4H_5O	63.79	C_4H_5O	92.15	C_4H_5O
77	0.33	$C_2H_5O_3$	0.31	$C_2H_5O_3$	10.13	$C_2H_5O_3$	20.32	$C_2H_5O_3$
87	54.29	$C_4H_7O_2$	66.39	$C_4H_7O_2$	9.27	$C_4H_7O_2$	11.56	$C_4H_7O_2$
91	2.58	$C_3H_7O_3,C_4H_{11}O_2$	2.38	$C_3H_7O_3,C_4H_{11}O_2$	19.88	$C_3H_7O_3,C_4H_{11}O_2$	38.10	$C_3H_7O_3,C_4H_{11}O_2$
100	7.11	$C_5H_8O_2$	11.27	$C_5H_8O_2$	23.18	$C_5H_8O_2$	28.79	$C_5H_8O_2$
113	1.31	$C_6H_9O_2$	5.84	$C_6H_9O_2$	100.00	$C_6H_9O_2$	100.00	$C_6H_9O_2$
117	1.35	$C_5H_9O_3$	1.30	$C_5H_9O_3$	7.64	$C_5H_9O_3$	13.02	$C_5H_9O_3$
129	0.35	$C_7H_{13}O_2$	0.38	$C_7H_{13}O_2$	12.08	$C_7H_{13}O_2$	15.27	$C_7H_{13}O_2$
130	0.09	$C_6H_{10}O_3$,monomer	0.11	$C_6H_{10}O_3$,monomer	3.13	$C_6H_{10}O_3$,monomer	4.58	$C_6H_{10}O_3$,monomer
141	0.07	$C_7H_9O_3$	0.10	$C_7H_9O_3$	11.26	$C_7H_9O_3$	13.62	$C_7H_9O_3$
149	0.13	$C_8H_5O_3$		$C_8H_5O_3$	10.82	$C_8H_5O_3$	13.62	$C_8H_5O_3$
165	0.16	$C_9H_9O_3$	0.17	$C_9H_9O_3$	10.93	$C_9H_9O_3$	14.20	$C_9H_9O_3$
187	—	$C_9H_{15}O_4$	0.46	$C_9H_{15}O_4$	19.01	$C_9H_{15}O_4$	14.61	$C_9H_{15}O_4$
199	0.01	$C_{10}H_{15}O_4$	0.41	$C_{10}H_{15}O_4$	10.67	$C_{10}H_{15}O_4$	10.05	$C_{10}H_{15}O_4$
215	0.03	$C_{10}H_{15}O_5$	0.33	$C_{10}H_{15}O_5$	7.27	$C_{10}H_{15}O_5$	8.03	$C_{10}H_{15}O_5$
231	0.02	$C_{11}H_{19}O_5$	0.03	$C_{11}H_{19}O_5$	9.75	$C_{11}H_{19}O_5$	6.59	$C_{11}H_{19}O_5$
255	—	$C_{12}H_{15}O_6$	0.05	$C_{12}H_{15}O_6$	5.55	$C_{12}H_{15}O_6$	4.43	$C_{12}H_{15}O_6$
260	—	$C_{12}H_{20}O_6$,dimer	0.01	$C_{12}H_{20}O_6$,dimer	2.27	$C_{12}H_{20}O_6$,dimer	2.41	$C_{12}H_{20}O_6$,dimer
267	—	$C_{13}H_{15}O_6$	0.03	$C_{13}H_{15}O_6$	4.37	$C_{13}H_{15}O_6$	3.61	$C_{13}H_{15}O_6$
279	0.02	$C_{14}H_{15}O_6$	0.01	$C_{14}H_{15}O_6$	3.05	$C_{14}H_{15}O_6$	2.88	$C_{14}H_{15}O_6$
287	—	$C_{14}H_{23}O_6$	0.01	$C_{14}H_{23}O_6$	3.58	$C_{14}H_{23}O_6$	2.50	$C_{14}H_{23}O_6$
299	—	$C_{15}H_{23}O_6$	0.03	$C_{15}H_{23}O_6$	6.42	$C_{15}H_{23}O_6$	3.33	$C_{15}H_{23}O_6$
311	0.03	$C_{16}H_{23}O_6$	0.05	$C_{16}H_{23}O_6$	5.15	$C_{16}H_{23}O_6$	2.89	$C_{16}H_{23}O_6$
327	—	$C_{17}H_{27}O_6$	0.01	$C_{17}H_{27}O_6$	3.05	$C_{17}H_{27}O_6$	2.17	$C_{17}H_{27}O_6$
376	—	$C_{17}H_{29}O_9$	—	$C_{17}H_{29}O_9$	0.97	$C_{17}H_{29}O_9$	0.67	$C_{17}H_{29}O_9$
390	—	$C_{18}H_{30}O_9$,trimer	—	$C_{18}H_{30}O_9$,trimer	0.75	$C_{18}H_{30}O_9$,trimer	0.55	$C_{18}H_{30}O_9$,trimer
520	—	$C_{24}H_{40}O_{12}$,tetramer	—	$C_{24}H_{40}O_{12}$,tetramer	0.25	$C_{24}H_{40}O_{12}$,tetramer	0.17	$C_{24}H_{40}O_{12}$,tetramer

the R group of ester OR, the monomer becomes unstable and degraded at low temperatures. In the second stage, the fragments are that of the monomer as in the first degradation stage with some changes in fragment abundance. In the last two stages, the main fragments are given in Scheme 2. The other fragments at these stages are those of monomer and polymer (Sch. 2), however, the other polymer fragments have limited abundance. These are dimer, trimer, tetramer and their fragments, and they are given in Table 1.

4 Conclusions

The γ-radiation induced polymerization of HEMA was carried out in aqueous solution to saturate –CH_2CH_2OH groups and that way to prevent intra- and intermolecular hydrogen bonding. In this case, the polymer might be linear, otherwise, cyclopolymerization would also be formed. The thermal degradation observed from TGA was mainly a combination of depolymerization and monomer fragmentation. The detail of the monomer degradation was



Sch. 2. MS fragmentation of polymer.

observed in GC-MS of the monomer; the degradation shown in the literature reported the recombination of fragments. The compounds obtained after degradation by Demirelli et al. (15) were not observed in our results. There are no anhydrides or cyclization products in the degradation, this is due to the polymerization being carried out in the presence of water.

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