Pyrolysis and Thermal Degradation of Ethylene−Carbon Monoxide Alternating Copolymers

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ABSTRACT: The thermal degradation behavior of E−CO alternating copolymers submitted to a variety of thermal conditions, both in a vacuum and in an inert atmosphere, has been investigated. The products obtained in the different thermal treatments were analyzed by GC/MS, and the structural changes occurring in the polymer chains were followed by FTIR and UV−vis. The influence of initial degradation reactions on polymer morphology was investigated with DSC, and it was found that thermally induced polymer degradation initiates in the amorphous parts of the samples. The initial reactions involve intramolecular cyclizations which produce cyclopentenone, furanic and oxydrylated structures in the chains, and intermolecular condensations causing cross-linking of polymer chains. Water is the only volatile product formed in this step. When chain scissions start developing, monomers and low molecular weight ketones are obtained as decomposition products. At higher temperatures the degradation embraces the whole polymer and proceeds with a competition of chain scissions, cyclizations, and cross-linking reactions involving macroradicals. The numerous fragments obtained from complete polymer degradation reflect the large structural modifications of the polymer chains.

Introduction

Ethylene−carbon monoxide (E−CO) alternating copolymers are thermoplastic materials with high crystallinity degree, high melting points, and good mechanical properties.[1−3] They are produced at low temperatures and pressures by slurry polymerization of carbon monoxide and ethylene, with Pd-based catalysts.[4,5]

The E−CO alternating copolymers have relatively poor thermal stability, and at the temperatures required for processing in the melted state they already undergo extensive chain degradation making them not melt processable. On the other hand, their insolubility in common organic solvents makes them practically unprocessable in solution. Therefore, successful industrial applications for E−CO copolymers could not be developed, until now.

The thermal degradation of such materials has already been investigated. Conti and Sommazzi[6] discussed the FTIR changes of E−CO copolymers and ethylene−propylene−CO terpolymers heated at temperatures near the melting point. Chien reported on the pyrolysis of the E−CO alternating copolymer at 500 °C, with identification of the products formed following chain fragmentation.[7] We have described in a previous paper the reactions taking place at relatively low temperatures that are responsible for the production of cyclic and cross-linked structures in thermally degraded E−CO samples.[8] In this work the thermal degradation behavior of E−CO alternating copolymers has been further investigated by submitting the polymer samples to a variety of thermal treatments, both in a vacuum and in an inert atmosphere. From analysis of the products obtained with polymer degradation and of the structural changes occurring in the polymer chains, with particular enphasis on the initial polymer decomposition reactions, mechanistic informations on the degradation process have been obtained.

Experimental Section

Materials. Three different E−CO alternating copolymer samples, kindly supplied by Istituto Donegani, Novara, Italy, were investigated. The samples were sinthesized with Pd-based catalysts, according to Shell patents.[9,10] Their characteristics are reported in Table 1.

Thermal Characterization. Thermogravimetric measurements were performed with a DuPont 951 horizontal balance under 60 cm^3/ min nitrogen flow. Differential scanning calorimetry (DSC) was carried out under nitrogen flow (60 cm^3/min) with a DuPont 910 Cell Base Module driven by a TA 2100 control unit.

Degradation Experiments. A Pyroprobe 1000 (CDS Instruments, USA) interfaced with a Hewlett-Packard GC-MS system (HP 5890 + HP 5970) was used for pyrolysis of polymer samples. Data acquisition was performed with CHEM-PC software (Hewlett-Packard) on a Vectra QS/165 PC. Pyrolysis conditions were as follows: T = 550 °C; heating rate 5 °C/ms; interface temperature 250 °C; pyrolysis time: 20 s.

Gas chromatographic separations were performed with the following temperature program: T = 30 °C for 5 min, ramp 20 °C/min to 250 °C; iso 250 °C for 5 min; injector temperature 250 °C.

Two different chromatographic columns were employed during the investigation: HP1, 0.2 mm, 12 m length, methylsilicone coated, 0.33 μm thickness; HP5, 0,25 mm. 30 m length, methylsilicone coated. 0.25 μm thickness.

Thermal volatilization analysis (TVA) under high vacuum were run in an all-glass system equipped with Pirani pressure gauges for monitoring the gaseous products formed during the thermal treatments.

Spectroscopic Analysis. FTIR spectra were collected on a 1710 Perkin-Elmer instrument, under control and data acquisition of Spectra-Calc (USA) software, with 4 cm^{-1} resolution. Polymer samples were measured in form of KBr pellets. Soluble products were in form of films cast from chloroform.

UV−vis spectra were determined with a Lambda 15 Perkin-Elmer system in hexafluoro-2-propanol solutions, 1 cm path length.

Results and Discussion

In our previous paper,[8] it has been shown that water formation is an important process in the course of E−CO thermal degradation. In order to detect the beginning

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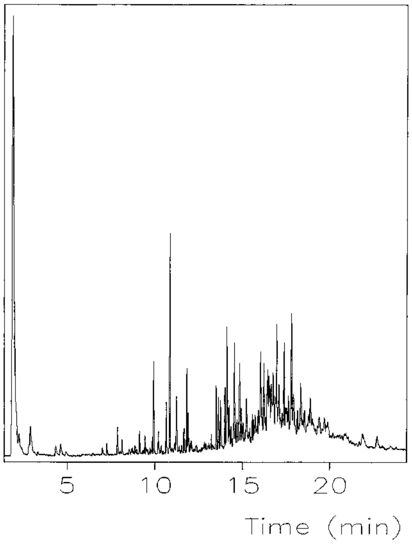


Figure 1. GC of products obtained from pyrolysis at 550 °C of E−CO copolymer S2, following the thermal treatments indicated in the text.

Table 1. Characteristics of Investigated E−CO Alternating Copolymers

sample	molecular wt apparent values from SEC M_n	M_w	[η] in *m*-cresol at 100 °C (cm^3/g)	crystallinity deg (%)	melting temp (°C)
S2	10200	32300	41	77	254
S4	not determined		250	44	255
S5	23000	54000	68	49	255

of water molecules production from dehydration of the copolymers structure, systematic step-pyrolysis experiments were performed on copolymer S2, starting at 200 °C.

The polymer sample was introduced in the pyrolysis unit and heated for 20 s at the following different temperatures, 200, 230, 250, 350, 400 and 550 °C, without removal from the instrument. The pyrolysis GC interface was initially set at 200 °C, and subsequently brought to 250 °C. After each 20 s thermal pulse, the GC/MS system was operated with the complete column heating program and the chromatogram of the eventually evolved species was collected.

From the treatment at 200 °C water was the only product obtained. No products were formed in the treatments at 230 and 250 °C, and it could be therefore concluded that the water evolved by heating at 200 °C was physically adsorbed and not originated from reactions within the polymer. In the succeeding treatments at 350 and 400 °C water was again the only product, coming this time from thermally induced dehydration reactions in the copolymer chains. The temperatures at which the formation of water molecules was revealed are higher than those reported in our previous work, where the conditions of sample treating were quite different. In the latter case, in fact, thermal treatments were carried out for 100 h, and degradation products accumulated.[8]

At the end of the successive thermal treatments, the copolymer sample was pyrolyzed at 550 °C, and the degradation products separated in the GC/MS. The pyrogram obtained is shown in Figure 1.

The same copolymer was also pyrolyzed directly at 550 °C, without any previous thermal treatment, and the decomposition products analyzed. The results obtained from the two pyrolyses at 550 °C were very similar, and may be compared in Figure 2, where the chromatograms of the low molecular weight region, up to 13 min retention time, are reported for the two cases. The peaks were reasonably separated and most of them could be identified through their mass fragmentation patterns, by comparison with the spectra in the spectrometer library. The structures of the identified compounds are reported in Table 2. In addition to CO, ethylene and water, a number of linear ketones with methyl, ethyl, and vinyl terminal groups were found, most of them in agreement with the results reported by Chien.[7] The methyl ester of 4-oxo-pentanoic acid (peak 15) has not been previously reported and is the fragment deriving from the CH_3−O−CO− end groups which are present in the E−CO copolymers.[11] Other identified compounds were five- and six-membered cyclic ketones, substituted furanes, bicyclic molecules, and aromatic hydrocarbons, with structures comparable to those already described in our previous work [8]

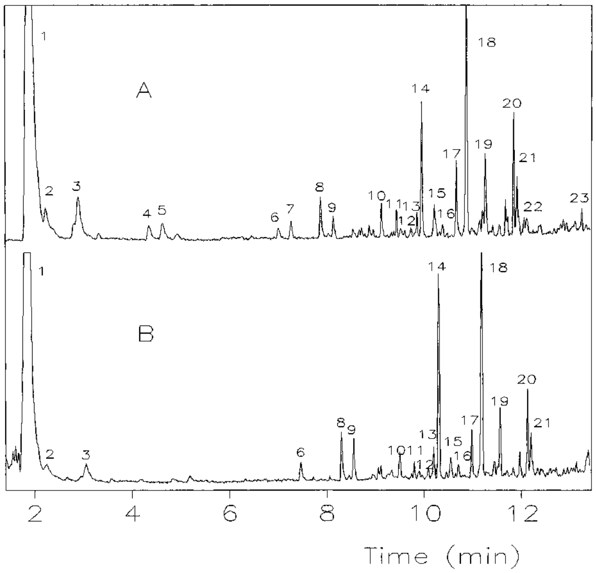


Figure 2. Comparison of products obtained from pyrolysis at 550 °C of sample S2 with previous thermal treatments (A) and without those treatments (B). Peak numbers refer to compounds listed in Table 2.

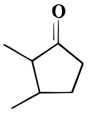
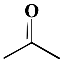
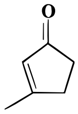
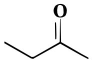
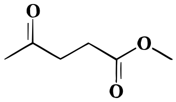
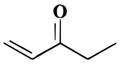
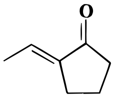
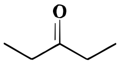
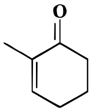
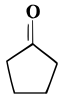
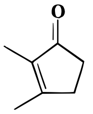
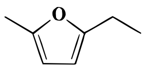
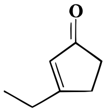
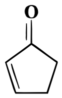
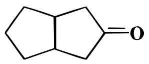
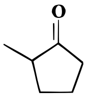
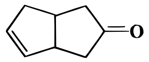
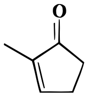
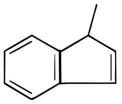
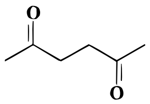
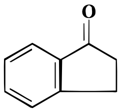
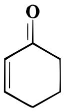
The principal difference between the products obtained from preheated samples and from an untreated polymer is the larger number of linear fragments with different end groups in the former case, together with the presence of higher molecular weight aromatic containing structures.

All the pyrolysis results support the mechanism of polymer degradation occurring not only through chain scissions and fragmentation but also with extensive development of intramolecular cyclization reactions, which take place with water production and give rise to the formation of the cyclopentenone, furanic, and aromatic structures.[8]

The copolymer samples were thermally degraded to high temperatures (450−500 °C) with a programmed temperature increase of 10 °C min. Degradations were carried out both under nitrogen in a thermobalance and in a thermal volatilization apparatus[12] under high vacuum (TVA) up to the end of production of decomposition compounds. This was appraised by the residues reaching constant weight in the thermogravimetric experiments and by the end of evolution of gaseous products in the TVA runs.

Polymer weight losses under nitrogen started at $T \geq 300$ °C, with maximum rates at $T \approx 400$ °C. Charlike polymer residues were on the order of 30% of the initial

Table 2. Products Obtained in the Pyrolysis at 550 °C of E−CO Copolymer Where Retention Times Refer to Chromatogram A of Figure 2

peak no.	retention time (min)	mol wt	mol structure	peak no.	retention time (min)	mol wt	mol structure
1	1.9	18−28	ethylene−CO water	13	9.8	112	
2	2.2	58		14	9.9	96	
3	2.9	72		15	10.2	130	
4	4.3	84		16	10.3	110	
5	4.6	86		17	10.6	110	
6	7.0	84		18	10.8	110	
7	7.3	110		19	11.22	110	
8	7.9	82		20	11.8	124	
9	8.1	98		21	11.9	122	
10	9.1	96		22	12.01	130	
11	9.4	114		23	13.2	132	
12	9.5	96					

sample weight in nitrogen, and ~10% in vacuo. When the polymer chains are decomposed at low pressure, chain fragments and small molecules produced are immediately vaporized and removed from the degradation oven, reducing their possibilities of reacting with the polymeric substrate for formation of cross-linked, nonvolatile structures.

In the case of vacuum degradation, chain fragments and oligomers may distill at high temperatures from the sample cell of the furnace and, as soon as they leave the heated zone of the vacuum line, condense on the glass walls. This high boiling fraction (HBF) of E−CO sample S2 was quantitatively collected by solvent dissolution, dried, and determined to be 40% by weight of the initial copolymer. The gaseous products volatile at room temperature amounted to 50% of the initial sample weight and were collected by condensation in liquid-nitrogen-cooled traps. From there they could be extracted and analyzed by injection in the GC/MS.

The chromatogram of the volatile products formed in the degradation under vacuum of sample S2 is shown in Figure 3. Numbers on the peaks refer to the compounds listed in Table 2. It is seen, also from these experiments, that the chain fragmentation produces, in addition to acetone and longer linear ketones, water and a mixture of saturated and unsaturated cyclic structures. The high boiling fractions were analyzed by FTIR, and the spectrum of the fraction obtained from sample S2 is compared with that of the starting copolymer in Figure 4. The principal spectral differences are as follows: a wide band is observed with a maximum at 3385 cm^{-1}, indicating the presence of −OH groups; a new absorption is observed at 3014 cm^{-1}, due to C−H stretchings of unsaturated structures; the

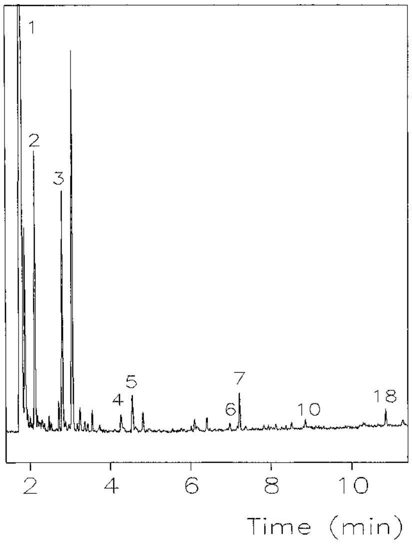


Figure 3. Chromatogram of volatile products obtained from thermal degradation of sample S2. Peak numbers refer to compounds in Table 2.

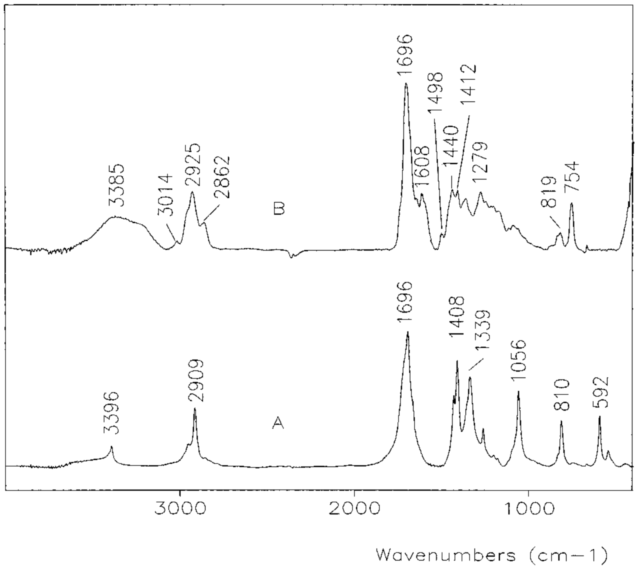


Figure 4. FTIR spectra of S2 copolymer (A) and of high boiling fractions (B) obtained from its thermal degradation under vacuum.

Table 3. Degradation Products Formed in the Isothermal Treatments of the S2 Sample

temp (°C)	time (min)	residue (%)	HBF (%)	gaseous products (%)
227	60	98		2
248	120	84		16
262	60	79	9	12
346	45	35	38	27

carbonyl peak is broadened and shifted at 1704 cm^{-1} from the 1692 cm^{-1} of the original copolymers; new absorptions appear in the region 1640−1600 cm^{-1}, indicating the formation of double bonds; the region 1500−1000 cm^{-1} becomes complex and less defined, with overlapping of multiple contributions while the intensity of the peak at 1408 cm^{-1}, typical of deformation of $-CH_2$ groups adjacent to carbonyl units,[13] is decreased; the absorbances at 1500, 819, and 754 cm^{-1} may be attributed to aromatic structures, likely of the same type as those detected in the pyrograms.

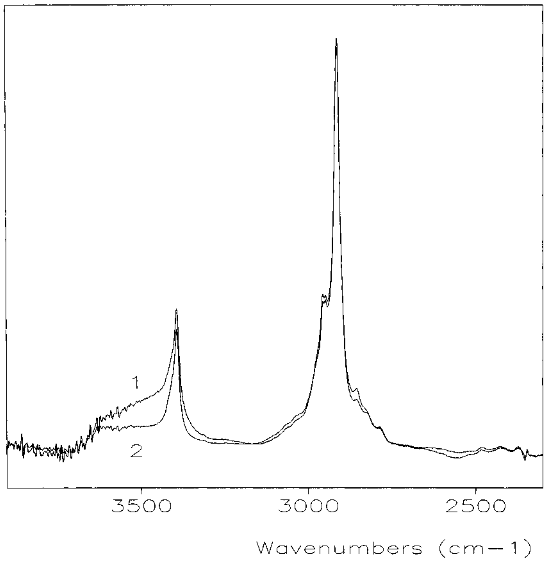


Figure 5. FTIR spectral changes of S2 E−CO sample before (1) and after (2) treatment at 180 °C for 240 min.

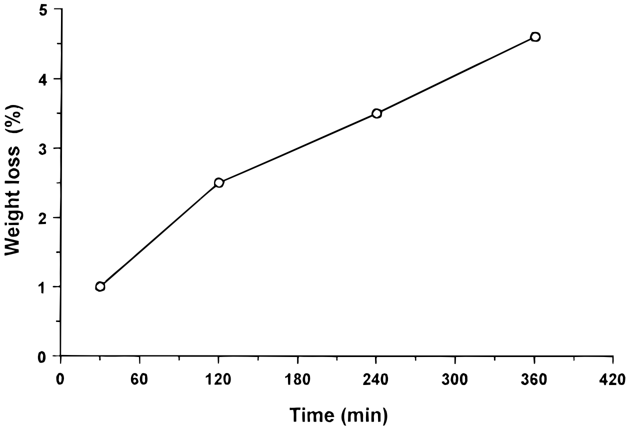


Figure 6. Amount of volatiles produced in the thermal treatments under vacuum at 230 °C of sample S5.

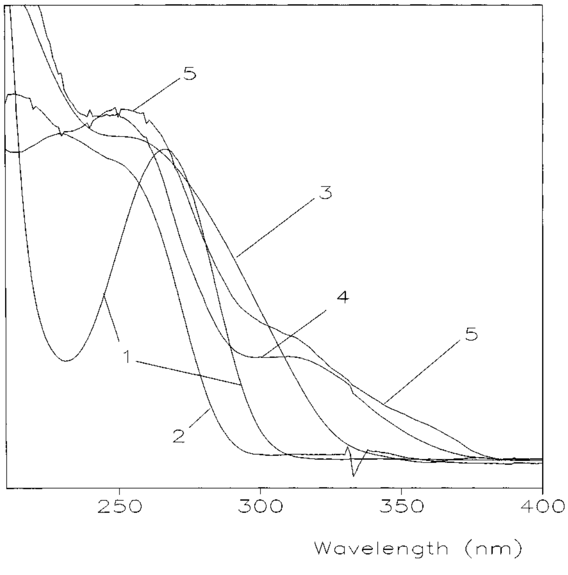


Figure 7. UV spectra of soluble fractions obtained after thermal treatments under vacuum of copolymer S5 at 230 °C for different times: (1) initial sample; (2) 30 min; (3) 120 min; (4) 240 min; (5) 360 min.

All the above spectral features completely support the hypothesis that the pyrolysis and, in general, the high temperature degradation of E−CO copolymers occurs with the chain fragmentation being in competition with other intramolecular and intermolecular reactions, leading to different cyclic and aromatic structures and cross-linked material.

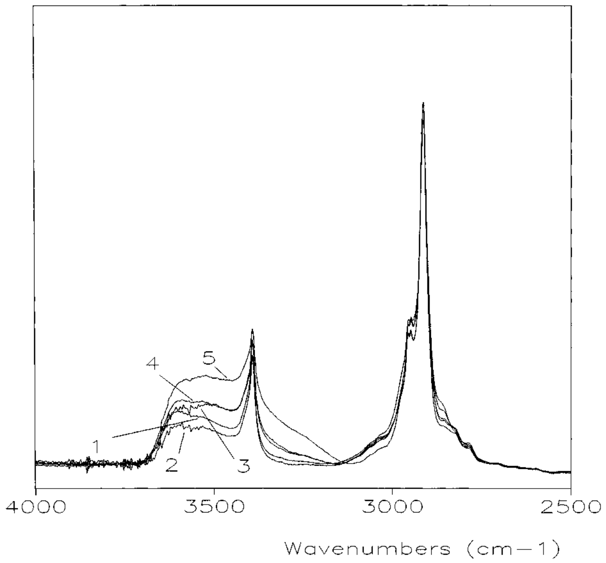


Figure 8. FTIR spectra in the region 4000−3000 cm^{-1} of copolymer S5 submitted to thermal treatments at 230 °C, under vacuum, for different times: (1) initial sample; (2) 30 min; (3) 120 min; (4) 240 min; (5) 360 min.

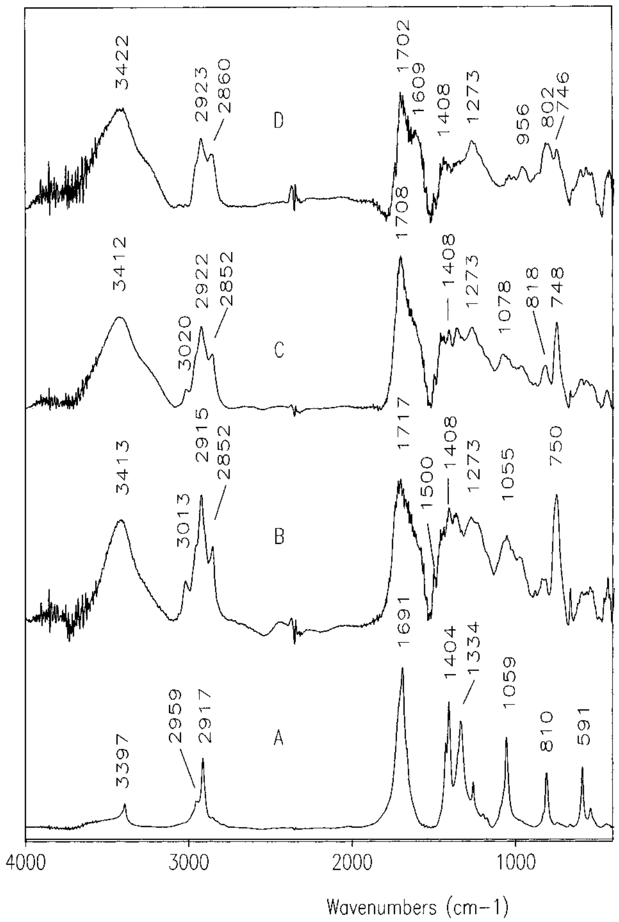


Figure 9. FTIR spectra of S2 samples treated under vacuum at different temperatures: (A) initial polymer; (B) polymer at 248 °C; (C) polymer at 262 °C; (D) polymer at 346 °C.

In order to investigate the initial steps of polymer decomposition, isothermal treatments at relatively low temperatures were performed, under high vacuum or in nitrogen flow.

The amount of adsorbed water was determined, for sample S2, by heating the polymer in a thermobalance at 150 and 180 °C, until it reached constant weight. Measured weight loss was 1%, and the only IR spectral change was the −OH stretching decrease, shown in Figure 5.

A sample of copolymer S5 was submitted to sequential 30 min treatments in the TVA system, at different temperatures ≤230 °C. After each treatment the polymer was removed for recording weight changes, IR and UV spectra, and DSC traces.

The weight decrease for loss of adsorbed water was 1%, as in polymer S2. The hygroscopic nature[8] of the E−CO copolymers was confirmed by the finding that when left in the atmosphere the samples rapidly readsorbed the water lost.

FTIR spectra of the aged samples did not show any new band, but only slight intensity changes occurring

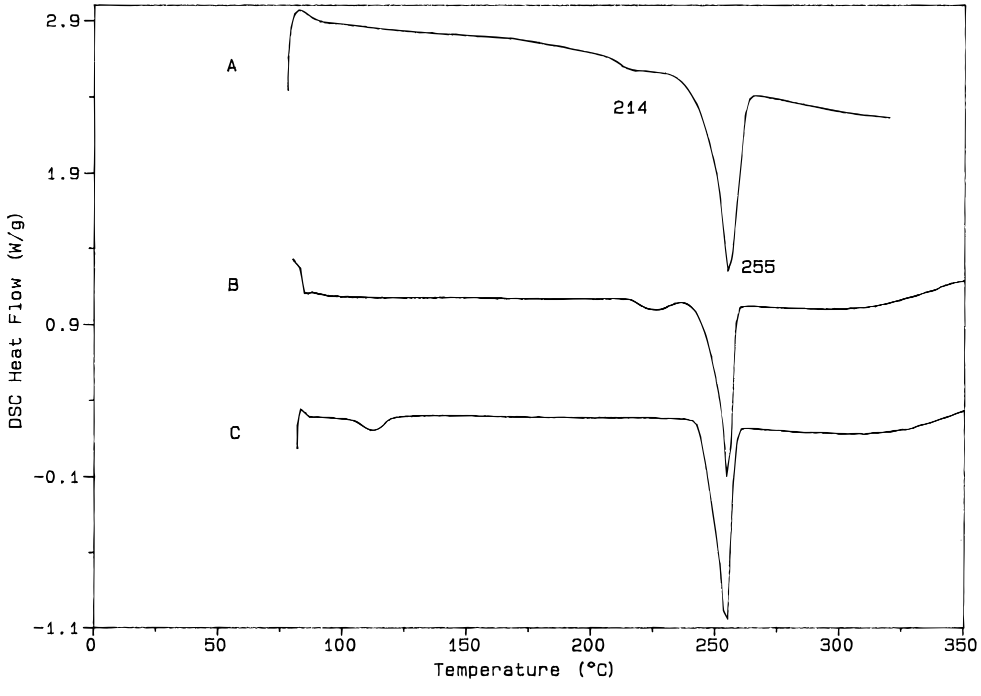


Figure 10. DSC curves of sample S5 for the initial sample (A) and samples after 30 min annealing at 200 °C (B) and at 230 °C (C).

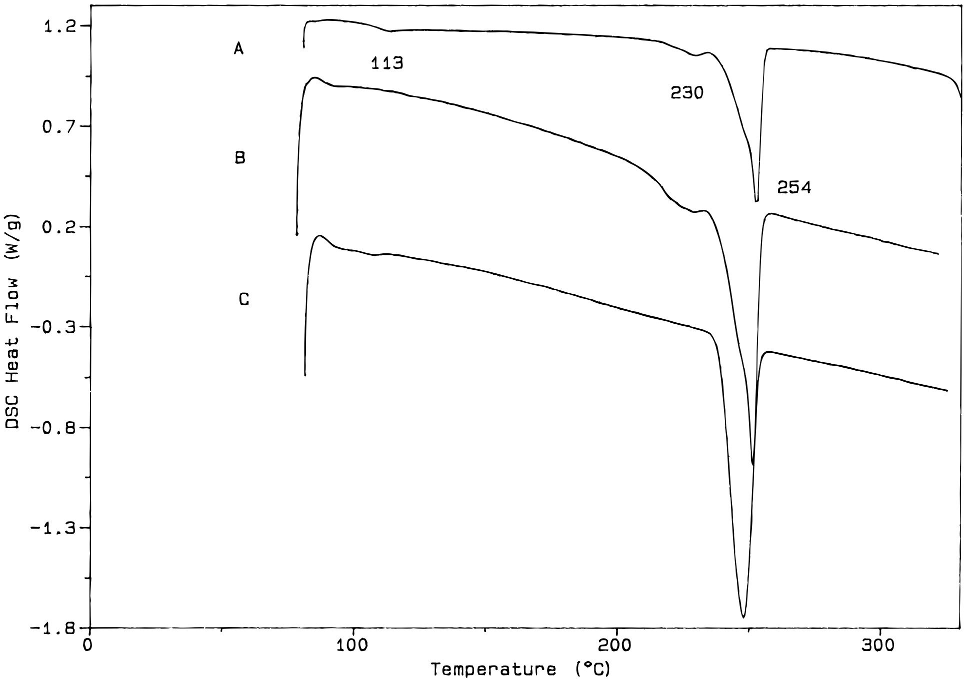


Figure 11. DSC curves of sample S2, before (A) and after annealing at 180 °C for 240 min (B) and at 230 °C for 360 min (C).

after the heating at 230 °C, with decreasing and broadening of the CO absorption at 1692 cm^{-1} and increasing intensities of the peaks at 1057, 812, 592 and 543 cm^{-1}, due to changes in morphology and chain packing,[14] as will be discussed later.

The polymer remained soluble in hexafluoro-2-propanol after all treatments, and no color development appeared. In the UV spectra of the copolymer heated at 230 °C the absorption between 210 and 250 nm increased.

The thermal treatments at 230 °C were extended up to 360 min, and larger changes were now detected in the polymer, with yellowing. In the experimental time interval the amount of volatile products increased at almost constant rate (Figure 6). At treatment times larger than 30 min, the polymer became partially insoluble, with the gel fraction increasing with time. The UV spectra of soluble fractions, Figure 7, reveal structural polymer modifications, with broadening of the peak in the region 210−250 nm and development of new absorptions between 300 and 380 nm. The latter modification may be reasonably ascribed to newly formed chromophores responsible for polymer discoloration.

Structural changes on the whole aged samples were followed by FTIR. The principal spectral modifications are shown in Figure 8, and concern the region of hydroxyl absorption, where it is seen that, after initial decrease of intensity due to removal of adsorbed water, absorbance increase with time, as a result of formation of new oxydrylated groups. This behavior is in agreement with that reported by Conti and Sommazzi.[6] As to the other parts of the spectra, the overall features of the regular E−CO copolymers are maintained, and only a slight broadening of the carbonyl peak, with slowly increasing absorbances around 1600 cm^{-1}, indicates double bond formation.

In all cases from pyrolysis at 550 °C of the aged samples, the same decomposition products as from the initial polymer were obtained.

Other sequential isothermal treatments under vacuum were performed on S2 sample, at different temperatures in the range 220−350 °C, for the time necessary to reach the end of evolution of gaseous products, as monitored by the pressure gauges in the line. Weights of polymer residues, and of high boiling fractions when present, were measured, and the results for the different treatments are summarized in Table 3.

The treatment at 227 °C produced a low quantity of gaseous products only, and the polymer residue turned a faint yellow. The FTIR spectrum of the residue was practically equal to that of the starting copolymer, with only a slight broadening of the carbonyl absorption. The gaseous products detected with the GC/MS were, in addition to water, CO, ethylene, and 2-butanone. The presence of these compounds clearly indicates that chain scissions had already occurred in the sample.

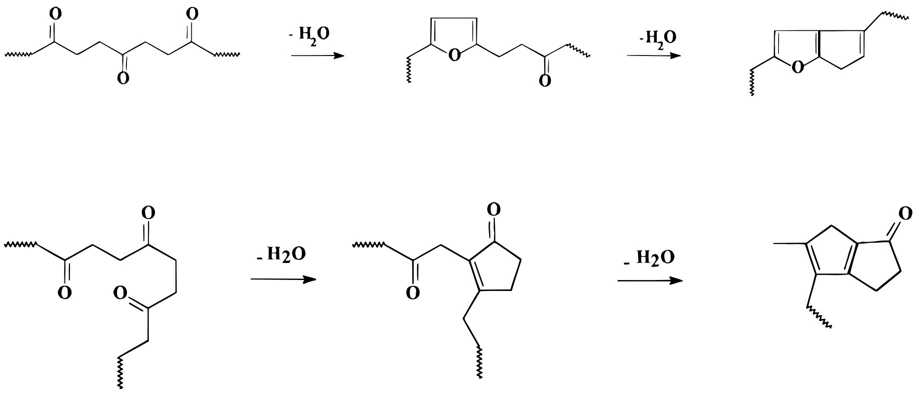
The treatment at 248 °C produced a larger amount of the same gaseous products and still no appearance of high molecular weight compounds condensed at the oven's exit. The polymer residue, however, showed large changes in the FTIR spectrum, as shown in Figure 9. A broad peak around 3420 cm^{-1}, due to −OH stretching, and new absorptions at 3020 and between 1640 and 1600 cm^{-1}, due to unsaturations, appear. The regular structure of the alternating E−CO copolymers is lost, as may be seen from the changes of the carbonyl peak, which becomes broad with the maximum shifted at 1708 cm^{-1}, and from the poorly defined spectrum shape in the fingerprint region between 1400 and 900 cm^{-1}.

Signs of aromatization also appear in the residue, as indicated by the new absorption at 1500 cm^{-1} and by the peak at 750 cm^{-1} attributed to out-of-plane deformations of hydrogen atoms in di- and trisubstituted aromatic rings.[15]

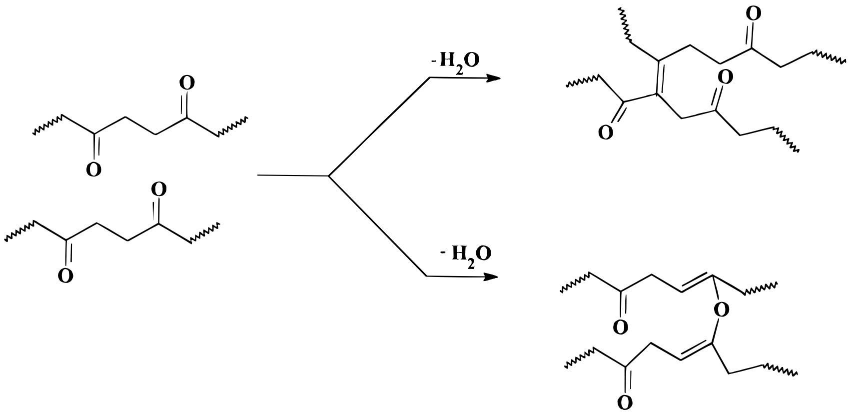
The thermal treatments carried out at 262 and 346 °C, over the copolymer melting points, produced a larger amount of volatile products and the appearance of high boiling fractions.

Acetone was now detected in the volatile compounds, in addition to the other low molecular weight molecules already observed. FTIR spectra of the polymer residues (Figure 9) showed the same type of modifications previously discussed, though to a larger extent. Building-up of aromatic structures is manifested by the

Scheme 1



Scheme 2

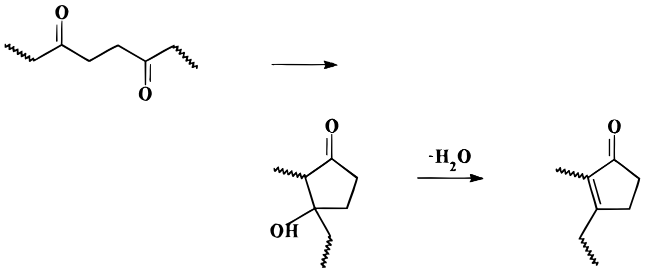


increasing with temperature of absorption at 1600 cm^{-1}. The growth of absorptions between 950 and 850 cm^{-1} also reveals that highly substituted aromatic structures are formed during the degradation.

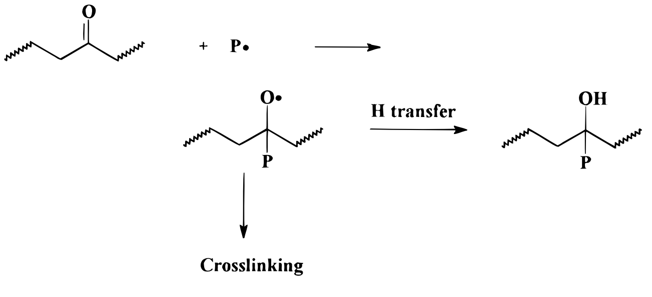
At 346 °C the formation of four-substituted aromatic rings appears favored, as shown by the higher absorption in the 900−820 cm^{-1} range, in comparison with the peak at 750 cm^{-1} connected to the less substituted structures.

The spectra of high boiling fractions were very similar to those obtained from the degradations at high temperatures (see Figure 4). They contain all the structural features found in the residues as above discussed.

Scheme 3



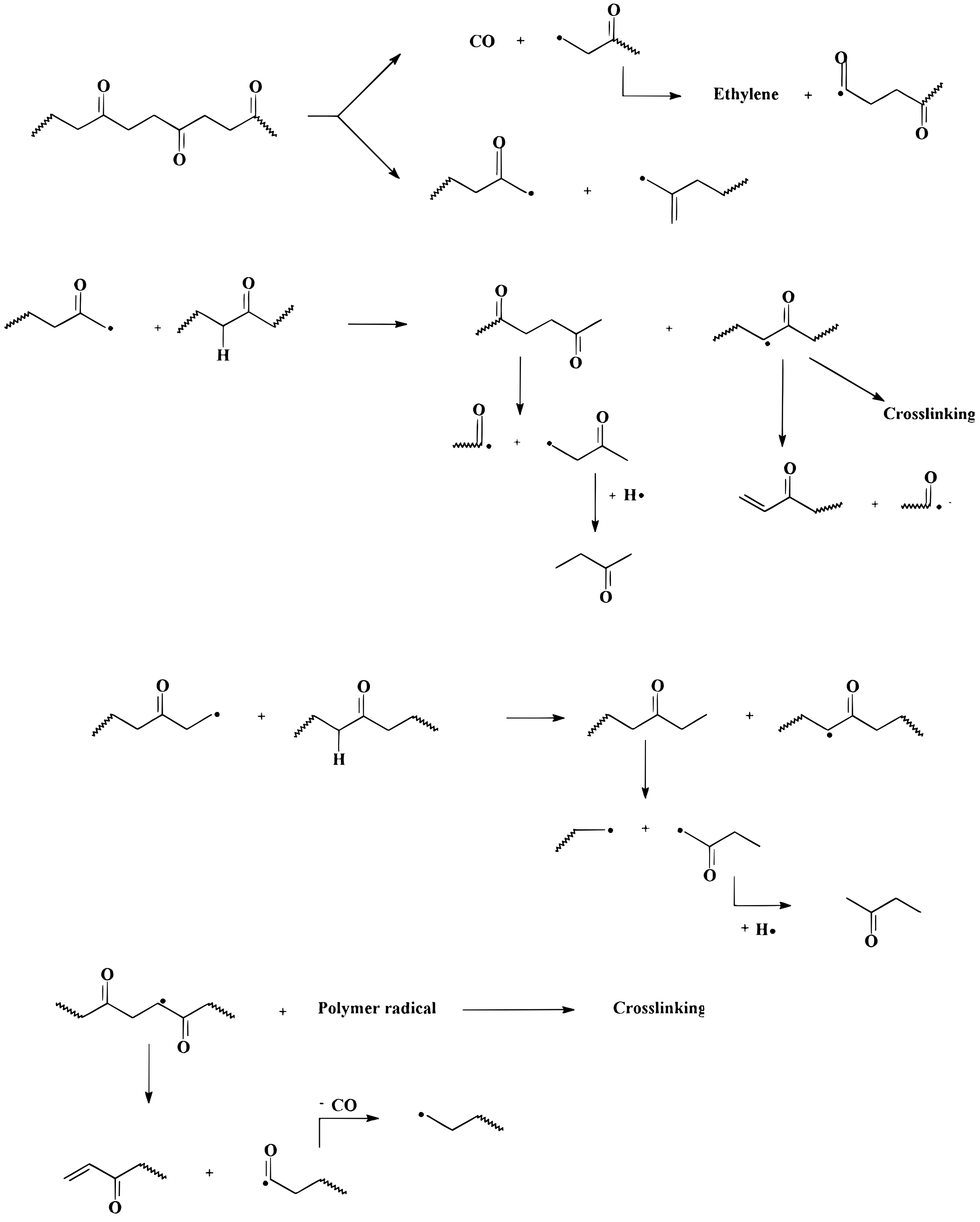
Scheme 4



Although structural chain modifications already take place at lower temperatures, particularly when thermal aging is being performed for a long time,[8] the above results demonstrate that the chain decomposition initiates at ca. 230 °C. At such a temperature, the crystalline structure of the copolymers is not affected by the degradation reactions, and the DSC traces of the E−CO copolymers after different thermal treatments show only thermally induced morphological changes. In Figure 10 are reported the DSC curves of initial sample S5 and the DSC curves after 30 min treatments at 200 and 230 °C. The annealing at 200 °C causes a shift to 224 °C of the 214 °C endothemic peak, due to the melting of defective crystalline fractions. The peak subsequently disappears with heating at higher temperature, merging in the main melting endotherm. Crystallinity degrees, calculated from the melting peak areas of DSC curves, increase to ca. 64% with annealings at $T \leq 200$ °C and to ca. 75% after heating at 230 °C. The indication that crystalline fractions do not participate to the solid state degradation process in the E−CO copolymers is further corroborated by the DSC curves of Figure 11 where comparison is made between sample S2 before and after annealing at 180 and 230 °C for quite long times. In the initial sample the melting endotherm at 113 °C may be due to the presence of an α crystalline phase, which by annealing transforms into the more common β phase.[14,16,17] The prefusion peak at 228 °C disappeared after heating at 230 °C, and the main melting peak remained unchanged. In the conditions of the latter treatment the polymer already showed coloration, cross-linking, and the appearance of new structural groups.

As copolymer molecules in the ordered parts of the material are scarcely affected by the thermal treatments at temperatures below the melting points, where however degradation already takes place, it is suggested

Scheme 5



that the process begins in the amorphous fractions of the E−CO copolymers. Degradation effects that appear first are water evolution and color development, which may be accounted for by intramolecular condensation reactions, like those proposed in Scheme 1.

Such reactions are more likely to occur in the flexible amorphous sections and in the dangling chain ends of the copolymer molecules not engaged in crystallites. The mobility of the chains in the amorphous phase influences such reactions, and we may expect chain ends to be the most reactive parts of the polymers, as they have the highest mobility. If the majority of chain ends are in the amorphous part of the polymers, a molecular weight effect can be envisaged in the initiation of low temperature thermal degradation. Some evidence of such molecular weight dependence may be found in the results previously reported (ref 8, Table 2) when, for the same heating, discoloration of sample S4, having higher molecular weights, was much lower that that of sample S2.

With more prolonged heatings, cross-linked structures build up as a result of intermolecular condensation reactions, as shown in Scheme 2.

In the early stages of degradation relevant amounts of hydroxyl groups are formed, and at the lower temperatures this may happen through intramolecular reactions like in Scheme 3.

When at higher temperatures chain scissions take place, −OH groups are also formed as a result of polymer radical addition to carbonyl groups, followed by hydrogen abstraction (Scheme 4).

The chain scissions start to develop at a temperature of ca. 230 °C, and ethylene, CO, and low molecular weight ketones are formed. At such relatively low temperatures the breaking of polymer chains produces macroradicals which may deactivate through intermolecular transfers, radical coupling and β- scisssions, according to the reactions shown in Scheme 5.

The result of such a reaction sequence is production of the volatile molecules, accumulation of conjugated unsaturations and formation of cross-linked structures.

In conclusion, the thermally induced initial degradation reactions in E−CO alternating copolymers develop in the amorphous parts of the samples, and consist of intramolecular cyclizations which produce cyclopentenone, furanic, and oxydrylated structures in the chains, and of intermolecular condensation reactions causing polymer cross-linking. At the beginning, water is the only product formed. When chain scissions start developing, monomers and low molecular weight ketones are obtained as decomposition products. At higher temperatures, the degradation embraces the whole polymer and proceeds with a competition of chain scissions, cyclizations, and cross-linking reactions involving macroradicals. Under such conditions, the numerous fragments obtained from complete polymer degradation reflect the large structural modifications of the polymer chains.

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