

# Thermal Degradation of EVA and EBA—A Comparison.

## I. Volatile Decomposition Products

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### SYNOPSIS

This is the first in a series of papers in which structural changes during thermal degradation of ethylene–vinyl acetate (EVA) and ethylene–butyl acrylate (EBA) copolymers are compared. EVA, containing 11.4 mol% vinyl acetate (VA) and EBA, containing 5.4 mol% butyl acrylate (BA), were pyrolyzed at 280°C in nitrogen for 30 min. In another series of pyrolysis, EVA containing 1.2, 2.2, and 11.4 mol% VA were treated at 150–190°C for 3 h. The volatile decomposition products were collected in cooled traps respectively gas bags and then analysed with GC-MS and ion-chromatography. EVA is rather labile. The main volatile decomposition product is acetic acid. A linear decomposition rate was found already at the lowest investigated pyrolysis temperature, 150°C. After 30 min at 280°C every 15th of the acetate side groups had been eliminated. EBA is much more stable to pyrolysis. Thirty minutes at 280°C resulted in a decomposition of one out of 1500 BA groups. Butene is the main volatile decomposition product. Ester pyrolysis is supposed to account for the degradation of both types of polymers. The big difference in reactivity is presumably due to conformational differences. The ester pyrolysis mechanism will result in random unsaturations in EVA and carboxylic groups in EBA. To a minor extent acetaldehyde is formed when EVA is degraded. According to the mechanisms suggested, carbonyl groups remain in the main chain. Contrary to what is reported for poly(butyl acrylate), no alcohol was formed when pyrolysing EBA. This indicates that adjacent acrylate groups are needed for alcohol formation. For both types of polymer, scissions of the main chain results in hydrocarbon fragments mainly. In addition, acrylate containing fragments are observed when EBA is degraded. EVA, however, does not give any acetate-containing fragments.

### INTRODUCTION

One of the major advantages when polyethylene was introduced was its unpolar, highly crystalline structure, which resulted in outstanding dielectric properties and chemical resistance. More recently, there has been an increasing demand for ethylene polymers with less ordered and more polar structure in order to obtain, e.g., softer, more rubberlike properties, improved adhesion, and improved ability to carry additives and fillers.

The usual way to obtain these structural changes is by copolymerization, for example, with vinyl acetate (VA). The call for such copolymers has meant a revival of the free radical high pressure processes. They are relatively easy to adapt to copolymerization with different polar monomers, whereas the low pressure processes mainly are restricted to  $\alpha$ -olefines.

Poly(ethylene–vinyl acetate)s (EVA) are so far the most widely used polar copolymers. They have a broad utility spectrum because of the low price and strong modifying effect of VA. Their tendency to evolve acetic acid (HAc) when heated is, however, a serious drawback.

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More expensive, but also more thermally stable alternatives are copolymers containing primary acrylates, e.g., ethyl or butyl acrylates (EEA, EBA). One disadvantage with ethyl acrylate is its penetrating smell, giving problems when handling the monomer.

As the copolymers are produced in high pressure processes, their general chemical structure are similar to LDPE; they contain a relatively high amount of short chain branches, 10–30/1000 carbons, a few long chain branches, and unsaturated groups.

In order to elucidate the differences in thermal properties between LDPE, EVA, and EBA, we have investigated a series of commercial polymers, free from all kinds of additives. The results are given in this paper and two others on changes in unsaturation and in side group structure and molecular weight changes.

## LITERATURE SURVEY

### Vinyl Acetate Polymers

HAc is the main decomposition product when EVA and poly(vinyl acetate) (PVAc) are pyrolyzed.<sup>1–10</sup> Small amounts of chain fragments as well as ketene, carbon monoxide, carbon dioxide, and water have also been observed. The latter degradation products are presumably formed during thermal decomposition of evolved HAc.<sup>11</sup>

All of the reported isothermal degradation studies of EVA were made at temperatures above 250°C. Using a modified molecular still, Grassie<sup>5</sup> found that PVAc is stable up to 190°C. With thermal volatilization analysis and a heating rate of 10°C/min., McNeill et al.<sup>4</sup> found that deacetylation starts at about 290°C both for PVAc and EVA copolymers containing 12–33% VA. The peak maximum was, however, observed at 30°C higher temperature for the copolymers. The authors suggest that this is due to the fact that every short sequence of VA units in the copolymers require its own initiation step.

Using UV spectroscopy, Gardner and McNeill<sup>12</sup> found that EVA with 12% VA contained 18.6% of the VA groups in blocks of two and 3.6% in triads or longer sequences. This rather high block content could not be explained by ordinary copolymerization statistics. Published reactivity ratios,  $r_1 = 1.2$ ,  $r_2 = 1.1$ ,<sup>13</sup> will give 5% of diads. This discrepancy may be a result of the special polymerization technique used or, possibly, some sort of monomer complex formation.

In isothermal studies in the temperature range 260–290°C, Razuvaev et al.<sup>3</sup> found a considerable deacetylation rate already at 260°C for EVA con-

taining 33% VA. They also noticed that the deacetylation was strongly catalyzed by SnCl<sub>2</sub>, HCl, and, to some extent, by evolved HAc. Inhibitors of radical reactions did not influence the deacetylation rate.

### Vinyl Acrylate Polymers

Poly(methyl acrylate) is the most stable polyacrylate. The volatile degradation products consist mainly of chain fragments, but also of carbon dioxide and methanol.<sup>6,14,15</sup>

Higher primary polyacrylates showed another degradation pattern.<sup>16–20</sup> The main decomposition products found at 315°C were carbon dioxide, alcohol, and the alkene corresponding to the alcohol, e.g., butene for poly(*n*-butyl acrylate).<sup>16</sup> In the beginning of the pyrolysis, no alcohol but equimolar amounts of carbon dioxide and alkene were evolved. Later on, alcohol was the main decomposition product. The degradation rate decreased somewhat with the size of the ester group.

Secondary polyacrylates, e.g., poly(isopropyl acrylate) (P-i-PA), show much less thermal stability than primary ones.<sup>20–23</sup> When degrading P-i-PA at 265°C, propene was evolved initially. Later on, carbon dioxide and possibly water were obtained. The ratio of carbon dioxide to propene was found to be approximately 0.6.<sup>21</sup>

Degradation studies of copolymers consisting of methyl(methacrylate) and ethyl acrylate or *n*-butyl acrylate showed that alcohol evolution decreased in the order: homopolymer > blockcopolymer > random copolymer.<sup>19</sup> The latter ones contained equal amounts of the two monomers.

## EXPERIMENTAL

### Materials

Data for the copolymers used are given in Table I. A copolymer containing 5.4 mol % butyl acrylate is designated EBA-5.4. EBA-5.4 and EVA-11.4 were pyrolyzed at 280°C. In a separate series, EVA-1.2, EVA-2.2, and EVA-11.4 were degraded at lower temperatures, 150–190°C.

### Degradation Procedure

Five grams of polymer was ground in a laboratory mill (Brabender, System Wiley), mixed with 24 g, 3 mm glass beads and loaded into a tubular glass reactor. It was heated by immersion in a thermostatted silicon oil bath. Nitrogen (AGA Nitrogen SR), containing less than 10 ppm oxygen, was used

Table I Samples Investigated

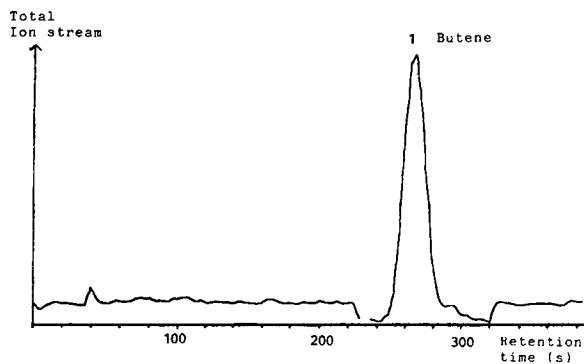
Sample	Commercial Name	Supplier	MI <sub>2</sub> (g/10 min)	Density (kg/m <sup>3</sup> )	Comonomer (wt. %)	Comonomer (mol %)	Unsaturation <sup>a</sup>				M <sub>w</sub> <sup>c</sup> LS <sup>c</sup> × 10 <sup>-3</sup>	LCB <sup>d</sup> /1000C	
							Trans $\frac{A_{965}}{A_{2010}}$	Vinyl $\frac{A_{910}}{A_{2010}}$	Vinylidene $\frac{A_{885}}{A_{2010}}$	M <sub>n</sub> <sup>b</sup> × 10 <sup>-3</sup>			M <sub>w</sub> <sup>b</sup> × 10 <sup>-3</sup>
LDPE	DFDS-6600	NESTE	0.31	921	—	—	< 0.1	0.3	0.7	20	167	299	1.0
EBA-0.8	DEX-915	NESTE	3.5	922	3.7	0.83	< 0.1	0.2	0.6	15	124	147	1.6
EBA-1.6	EBA-907	NESTE	1.1	923	6.9	1.6	< 0.1	0.3	0.7	16	136	145	1.1
EBA-5.4	DXM-410	NESTE	4.0	925	20.6	5.4	< 0.1	0.5	0.8	21	123	187	1.0
EVA-1.2	DQD-1824	UCC	0.9	928	3.5	1.2	Disturbance	< 0.1	0.2	22	103	97	1.5
EVA-2.2	Baylon V18T	BAYER	0.5	928	6.4	2.2	Disturbance	< 0.1	0.7	29	375	—	1.1
EVA-11.4	Evathene-2805	ICI	5.0	950	28.0	11.4	Disturbance	—	—	—	—	—	—

<sup>a</sup> Relative number of unsaturations calculated from IR absorbance for respective unsaturation peak at 965, 910, and 885 cm<sup>-1</sup> divided by the absorbance for the reference peak at 2010 cm<sup>-1</sup>.

<sup>b</sup> Determined by size exclusion chromatography. Refractive index detector.

<sup>c</sup> Determined by light scattering coupled on line to the size exclusion chromatography.

<sup>d</sup> LCB/1000 C = number of long chain branches per 1000 carbons.



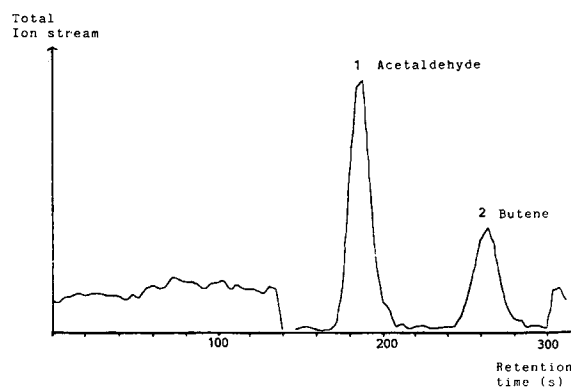
**Figure 1** GC-MS of more volatile decomposition products from EBA, after 30 min pyrolysis at 280°C.

as a carrier gas. The gas stream was dried and purified by molecular sieve (Altech gas purifier, Novakemi) and preheated in a glass coil in the silicon oil bath. The apparatus was purged for 15 min before heating.

#### Analysis of Volatile Degradation Products

The volatile components were analyzed by three different methods:

1. Analysis of more volatile components: The gas from the degradation reactor was collected in a Linde bag and later on injected by syringe into a gas chromatograph-mass spectrometer (GC-MS). A Chromosorb 102 (2 m × 2.1 mm) column was used at 100°C. The system was calibrated for butene by a standard mixture of butene and nitrogen (46 ng butene/mL).
2. Determination of evolved acetic acid: The decomposition products were collected in an U-tube cooled with liquid nitrogen. After the pyrolysis, the tube was closed and heated to room temperature. The content in the trap was then transferred to an ion chromatograph (Dionex system 10) in several portions of 0.5 mM Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> buffer, which also was used as eluent. The separation was carried out by an anion exchanger (precolumn 150 × 3 mm,



**Figure 2** GC-MS of more volatile decomposition products from EVA, after 30 min pyrolysis at 280°C.

two separation column 350 × 3 mm). The system was calibrated by ultrapure sodium acetate (Merck), dried at 110°C for 2 h. The detection limit of the conductometric detector used was about 0.3 ppm acetic acid.

3. Analysis of low volatility components: The decomposition products were collected in an U-tube, cooled by liquid nitrogen as in 2. The components were then distilled into another cooled trap (SIK valve), which later was connected to the GC-MS equipment. During this procedure, the more volatile components, including HAc, were only partly transferred to the analyzing system in order to avoid overloading.

#### RESULTS

The dominating part of the volatile products obtained from the two polymers pyrolyzed at 280°C contained relatively low boiling components. Analysis according to method 1 reveals that the major part of this fraction consists of butene from EBA (Fig. 1) and butene and acetaldehyde from EVA (Fig. 2). The identification of these compounds were made by controlling the mass spectra and retention time by adding these substances. The GC-MS spectra of the degradation products of EBA contained a small peak with a retention time of 40 s. This sub-

**Table II** Main Decomposition Products after 30 Min of Pyrolysis at 280°C

Sample	Butene		Acetaldehyde		Acetic Acid	
	(mg/kg)	(mol/kg)	(mg/kg)	(mol/kg)	(mg/kg)	(mol/kg)
EBA-5.4	62	0.0011	0	0	Trace	Trace
EVA-11.4	13	0.00023	26	0.00059	13000	0.22

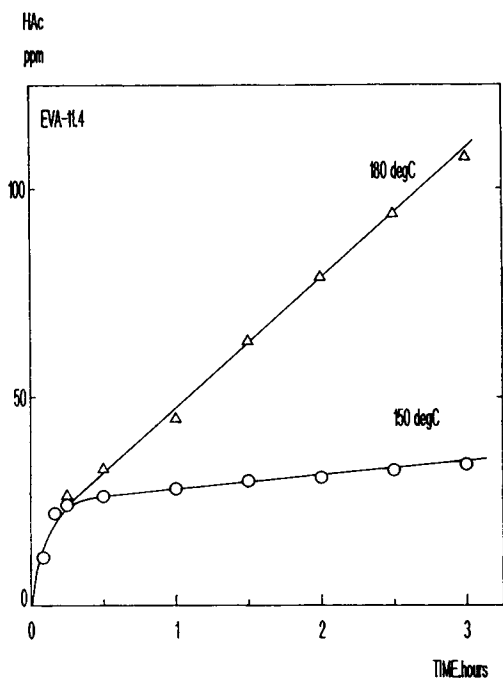


Figure 3 Formation of acetic acid from EVA-11.4 at 150 and 180°C.

stance has not been further analyzed by mass spectrometry. The retention time indicates that it consists of carbon dioxide.

In Table II the amount of acetic acid determined by ion chromatography (method 2) and the amount of butene determined by GC-MS is given. A rough estimation of evolved acetaldehyde is made, using the same response factor as for butene.

The amount of HAc evolved from EVA-11.4 in-

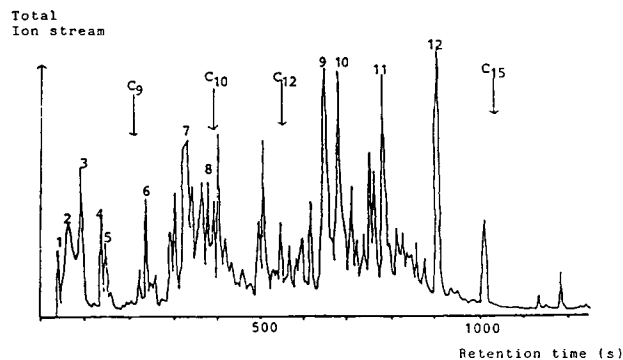


Figure 4 GC-MS of decomposition products from EBA, after 30 min pyrolysis at 280°C.

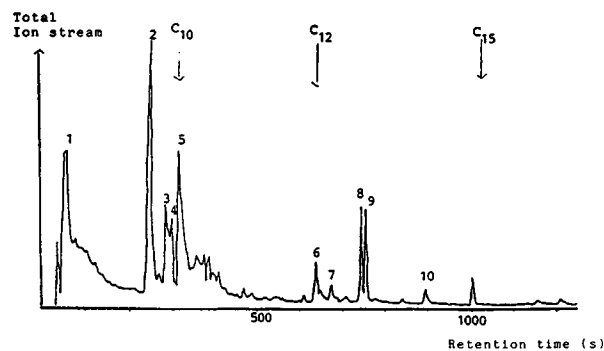
dicates that every 15th acetate group was split off after 30 min at 280°C. As calculated, only one out of 5500 acetate groups has been transformed into acetaldehyde. The small amount of butene is possibly due to the degradation of the hydrocarbon chain. The butene evolution from pyrolyzed EBA is considerably higher. If all butene comes from the acrylate groups, one out of 1500 of these groups are degraded. As the deacetylation rate of EVA was so fast at 280°C, we also used lower pyrolysis temperatures, 150–190°C. The result is given in Figures 3 and Table III.

The HAc evolution curves show a fast initial rate followed by a slower increase, linear in time but increasing with temperature. The rates of this latter part of the deacetylation are given in Table III. The deviation between reruns was about  $\pm 10\%$ . The changeover point in the curves are positioned at 2.7 and 20 ppm for EVA-1.2, EVA-2.2, and EVA-11.4,

Table III Deacetylation Rate of EVA at 150–190°C

Sample	Temperature (°C)	Deacetylation Rate <sup>a</sup> (ppm/h)	Normalized <sup>a</sup> Deacetylation Rate (ppm/h mol % VA)
EVA-1.2	150	<0.3	—
EVA-1.2	160	< 0.3	—
EVA-1.2	170	0.30	0.25
EVA-1.2	180	0.84	0.70
EVA-1.2	190	3.0	2.5
EVA-2.2	150	0.40	0.18
EVA-2.2	160	0.44	0.20
EVA-2.2	170	0.74	0.34
EVA-2.2	180	1.1	0.51
EVA-11.4	150	2.8	0.25
EVA-11.4	180	31	2.7

<sup>a</sup> Calculated from the second linear part of the degradation curves.



**Figure 5** GC-MS of decomposition products from EVA, after 30 min pyrolysis at 280°C.

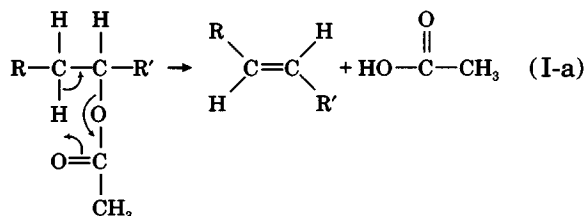
respectively. The more volatile fractions could not be separated by the column used in method 3. Consequently, they are found in peak no. 1 in the chromatograms (Figs. 4 and 5).

Investigation of the mass spectras obtained from the other components shows that the degradation products of EBA-5,4 contained hydrocarbon chain fragments (peaks: 3, 4, 5, 7, 8, 9, and 11) as well as butyl acrylate containing chain fragments (peaks: 6, 10, and 12). There are also traces of acetic acid (peak 2).

EVA-11.4 gave a lower number of peaks and lower quantities of heavier fractions than EBA-5.4. Hydrocarbon chain fragments are present (peaks: 2, 3, 4, 5, 8, and 9). Peaks 6, 7, and 10 gave a fragmentation pattern typical for oxygen containing compounds, e.g., peaks in the mass series 31, 45, 59, . . .<sup>23</sup> Their structure have not been revealed. The fragmentation pattern is, however, not consistent with acetate containing compounds.

## DISCUSSION

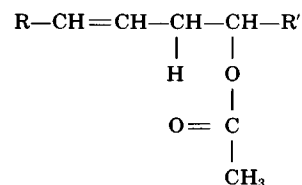
In accordance with earlier investigations of EVA and PVAc, our measurements show that HAc is the dominating degradation product from EVA. The formation of HAc is due to ester pyrolysis (I-a). This reaction, well known from low molecular acetates,<sup>24</sup> is generally accepted also for EVA and PVAc<sup>1,5,6</sup>:



As mentioned above, Grassie<sup>5</sup> considered PVAc to be stable up to 190°C. McNeill found EVA to be more stable.<sup>4</sup> All earlier isothermal pyrolysis experiments concerning EVA have been carried out at temperatures higher than 250°C. In our experiment we found a measurable HAc evolution already at the lowest investigated temperature, 150°C.

The degradation curves in Figure 3 show a fast initial HAc release followed by a slower constant deacetylation rate. The HAc evolution increases with temperature and VA-content. We consider the fast initial release to originate from the presence of dissolved HAc in the samples, formed during processing and storage. The solubility of HAc in the copolymers increases with the VA-content, which explains why the initial release is increasing with the VA-content of the copolymers.

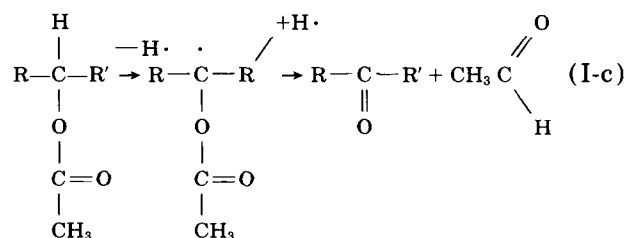
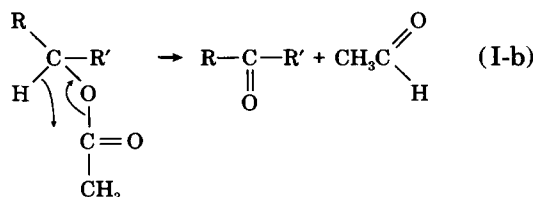
The second part of the degradation curves reveal the actual thermal stability of the polymers at the pyrolysis conditions used. EVA-11.4 shows the highest degradation rate. In this polymer the content of acetate blocks must be higher than in the other polymers. As mentioned before, McNeill et al.<sup>4</sup> suggested that every short sequence of VA units require its own initiation step in the copolymers. The initiation step leads to the following allyl activated structure<sup>6</sup>:



There should also be an increased catalytic effect of HAc in EVA-11.4 due to the higher degradation rate and increased solubility of HAc in this more polar copolymer. EVA-2.2 shows a somewhat anomalous behavior, with a comparably high degradation rate at low temperatures as well as a small temperature effect. This copolymer is produced in an autoclave reactor in contrast to EVA-1.2, which is a tubular reactor quality. EVA-2.2 shows a rather high molecular weight and a broad molecular weight distribution. It has also a high content of vinylidene unsaturation (see Table I). The different manufacturing processes might also influence the tendency to block formation.

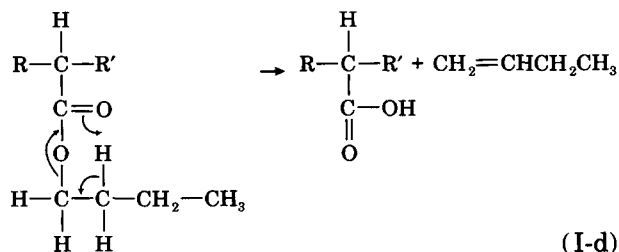
The formation of acetaldehyde has not previously been reported in pyrolysis of EVA. The amount found in our experiments is much lower (400 times) than the HAc evolved, but is in fact comparable with

the butene formation in EBA. Both molecular and radical mechanisms could be suggested:



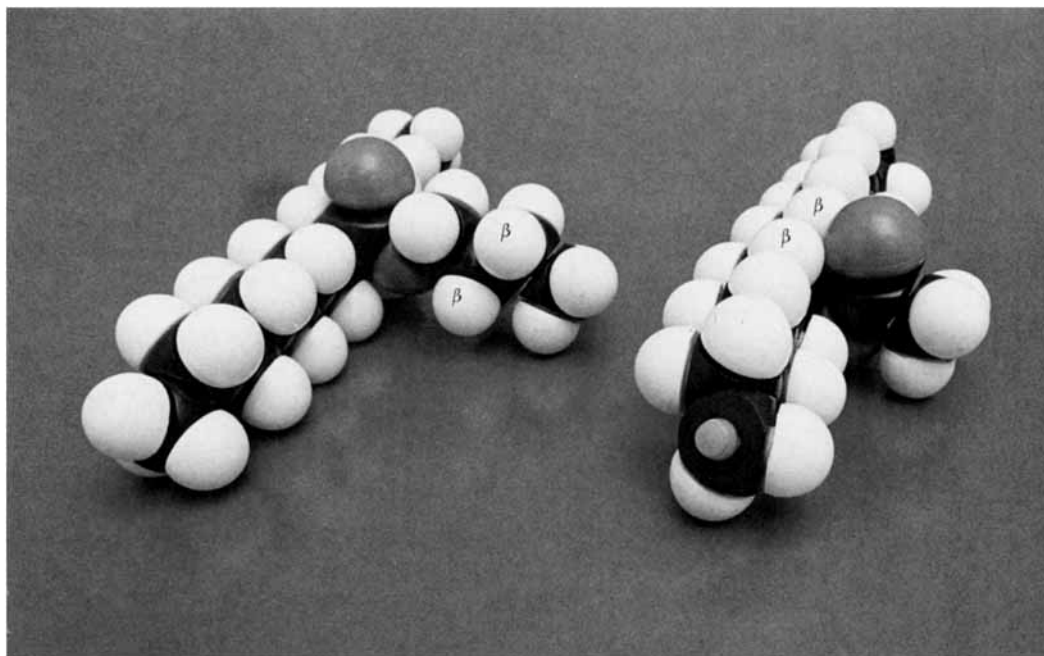
I-b and I-c are both a result of the weakness of the tertiary carbon-hydrogen bond. After evolution of acetaldehyde, the chain should contain carbonyl groups and this structure was actually found in the remaining polymer, as referred to in Paper II.<sup>25</sup> We did not detect any decomposition products from acetic acid, such as ketene, methane, and water, which have been identified by other workers using considerably higher temperatures, e.g., 500°C.<sup>8</sup>

In EBA the main decomposition product, butene, is most likely formed by ester pyrolysis:

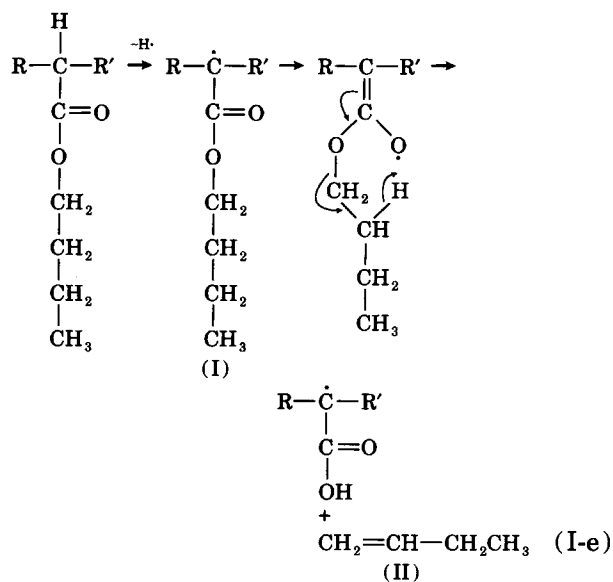


In spite of its similarity with the acetate pyrolysis of EVA, the butene formation is much slower than the formation of acetic acid. The main reason for this could well be an effect of conformational differences. In the EVA molecule the carbonyl oxygen is close to the hydrogen atoms connected to the  $\beta$ -carbons in the main chain. The distance is considerably larger between the carbonyl oxygen and the hydrogens on the  $\beta$ -carbon in the side group. This difference can be seen in Figure 6, where the ester groups are in their most favorable conformation.<sup>26</sup> An additional reason is that more energy is needed to form vinyl end groups than internal double bounds.<sup>27</sup>

As an alternative to the above-mentioned molecular mechanism a radical mechanism could be postulated:

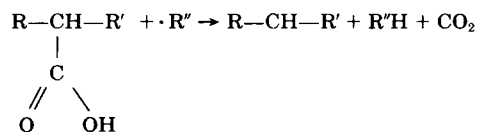


**Figure 6** Space filling models of the most favorable conformation of EBA and EVA. (Reactive hydrogens marked  $\beta$ .)



Butyl acrylate is known to have a chain transfer effect in the copolymerization with ethylene. This will create acrylate end groups. The butyl acrylate containing fragments observed in the degradation of EBA-5.4 might be due to chain cleavage near such ends and/or near acrylate groups within the chain. As discussed later in this series of papers,<sup>28</sup> EBA shows a higher tendency to chain cleavages than LDPE. This could be due to  $\beta$ -scissions adjacent to the macroradical I and II in reaction (I-e).

As mentioned above, our GC-MS analysis indicated that carbon dioxide was evolved when pyrolyzing EBA-5.4 at 280°C. Grassie and Fortune<sup>29</sup> found a considerable decarboxylation in the thermal degradation at 315°C of a copolymer of methyl methacrylate and butyl acrylate. They suggested a radical mechanism<sup>30</sup>:



Butanol is one of the dominating decomposition products when poly(butyl acrylate) is pyrolyzed.<sup>16</sup> We did not find any alcohol however, when degrading the random copolymer EBA-5.4. This is in accordance with the result of pyrolysing random copolymers of methyl methacrylate and other acrylates.<sup>19,29-33</sup> For alcohol formation, adjacent acrylate groups are obviously necessary.

## CONCLUSIONS

Pyrolysis at 280°C of random EVA and random EBA gives acetic acid and butene, respectively, as the

main volatile product. In both cases ester pyrolysis is suggested to account for the result. EBA is, however, much more stable than EVA, which we suggest is mainly due to conformational reasons. The ester pyrolysis mechanism will result in main chain unsaturation in EVA and carboxylic groups in EBA.

Contrary to earlier degradation studies, we noticed an HAC evolution already at 150°C, which was the lowest pyrolysis temperature used.

To a minor extent, acetaldehyde is formed when EVA is degraded. According to the mechanism suggested, carbonyl groups remain in the polymer chain.

Contrary to what is reported for poly(*n*-butyl acrylate) no alcohol is formed from random EBA. This supports earlier findings that adjacent acrylate groups are needed for alcohol formation in acrylate containing polymers.

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