

Thermal Degradation of EVA and EBA—A Comparison.

III. Molecular Weight Changes

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SYNOPSIS

This is the third in a series of papers in which the thermal degradation of ethylene–vinyl acetate (EVA) and ethylene–butyl acrylate (EBA) copolymers are compared. The EBA samples contained 0.8, 1.6, and 5.4 mol % butyl acrylate (BA), respectively, and the EVA samples 1.2 and 6.7 mol % vinyl acetate (VA). The samples were heated in nitrogen in a tubular oven at 285–390°C, for 6–120 min. The molecular weight distribution (MWD), long chain branching, and gel content were analyzed with size exclusion chromatography (SEC). The columns were connected to refractive index, viscometric, and light scattering detectors. EVA gave a pronounced molecular enlargement at all degradation temperatures. In EVA-6.7, gel was formed at all degradation levels, whereas the low content sample, EVA-1.2, did not form any visible amount of gel. The strong tendency to molecular enlargement is due to allyl radicals formed after thermal deacetylation and the formation of internal double bonds. These macroradicals will combine or, less frequently, add to double bonds. The EBA copolymers show a more polyethylenelike degradation behavior. At 285°C molecular enlargement dominates, but already at 333°C a net reduction in molecular size is observed. At high temperatures, ester pyrolysis of the BA groups give carboxylic groups and anhydrides. Alkaline treatment will not give any appreciable change in MWD, showing that the anhydride formation is mainly intramolecular. The chain scission increases with the BA content. This is probably due to β -cleavage of tertiary macroradicals formed in the chain at the acrylate or carboxylic side groups.

INTRODUCTION

In this series of investigations the thermal stabilities of ethylene–butyl acrylate (EBA) and ethylene–vinyl acetate (EVA) copolymers are compared. In the first two papers the volatile decomposition products and the changes in side group structures and unsaturations have been studied.^{1,2}

As is well known from practical work, EVA is thermally labile and evolves acetic acid (HAc). In our first paper in this series,¹ we reported that HAc was evolved already at the lowest investigated temperature, 150°C. After about 30 min at 333°C the deacetylation was completed. Although HAc was the

main volatile degradation product, minor amounts of acetaldehyde were also evolved. The formation of HAc is due to ester pyrolysis and is accompanied with the formation of double bonds in the polymer chain. As is the case for PVC, the decomposition is catalyzed by the acid decomposition product. In blocks of vinyl acetate (VA), an allyl activation effect contributes. Weight loss measurements indicate a decreased tendency to main chain cleavage with increasing VA content.

In EBA, the thermal degradation also results in ester pyrolysis. In this case, however, an unsaturated volatile product, butene, is formed and the acid residue remains in the polymer as carboxylic groups. These groups were found to partly convert to anhydrides. Dekarboxylation was also observed. It was suggested that the higher stability of EBA compared to EVA is mainly due to conformational reasons.

As is the case for polyethylene, main chain scis-

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sion also occurs. The rate was low at moderate temperature. For EBA, acrylate containing fragments were observed, which would imply that chain cleavage adjacent to the acrylate groups are favored. Furthermore, weight loss measurements show that the presence of butyl acrylate (BA) groups increase the tendency to main chain cleavage.

Several of these structural changes should influence on the molecular weight distribution (MWD), the long chain branching (LCB), and possibly, result in gel formation. In this paper such changes are studied.

EXPERIMENTAL

Materials and Thermal Degradation

The virgin polymers (Table I) and degraded samples used in our second paper² are further investigated in this study. The thermal degradation was performed in ultrapure nitrogen in a tubular oven at 285, 333, 350, 370, and 390°C for 6–120 min. For experimental details see Ref. 2.

Size Exclusion Chromatography

The molecular weight distribution (MWD), long chain branching (LCB), and the content of gel and microgel were determined by size exclusion chromatography (SEC).

The chromatograph, Waters Model 200, was equipped with a refractive index detector (RI), a Fica capillary viscometer (OLV) and a Chromatix KMX-6 low angle laser light scattering photometer (LS).

Details of the SEC-analysis system have been described earlier.³

Experimental Parameters

The sample solutions were prepared according to a standardized procedure, including the mixture of 40 mg sample in 20 mL Trichlorobenzene (TCB). After dissolution 3 h at 135°C in nitrogen, the solution was filtered through a 0.45 μm asbestos filter.

Data for the LS determinations were

- Wave length = 633 nm
- Refractive index of solvent $n = 1.503$
- Second virial coefficient, $2A_2 = 6 \times 10^{-4}$ (for polyethylene)
- Refractive index increment, $dn/dc = -0.104$

MWD and LCB

Use of both RI and OLV allows for the determination of MWD and LCB. The determination is improved by the additional use of LS, which measures the absolute value of M_w (M_w -LS).

The calculations of MWD and LCB follow the procedure developed by Drott and Mendelsson.⁴

The following Mark-Houwink relation, valid for polyethylene, was used⁵:

$$[\eta] = 3.92 \times 10^{-4} M_w^{0.725}$$

LCB was determined by the Zimm-Stockmayer relation for polydisperse samples⁶:

$$\langle g_3 \rangle_w = \frac{6}{n_w} \left[0.5 \left[\frac{2 + n_w}{n_w} \right]^{0.5} \times \ln \left[\frac{(2 + n_w)^{0.5} + n_w^{0.5}}{(2 + n_w)^{0.5} - n_w^{0.5}} - 1 \right] \right]$$

$\langle g_3 \rangle_w$ is the weight average of the quotient between the squared gyration radii of three-star branched and linear molecules of the same molecular weight in theta solution. n_w is the weight average of the number of branch points per molecule. $\langle g_3 \rangle_w$ was calculated from the viscometric measurements⁷

$$g' = \langle g_3 \rangle_w^b$$

$$g' = [\eta]_{\text{branched}} / [\eta]_{\text{linear}}$$

The value of b was taken as 0.7 according to calibrations using NMR, carried out in our laboratory,³ on polyethylene samples.

The difference between the output signal from the RI and LS detector is illustrated in Figure 1, which refers to silane crosslinking of grafted polyethylene. The output signal from the RI detector is a measure of the concentration in the eluent. The abscissa is given in counts, e.g., approx. 5 mL portions of the elution volume V_e . V_e is inversely related to the molecular weight. In the ordinary data treatment, the ordinates are normalized and the abscissa is expressed in molecular weight (M). This transformation results in ordinary MWD curves, where the relative concentration (C_r), i.e., the relative number of molecules, is given against molecular weight.

The output signal of LS is a measure of molecular weight times concentration ($M \times C$).

High molecular fractions are therefore enhanced: on the other hand, the sensitivity in the low molec-

Table I Samples Investigated

Sample	Commercial Name	Supplier	MI ₂ (g/10 min)	Density (kg/m ³)	Comonomer		Unsaturation ^a				M_w^- LS ^c × 10 ⁻³	LCB ^d 1000 C	
					(wt %)	(mol %)	Trans $\frac{A_{965}}{A_{2010}}$	Vinyl $\frac{A_{910}}{A_{2010}}$	Vinylidene $\frac{A_{885}}{A_{2010}}$	M_n^b × 10 ⁻³			M_w^b × 10 ⁻³
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		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						

^a Relative number of unsaturations calculated from IR absorbance for respective unsaturation peak at 965, 910, and 885 cm⁻¹ divided by the absorbance for the reference peak at 2010 cm⁻¹.

^b Determined by size exclusion chromatography. Refractive index detector.

^c Determined by light scattering coupled on line to the size exclusion chromatograph.

^d LCB/1000 C = number of long chain branches per 1000 carbons.

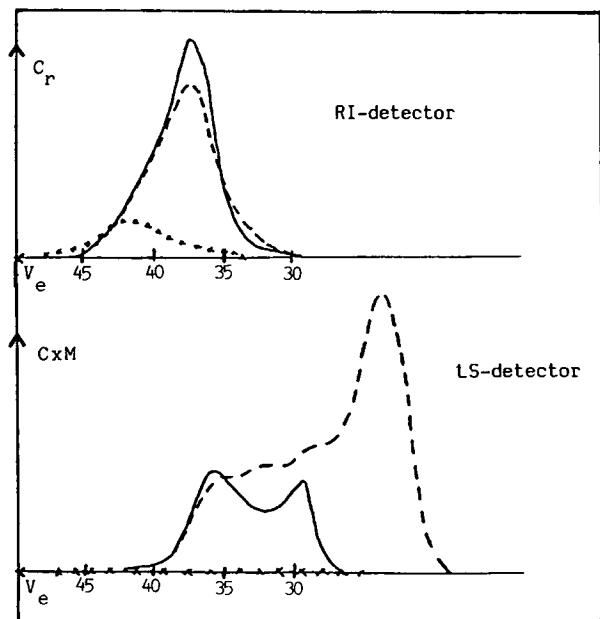


Figure 1 Comparison between refractive index and light scattering detector: (—) untreated LDPE-2; (---) LDPE-2 after grafting with vinyl-trimethoxy silane according to the sioplas method¹⁷; (xxx) grafted polymer after addition of crosslinking catalyst and water treatment.

ular region is poor. This difference between RI and LS measurement is clearly demonstrated in Figure 1. The enhanced sensitivity of LS for large molecules allows for a qualitative detection of microgel and traces of soluble giant molecules. The SEC measurements in this investigation is illustrated by Figures 2–4 and 10. In these figures the RI measurements are given as MWD curves and the LS curves as untreated chromatograms. As the ordinate is not normalized, it is a measure of the absolute value of $M \times C$. The V_e values equivalent to the detection limits for the RI detector are indicated by arrows in the LS chromatograms.

The data obtained from the SEC analysis are summarized in Table II. In the column to the right the relative changes in the number of molecules due to chain cleavages or combinations are given in percent according to

$$\frac{M_n^{-1} - M_{n0}^{-1}}{M_{n0}^{-1}} \times 100\%$$

where M_{n0} and M_n are the number average molecular weights for the undegraded and degraded polymers, respectively.

Content of Macrogel

The gel content of degraded samples were calculated from the reduction in curve areas of the original RI chromatograms by comparison with the chromatogram areas of the undegraded samples.

This procedure is based on the fact that gel is not passing the asbestos filter used for preparation of the sample solution.

RESULTS

At 285°C the molecular enlargement reaction dominate in LDPE (Fig. 2). The enlargement is more pronounced in EVA (Fig. 3). In EVA-6.7, it has resulted in a large amount of gel. (Fig. 5). The changes in M_w -LS for the soluble part of this sample degraded at 285°C is given in Fig. 6. M_w -LS increases strongly with degradation time up to 90 min. After 120 min of degradation, the soluble fraction has about the same molecular weight as the original sample. The gel content, however, has increased from 20 to 40 wt % during this period. These changes are clearly illustrated in Figure 3.

At 333°C the molecular enlargement in EVA is still more accelerated. After 90 min the M_w -LS is more than doubled for EVA-1.2 (Fig. 7), but no gel was observed. For EVA-6.7, however, the gel formation is very rapid (see Fig. 5). Already after 24 min of degradation, the gel content curve flattens out at about 80 wt %. The soluble part has a low molecular weight (see Fig. 3). At these degradation conditions nearly all of the acetate groups have been split off.² The gel formation is linearly related to the reduction in VA content (Fig. 8), excluding short degradation time (333.6 min) and low VA losses.

As shown in our previous paper in this series,² there is only a minor reduction in BA content in the EBA copolymers when degraded at 285°C. The changes in molecular weight for these copolymers are similar to those obtained for LDPE (Figs. 4 and 6). The tendency to molecular enlargement is, however, less pronounced. At 333°C the molecular diminishing reactions are dominating for both LDPE and EBA (Fig. 7). The increase in the relative number of molecules are given against time and BA content in (Fig. 9). The chain cleavage increases linearly with time and initial content of the comonomer.

EBA-0.8 and EBA-1.6 have also been degraded at 350, 370, and 390°C for 24 min. Chain scission and branching are rapidly increasing with temper-

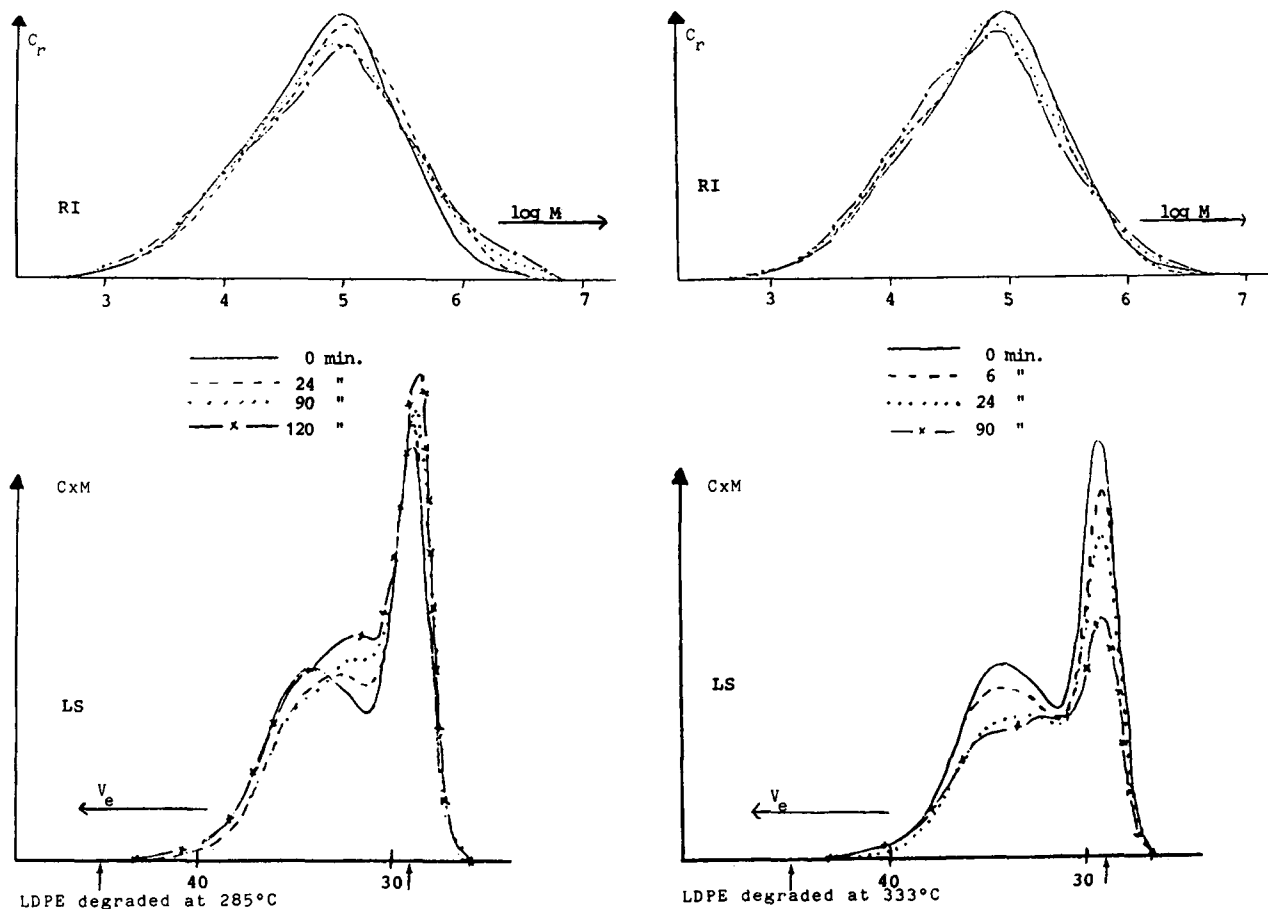


Figure 2 SEC chromatograms obtained with RI and LS detectors of LDPE degraded at 285 and 333°C.

ature. The influence of the BA content is marked also at these higher temperatures (see Table II). Even at this extensive degradation, no gel was formed—on the contrary, the high molecular weight tail is rapidly diminishing (Fig. 10).

The changes in intrinsic viscosity $[\eta]$ for the soluble part of the polymers degraded at 333°C is given in Figure 11. $[\eta]$ decreases with time for LDPE and EBA, while it increases for EVA 1.2. These changes are related to the earlier discussed changes in molecular weight.

Naturally, $[\eta]$ is also influenced by the changes in LCB. In LDPE the branching is increasing with degradation. In EBA there is a slight drop in LCB at moderate degradation conditions, reducing $[\eta]$. More intense degradation result in an increase in LCB. LCB data for the EVA copolymers is rather inconsistent due to the formation of chain double bonds, counteracting the effect of branching on molecular size.

DISCUSSION

LDPE

In the LDPE sample molecular enlargement reactions dominate at 285°C. In the second paper in this series,² it was found that there was little change in unsaturation at 285°C. Accordingly, the rate of β -scission is small and combinations of macroradicals dominates over disproportionation.

At 333°C the vinyl unsaturation increases,² indicating an increased tendency to β -scission and/or disproportionation. This is supported by the MWD and LS curves (Fig. 2). These observations are in accordance with earlier investigations, carried out at this laboratory.⁸⁻¹⁰

Obviously, the temperature dependence of the molecular enlarging reactions are smaller, than that of the molecular diminishing reactions, leading to a balance at a temperature slightly below 330°C.

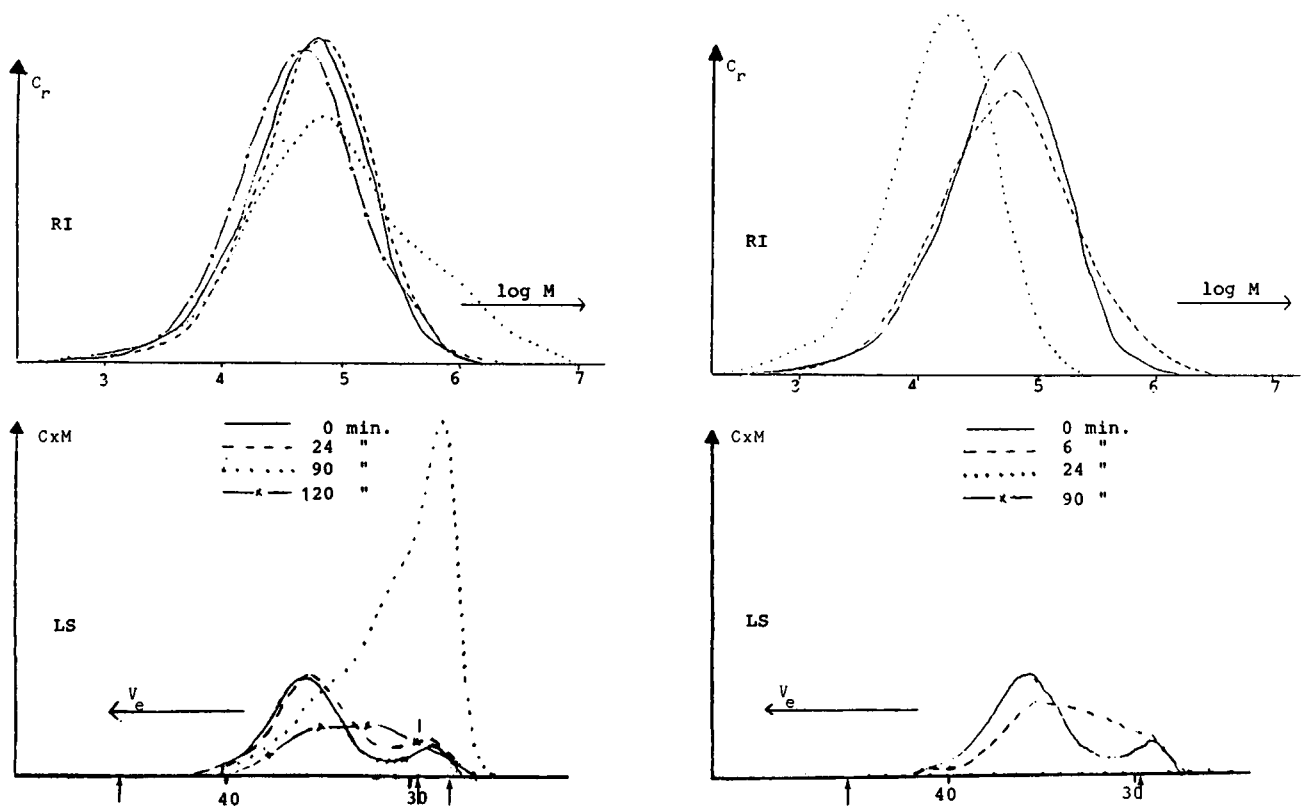


Figure 3 SEC chromatograms obtained with RI and LS detectors of EVA-6,7 degraded at 285 and 333°C.

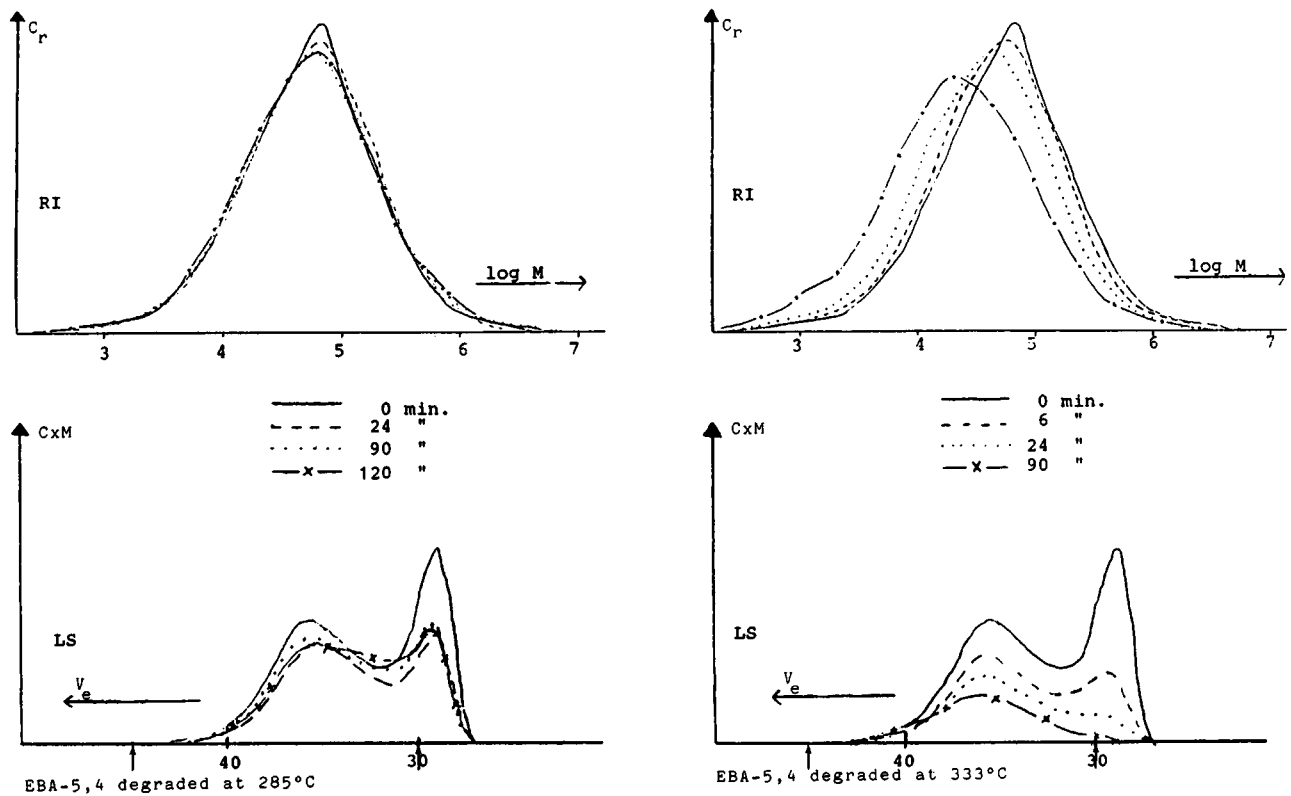


Figure 4 SEC chromatograms obtained with RI and LS detectors of EBA-5,4 degraded at 285 and 333°C (soluble part).

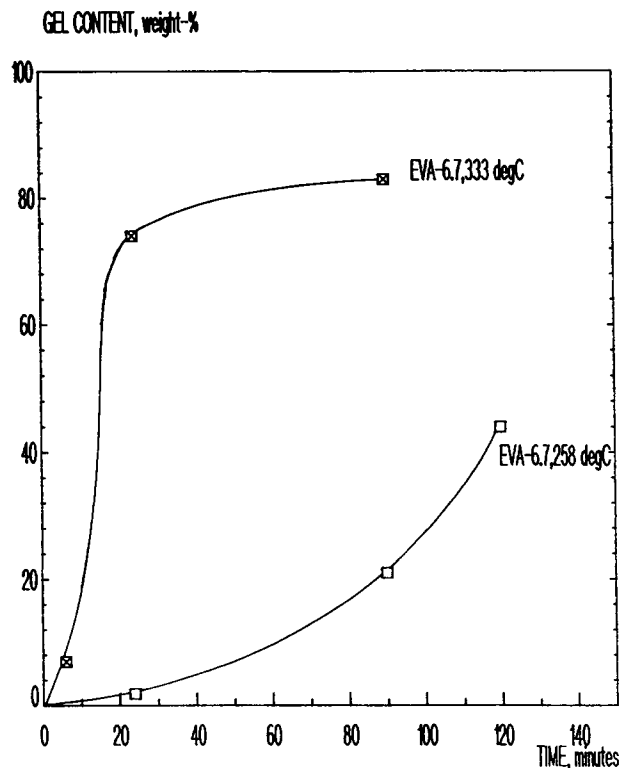


Figure 5 Gel formation when degrading EVA-6,7 at 285 and 333°C.

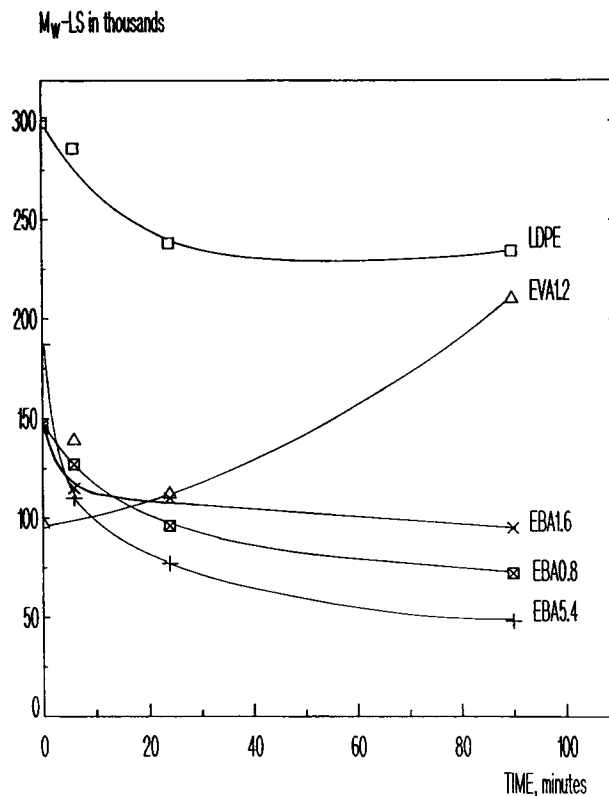


Figure 7 Molecular weight changes measured with light scattering for samples degraded at 333°C.

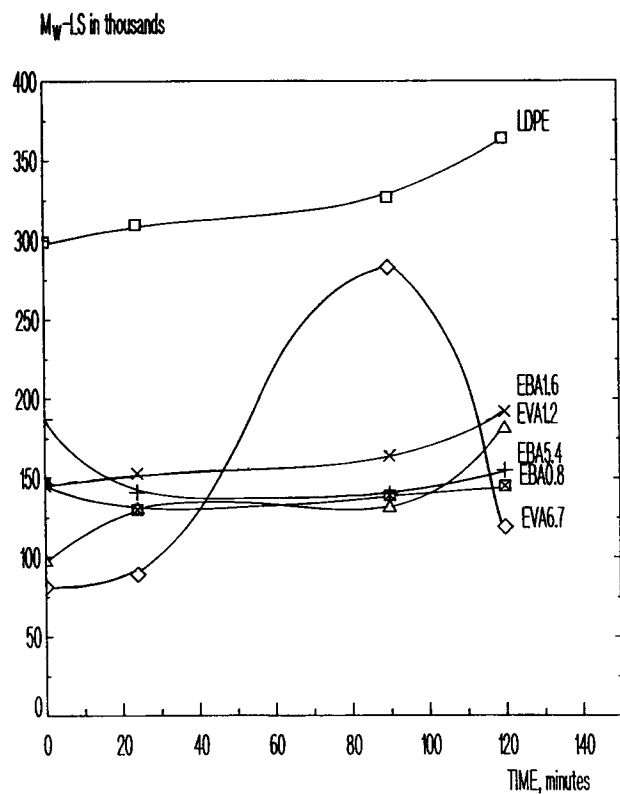


Figure 6 Molecular weight changes measured with light scattering for samples degraded at 285°C.

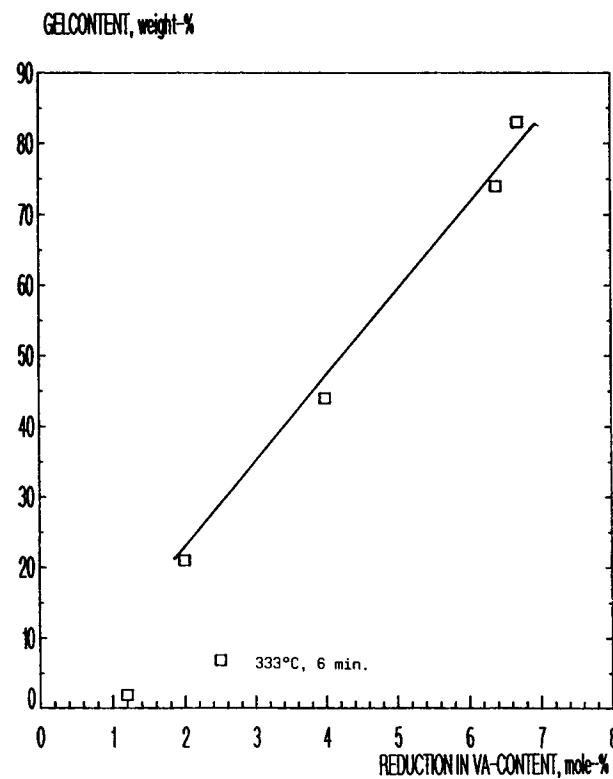


Figure 8 Gelformation vs. reduction in VA-content for EVA-6,7.

Table II SEC Analysis Data

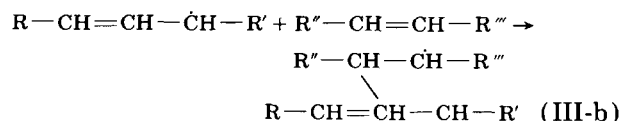
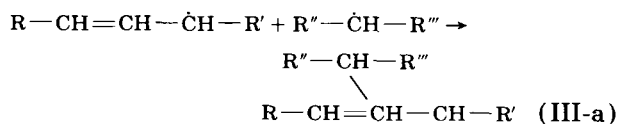
Sample	Degradation		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w\text{-LS} \times 10^{-3}$	LCB/1000 C	[η] (dL/g)	$\frac{M_n^{-1} - M_{n0}^{-1}}{M_{n0}^{-1}} \times 10^{-2}\%$
	Temp (°C)	Time (min)						
LDPE	—	—	20	167	299	1.02	0.98	
	285	24	23	186	310	1.26	0.98	-13
	285	90	20	221	327	1.26	0.98	0
	285	120	18	262	364	1.23	0.98	11
	333	6	19	143	286	1.20	0.93	5
	333	24	19	155	238	1.11	0.88	5
	333	90	19	167	234	1.64	0.80	5
EBA-0.8	—	—	15	124	147	1.60	0.76	0
	285	24	15	109	130	1.47	0.77	0
	285	90	18	106	139	1.30	0.79	-17
	285	120	17	114	145	1.13	0.83	-12
	333	6	18	197	127	1.18	0.80	-17
	333	24	16	91	96	1.65	0.69	-6
	333	90	12	89	72	2.13	0.58	25
	350	24	12	67	62	1.92	0.59	25
	370	24	8.3	44	30	2.93	0.43	80
	390	24	4.1	18	16	4.1	0.27	266
EBA-1.6	—	—	16	136	145	1.08	0.92	
	285	24	22	155	153	1.16	0.95	-26
	285	90	22	140	164	0.95	0.97	-26
	285	120	14	145	192	0.98	0.94	13
	333	6	19	107	115	0.95	0.89	-16
	333	24	16	100	110	1.26	0.77	3
	333	90	10	87.3	95	1.64	0.62	54
	350	24	11	72.2	61	2.41	0.55	47
	370	24	6.4	47.1	55	3.25	0.40	150
	390	24	3.4	24.2	22	5.66	0.24	370
EBA-5.4	—	—	21	123	187	1.04	0.90	
	285	24	21	120	141	1.4	0.82	0
	285	90	21	139	140	1.68	0.77	0
	285	120	20	128	155	1.26	0.84	5
	333	6	18	110	110	1.46	0.76	17
	333	24	13	83	77	1.92	0.63	62
	333	90	6.9	59	48	2.00	0.51	204
EVA-1.2	—	—	22	103	97	1.46	0.81	
	285	24	26	112	130	1.32	0.87	-15
	285	90	20	106	131	1.01	0.90	10
	285	120	22	132	181	1.12	0.91	0
	333	6	22	106	139	1.13	0.83	0
	333	24	24	113	112	1.47	0.80	-8
	333	90	17	190	210	1.11	0.93	29
EVA-6.7	—	—	17	87	81	0.99	0.84	
	285	24	24	103	89	0.91	0.93	-29
	285	90	21	317	283	1.16	1.06	-19
	285	120	21	88	119	—	—	-19
	333	6	19	128	81	1.15	0.86	-10
	333	24	7.8	24	—	—	—	118
	333	90	—	—	—	—	—	—

EVA

Compared with polyethylene, EVA shows a totally different behavior. The crosslinking tendency is much more pronounced at 285°C and is increasing with temperature. It is linearly related to the formation of internal double bonds.

Such crosslinkings could be due to either Diels-Alder reactions or combination of macro allyl radicals. The Diels-Alder reaction calls for the presence of conjugated double bonds, which is a possibility even in random copolymers. We have, however, found that the gel cannot be dissolved by treatment with maleic anhydride, which is the standard method for breaking Diels-Alder structures.¹¹

Crosslinking via randomly distributed double bonds could possibly occur after abstraction of hydrogen in allyl position. The resonance stabilized radical is likely to combine with other macroradicals (III-a). A less frequent alternative is addition to double bonds (III-b).



In our second paper in this series,² it was noticed that the increase in vinyl end groups was much less in EVA than in LDPE. This might be a result of a reaction between allyl activated macroradicals and vinyl end groups. Another explanation for the low content of vinyl end groups is the chance for a macroradical to react with an allyl activated radical instead of undergoing β -scission or disproportionation.

EBA

In our second paper,² it was shown that the pyrolysis of EBA results in the formation of butene, carboxylic groups remaining in the polymer. The carboxylic groups are partly converted to anhydrides. In that paper it could not be decided whether the anhydride formation was inter- or intramolecular. To investigate this point further, SEC analysis was performed on EBA-6.7, degraded for 90 min at 333°C, before and after titration with alcoholic KOH. In Ref. 2 it was shown that this titration totally transformed the anhydride and carboxylic groups to carboxylates. In the present investigation no difference in MWD between titrated and untitrated sample could be detected with the RI detector. The LS de-

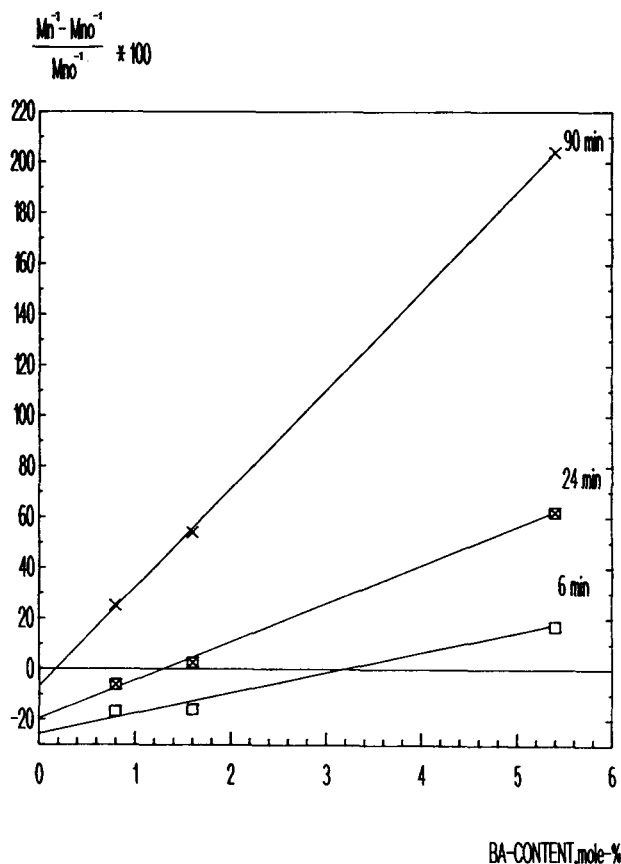
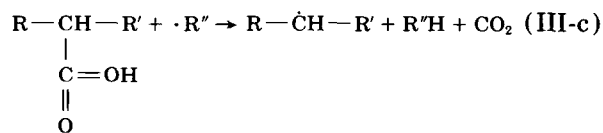


Figure 9 Increase in the relative number of molecules for the EBA copolymers degraded at 333°C.

tor, on the other hand, showed a small reduction in the high molecular part of the titrated sample (Fig. 12). The LS detector is extremely sensitive to these big molecules. It can therefore be concluded that the content of inter molecular anhydride groups is small and that the anhydride formation is mainly intramolecular. The SEC analysis further showed that the number of molecules increased with BA content and degradation (Fig. 9). It is not likely that the observed reduction in molecular weight is due to chain scissions after decarboxylation. Indeed Grassie and Fortune have proposed¹² the following decarboxylation reaction for carboxylic groups formed in a methyl methacrylate (*n*-butyl acrylate) copolymer giving a secondary radical which could induce β -scission:



They did not, however, find any relation between carbon dioxide formation and chain scission.¹²⁻¹⁵

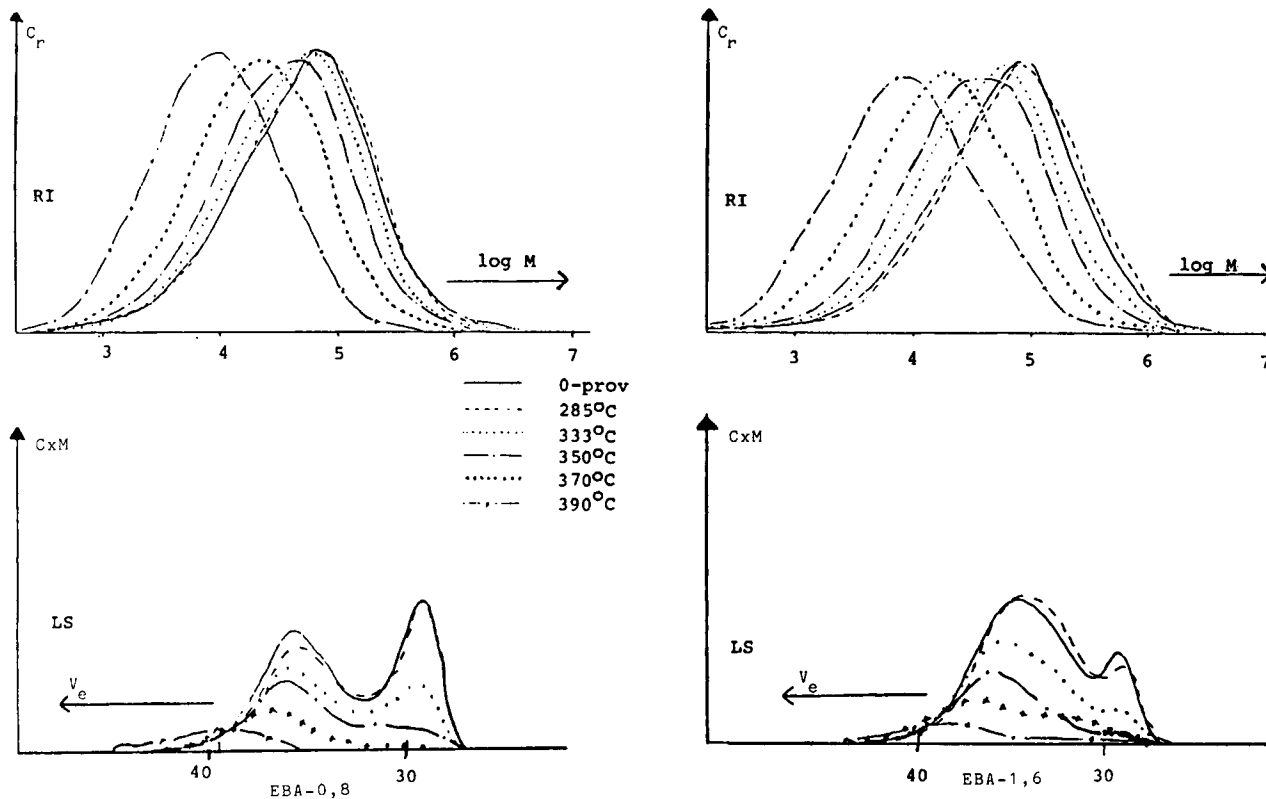


Figure 10 SEC chromatograms obtained with RI and LS detectors for EBA-0,8 and EBA-1,6 degraded for 24 min at temperatures between 285 and 390°C.

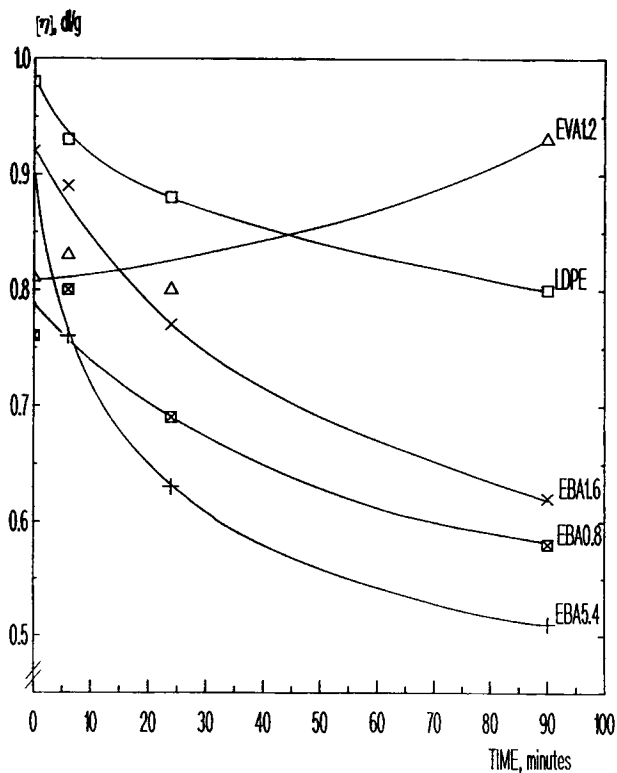
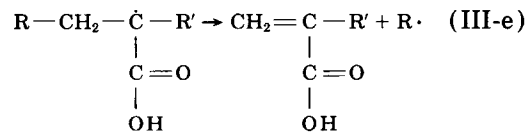
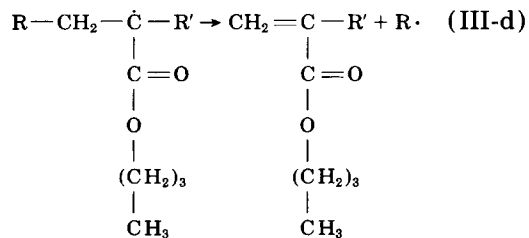


Figure 11 Changes in intrinsic viscosity for samples degraded at 333°C.

Furthermore, the macroradical formed should give a vinyl end group at β -cleavage. We did, however, not find any relation between BA content and formation of vinyl end groups.²

On the other hand, if the molecular weight reduction occurs before decarboxylation via β -cleavage of a tertiary radical adjacent to the BA group, the resulting vinyl group is conjugated with the carbonyl group. This vinyl group absorbs at 940 cm^{-1} .¹⁶ It is masked by the butyl ester absorption and is therefore not possible to detect in our investigation. We therefore suggest the following scheme for chain cleavage related to acrylate groups:



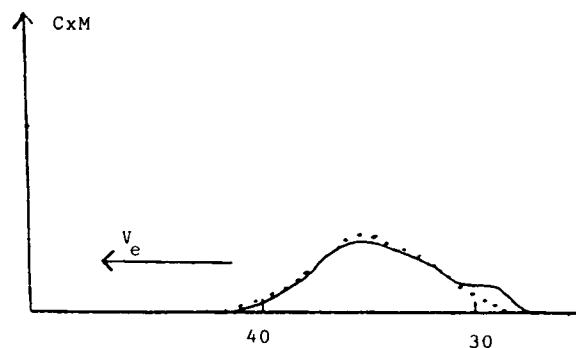


Figure 12 Light scattering chromatogram for EBA-1,6 degraded for 90 min at 333°C, before (—) and after (···) titration with KOH.

CONCLUSIONS

Both chain cleavage and molecular enlargement occur at thermal degradation of LDPE and EBA. At 285°C the molecular enlargement reactions dominate, but already at 333°C molecular diminishing reactions takes over. In LDPE, chain cleavages is due to β -scission. The macroradicals formed will terminate by disproportionation or combination. The tendency to disproportionation is increasing with temperature. Combination leads to long chain branching and molecular enlargement.

EBA shows a stronger tendency to chain cleavage than LDPE. This is due to the higher content of tertiary positions and resonance stabilization of radicals formed at the acrylate groups. The acrylate group will also form carboxylic groups and anhydrides. The latter are mainly intra molecular, and will thus not result in molecular enlargement.

EVA gave a pronounced molecular enlargement at all degradation temperatures. Above a fairly low VA content it also resulted in gel at all degradation levels tested. The strong tendency to molecular enlargement is assumed to be due to combination of allyl radicals obtained after deacetylation and the formation of internal double bounds. These macroradicals will combine, or less frequently, induce oligomerization to larger molecules.

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