

## Oxidative Degradation of Poly(ethyl Acrylate)\*

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### Synopsis

The oxidative degradation of poly(ethyl acrylate) was investigated by infrared spectrophotometric techniques, and the volatile degradation products were determined by vapor-phase chromatographic analysis. During the course of degradation, no change in the spectrum of the polymer, indicating the formation of other moieties, was detected. There was only a generally uniform decrease of all the existing absorption bands with the exception of the 5.75–5.85  $\mu$  ester-ketone carbonyl region. This decrease of absorption proceeded appreciably slower than the rate previously reported for the degradation of poly(ethylacrylate). The reported formation of carboxylic acid groups detected in the spectrum of degraded polymer was not substantiated in this study. In contrast to degraded poly(ethyl acrylate), the low molecular weight, volatile polymer formed on oxidation was highly oxidized. In addition, the highly volatile degradation products were identified as carbon dioxide, water, ethyl acetate, and ethyl alcohol. No monomer, ethyl acrylate, could be detected among the volatile products. A methanistic pathway was postulated based on these results. Initially, there is attack of molecular oxygen at the tertiary carbon atoms of the polymer chain to form hydroperoxide groups. Subsequent decomposition of the hydroperoxides results in random chain scission eventually giving low molecular weight polymeric units. Further oxidation of the low polymer units leads to the observed product formation.

### INTRODUCTION

The number of studies concerned with the thermal degradation of polyacrylates has been relatively small. Madorsky and Straus<sup>1,2</sup> have investigated the thermal degradation of poly(methyl acrylate) at 292–399°C. *in vacuo*. Unlike poly(methyl methacrylate), which depolymerizes to monomer,<sup>3</sup> poly(methyl acrylate) degraded to a variety of relatively low molecular weight products. From a study of the rate of degradation as a function of temperature, an activation energy of 37 kcal. was determined for the initial degradation reaction.

Steele and Jacobs<sup>4</sup> examined the oxidative, pyrolytic degradation of poly(ethyl acrylate). These investigators employed viscometric techniques, rate studies of oxygen absorption, and titration methods to follow changes in the bulk of the polymer. Volatile degradation products were examined by mass spectrometric methods. It was reported that car-

\* Presented, in part, at the Battelle Institute Symposium on the Thermal Stability of Polymers, Columbus, Ohio, December 1963 and the Metropolitan Regional Meeting, American Chemical Society, New York, January 1964.

boxylic acid groups were present in appreciable quantities after relatively short periods of exposure to air at 100°C. The authors postulated the initial oxidation step to be the attack of oxygen at the tertiary carbon atoms of the polymer chain,<sup>5-7</sup> with consequent hydroperoxide formation. Subsequent decomposition of the hydroperoxides resulted in chain scission. From a study of the rate of change of the intrinsic viscosity of the oxidized polymer, the activation energy for the chain scission process was calculated to be 28.6 kcal./mole.

As part of a continuing program concerned with the degradation of polymeric materials, it was of interest to investigate the oxidative degradation of acrylonitrile copolymerized with a variety of acrylic monomers. One such copolymer was prepared from a 9:1 weight ratio of ethyl acrylate to acrylonitrile. Examination of this sample at 200°C. in air by means of infrared spectrophotometric monitoring of functional group changes revealed a degradation process considerably different than that proposed for each pure polymer.<sup>4,8</sup> The actual observations were consistent with volatilization of the acrylate portion of the copolymer. As the time of exposure increased, an increase in the nitrile portion of the polymer was noted. However, during this process no significant degradation of the nitrile system was observed. More significant was the observation that no evidence for the formation of carboxylic acid species as proposed by Steele and Jacobs<sup>4</sup> could be obtained from the spectrum of the degraded polymer. Because of these differences with already reported data on the homopolymers, it was deemed necessary to re-examine the degradation of poly(ethyl acrylate).

On the basis of previous results in other systems,<sup>8-10</sup> it was expected that the necessary information regarding the degradation process could be obtained by monitoring the bulk phase of the polymer continuously by using infrared spectrophotometric techniques. In addition, it was of interest to determine the nature of the volatile degradation products by using vapor-phase chromatographic separation and identification techniques. This combination of methods was expected to yield sufficient information to ascertain the major aspects of the oxidative degradation process.

## EXPERIMENTAL

All oxidative degradation rate data were determined from spectra recorded with a Beckman IR-5A infrared spectrophotometer equipped with sodium chloride optics. High resolution spectral data were obtained by using a Beckman IR-9 grating spectrophotometer. Degradation product analyses were carried out, in part, by using an F and M Model 720 dual-column, programmed-temperature vapor-phase chromatograph.

For comparison with samples prepared in this laboratory, a sample of poly(ethyl acrylate) prepared by emulsion techniques, supplied by the Rohm and Haas Company, was examined under the same conditions as those employed for the synthetic material.

### Preparation of Poly(ethyl Acrylate) Films

A mixture of 30 ml. of freshly distilled ethyl acrylate and 45 ml. of benzene was heated to reflux under an atmosphere of dry nitrogen. Benzoyl peroxide (5 mg.) was added to the refluxing monomer solution. After 2 hr. at reflux, the crude reaction mixture was steam distilled to remove monomer. The resulting precipitated polymer mass was dried *in vacuo*. The polymer was redissolved in dry benzene or 1,2-dichloroethane immediately prior to film preparation. Circular films 38 mm. in diameter of approximately 4 mg. in weight, were prepared by evaporation of a small volume of polymer-benzene solution. Since films prepared in this fashion yielded excellent spectra, this technique was used throughout this investigation.

### Thermal Degradation Studies

**Intermittent Infrared Spectral Monitoring.** The films prepared as described in the previous section were heated in the low temperature region (72–160°C.) in the following manner. The coated salt plate, mounted in an asbestos holder, was placed in an oven; after specified time intervals, the plate was removed from the oven, desiccated until cool, and the spectrum determined. The process was repeated until a significant number of spectra were obtained on each sample to allow the correlation of functional group changes with time of heating. Typical data for the two major bands, the 3.35  $\mu$  carbon-hydrogen stretching frequency and the 5.75  $\mu$  ester carbonyl frequency, at 125 and 160°C. summarized in Tables I and II, respectively.

TABLE I  
Changes in the Major Infrared Bands with Time of Heating at  
125°C. Using the Intermittent Techniques

Time, hr.	Absorbance	
	3.35 $\mu$	5.75 $\mu$
0	0.137	0.93
48	0.137	0.91
72	0.125	0.92
413	0.122	0.79
1157	0.105	0.66

**Continuous Infrared Spectral Monitoring.** At elevated temperatures (160–240°C.), the degradation rate increased greatly, facilitating the use of a continuous monitoring technique. The heated cell utilized was a simplified variation of that described by Conley and Bieron.<sup>11</sup> The overall cell was designed for the beam path of the instrument. The temperature within the cell was controlled and indicated by the single thermocouple placed at one-half the radius of the sodium chloride disk. The absorbance data were collected by using the baseline method described by Wright.<sup>12</sup>

TABLE II  
Changes in the Major Infrared Bands with Time of Heating  
at 160°C. Using the Intermittent Technique

Time, hr.	Absorbance	
	3.35 $\mu$	5.75 $\mu$
0	0.125	0.865
26	0.125	0.865
141	0.110	0.760
165	0.110	0.760
237	0.100	0.730
477	0.080	0.560
573	0.070	0.500
1317	0.040	0.210

The values so obtained were converted to fit a per cent weight remaining scale in order to correct for any small changes in film thickness of the various samples undergoing oxidative degradation. The band absorbance at initial time for each run was taken as 100% of the sample weight remaining and the base line equal to zero. Again, the two bands monitored were the carbon-hydrogen stretching vibration at 3.35  $\mu$  and the 5.75  $\mu$  ester carbonyl vibration. Typical data obtained by this technique are summarized in Table III for oxidative degradation of poly(ethyl acrylate) at 220°C.

TABLE III  
Continuous Infrared Monitoring of the Oxidative  
Degradation of Poly(ethyl Acrylate) at 220°C.

Time, min.	Absorbance		Weight remaining, %	
	3.35 $\mu$	5.75 $\mu$	3.35 $\mu$	5.75 $\mu$
0	0.243	0.837	100	100
15	0.221	0.807	91	96
30	0.204	0.782	84	93
45	0.195	0.765	80	91
60	0.170	0.735	70	88
75	0.158	0.715	65	85
90	0.146	0.675	60	81
105	0.125	0.635	51	76
120	0.113	0.595	46	71
135	0.107	0.555	44	66

**Product Analysis Method.** A film of thickness approximately equal to those deposited on the sodium chloride disks was cast on an aluminum strip 36 in. in length and 2 in. wide. At regular intervals, the strip was dented to separate the layers when the strip was coiled. The coiled strip was placed in the pyrolysis chamber as shown in Figure 1. The heater used was the same unit utilized to heat the sodium chloride disks to temperature for

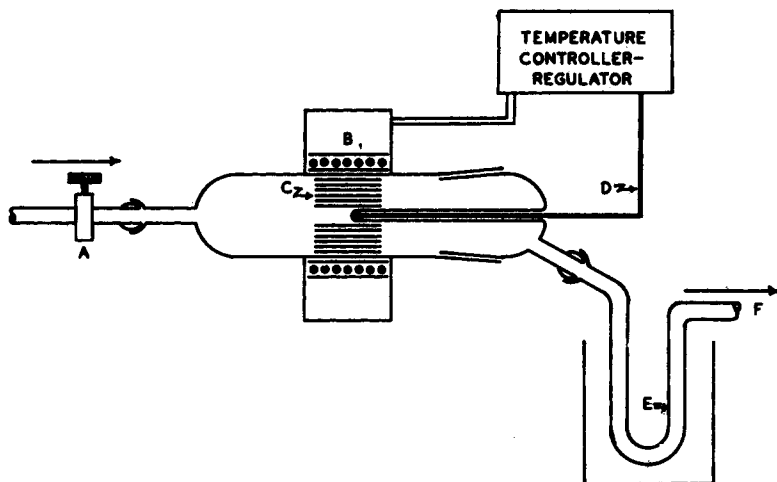


Fig. 1. Pyrolysis chamber used to collect volatile degradation products from the oxidation of poly(ethyl acrylate): (A) oxygen or air inlet valve; (B) movable heating unit; (C) coated aluminum coiled strip; (D) thermocouple; (E) U-tube trap for condensing organic volatile fragments; (F) exit gas stream to secondary collection system.

the continuous infrared monitoring of the film samples. The pyrolyses were carried out under the same conditions as employed in the spectral monitoring study. The pyrolysis products were collected by condensing the volatile components in a Dry Ice-acetone trap. The noncondensable component, carbon dioxide, was absorbed in a preweighted Ascarite-filled tube.

Examination of the liquid pyrolyzates was carried out by using vapor-phase chromatographic techniques in conjunction with infrared examination of the trapped products. All separations were effected by using a 6-ft. Ucon L-550X column with the following instrument conditions: helium flow rate, 60 ml./min.; detector block temperature, 342°C.; injection port temperature, 270°C.; detector current, 100 mg.; column temperature, 75°C.

## RESULTS AND DISCUSSION

The degradation of poly(ethyl acrylate) in air was examined by infrared monitoring of the changes occurring in the bulk phase at temperatures of 72, 125, and 160°C. Below 150°C., the reaction proceeded slowly, necessitating in these initial experiments extended exposure times. The spectrum of a typical poly(ethyl acrylate) film sample and the generalized structural formulation are indicated in Figure 2. At 72°C., no changes were detected in the spectrum after 47 hr. of exposure in air. Tables I and II indicate the slow changes occurring at 125 and 160°C. It was noted in these cases that all bands decreased in intensity at approximately the same rate and no new bands, even at the 160°C. temperature, could be detected.

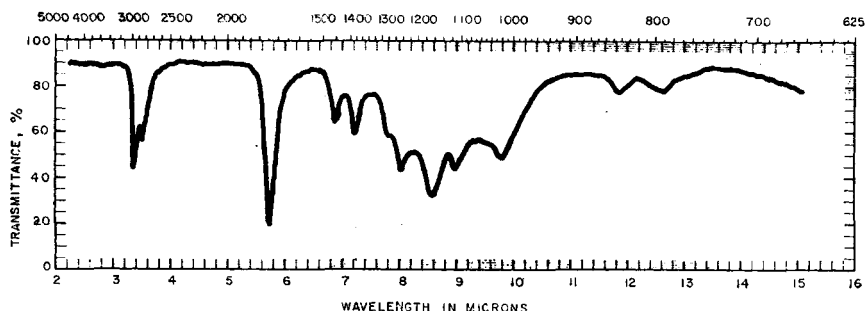


Fig. 2. Spectrum of poly(ethyl acrylate).

These data do not agree with the reported observations by Steele and Jacobs,<sup>4</sup> in which carboxylic acid species were detected after only 8 hr. at 100°C. In addition, these investigators report titration of these species with sodium methoxide. Since no evidence could be obtained to support acid formation in this temperature range, it was concluded that the titration data most probably result from the reaction of the hydroperoxide groups formed during the initial oxidation reaction with sodium methoxide.

Further substantiation of this conclusion was obtained in the elevated temperature range of 180–240°C. At these temperatures the reaction rate was sufficiently rapid so that continuous spectral monitoring techniques could be used at the reaction temperature. With this technique, it was possible to record a complete spectrum (2–16  $\mu$ ) on the spectrophotometer every 15 min. or a region of the spectrum of interest approximately every 3 min. Again, the presence of carboxylic acid functional groups could not be substantiated. The possibility still remained that the concentration of the acid species may never be high enough to allow their detection spectrophotometrically. Fortunately, in this particular system low concentrations (2–5%) are readily detectable by the method utilized. Since Steele and Jacobs<sup>4</sup> report as high as 30% acidic material, we can only conclude their interpretation as to the nature of these species to be erroneous.

As observed in the lower temperature region, all bands were decreasing at relatively the same rate, the only exception being the rate decrease of the carbonyl group absorption at 5.75  $\mu$ . At temperatures between 180 and 240°C., this absorption decreased more slowly than the disappearance of the aliphatic portion of the system as monitored at 3.35  $\mu$ . Since no other functional groups appeared, it was presumed that a new functional group closely related to the ester carbonyl was being produced as an intermediate stage in the oxidative degradation. A composite series of spectra indicating these changes is shown in Figure 3.

From the observed changes it was concluded that the most likely new carbonyl species which could be formed were ketonic functional groups resulting from chain scission on decomposition of the hydroperoxides present. In order to test this proposal, high resolution spectral examination of heated

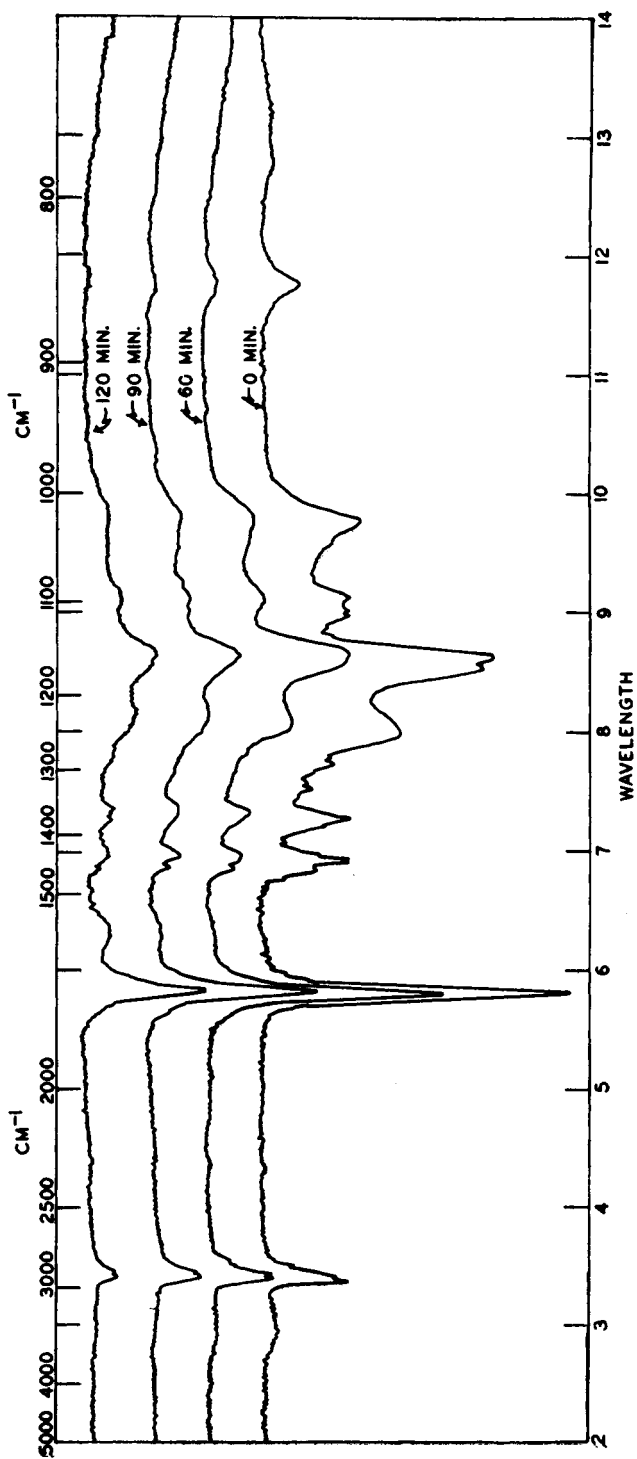


Fig. 3. Composite of spectra indicating the band changes observable on air oxidation at 200°C.

films was undertaken, since a shift to longer wavelength (lower wave number) should be expected if these groups are formed in significant amounts. Indeed a shift of the carbonyl absorption from  $1735\text{ cm.}^{-1}$  ( $5.75\ \mu$ ) to  $1725\text{ cm.}^{-1}$  ( $5.80\ \mu$ ) initially appearing as a small shoulder on the ester carbonyl band was observed. This observation gives strong support to the proposed formation of ketonic species. In addition, the spectra were scrutinized for acidic species and again no support for acid formation could be gained lending further credence to our original conclusion.

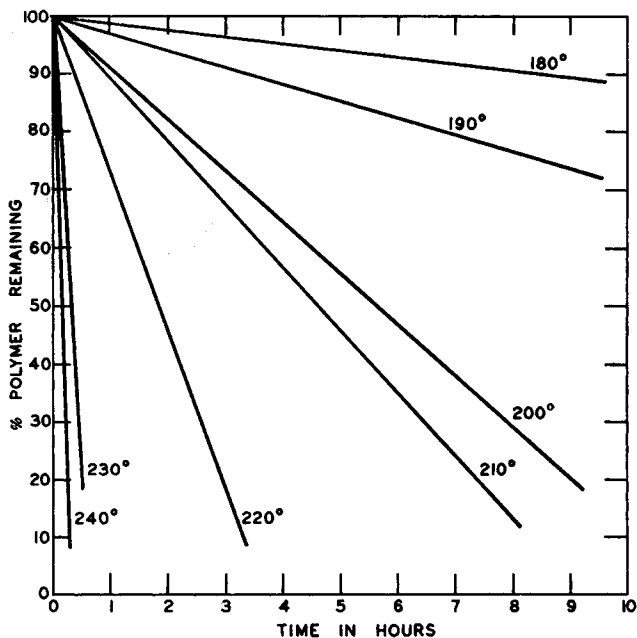


Fig. 4. Plots of the per cent polymer remaining as determined from the absorbance change at  $3.35\ \mu$  (carbon-hydrogen stretching vibration) vs. time.

Since the two most intense bands in the infrared spectrum at  $3.35\ \mu$ , carbon-hydrogen stretching vibration, and  $5.75\ \mu$ , carbonyl absorption, could readily be monitored, a kinetic evaluation was attempted. Due to the in-growth of ketonic species at  $5.85\ \mu$  interfering with the ester vibration (see Table III, for typical data), the changes were best followed by observing the decrease of  $3.35\ \mu$  absorption band. Using this band, a series of straight line plots of the change in per cent polymer remaining as a function of oxidation time at temperatures of 180, 190, 200, 210, 220, 230, and  $240^{\circ}\text{C}$ . could be constructed. These data are graphically represented in Figure 4. Since the change in polymer concentration is due to volatilization of fragments from the polymer surface, the apparent zero-order kinetic relationship was not unexpected. From the slopes of the lines at each temperature, a series of rate constants was obtained. These rate data are summarized in Table IV.



TABLE IV  
Summary of the Rate Data for the Oxidative Degradation of  
Poly(ethyl Acrylate) in Air between 180 and 240°C.

Temperature, °C.	$1/T \times 10^3$	Rate constant $k$ , hr. <sup>-1</sup>	$-\log k$
180	2.21	0.64	3.194
190	2.16	1.28	2.893
200	2.12	9.3	2.040
210	2.07	11.9	1.920
220	2.03	27.4	1.570
230	1.99	221.6	0.654
240	1.95	472.2	0.326

From the values of  $-\log k$ , the best curve through these points was determined by a stepwise linear regression analysis. All calculations were carried out using a standard program on an IBM 1620 computer. The slope so obtained when multiplied by  $2.303R$  gave an activation energy of  $50.9 \pm 4.5$  kcal. Figure 5 shows a diagrammatic construction of the activation energy plot. The value for the activation energy is consistent with those reported for degradation processes involving volatilization of low molecular weight species via a random chain scission process.<sup>13</sup> The value

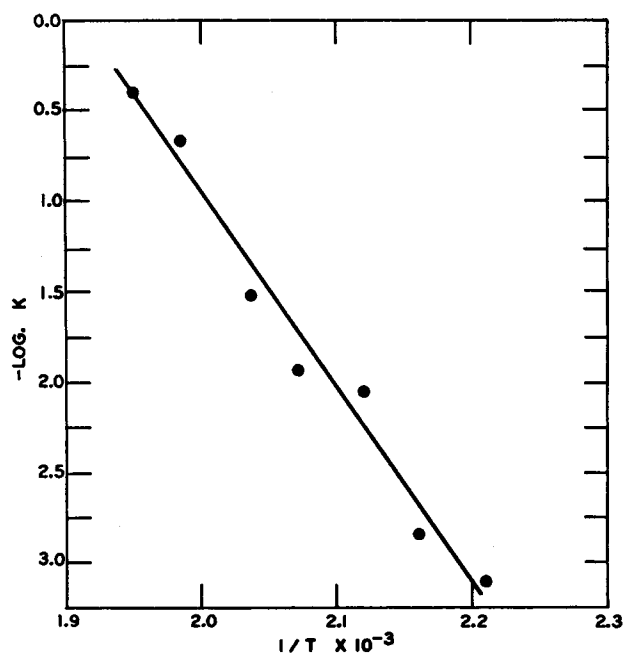


Fig. 5. Graphic representation of the change in rate constant vs. the reciprocal of the absolute temperature for estimation of the activation energy of poly(ethyl acrylate) oxidative degradation.

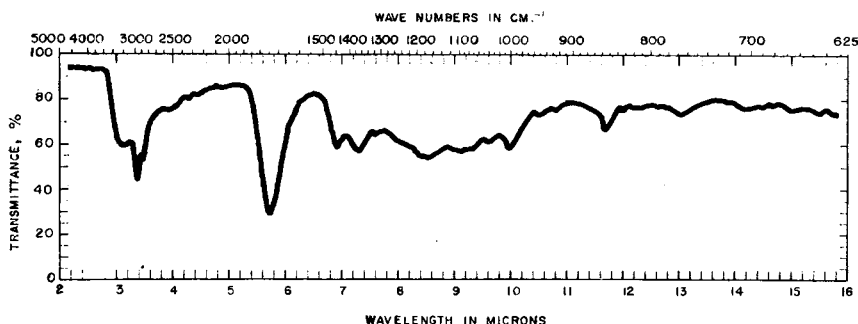


Fig. 6. Typical spectrum of oxidized, volatile, low-polymeric acid-ester fragments.

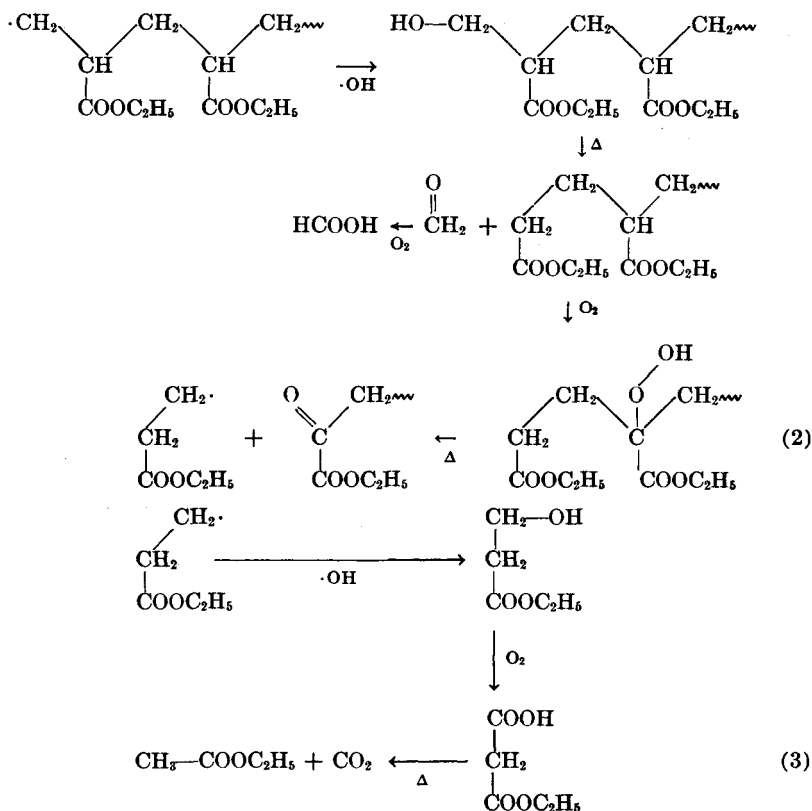
obtained here for the activation energy for oxidative chain scission of poly(ethyl acrylate) to give volatile fragments, is in excellent agreement with the value obtained for hydroperoxide decomposition in polystyrene and various deuterio-substituted polystyrenes reported by Beachell and Nemphos.<sup>14</sup> Interestingly, these investigators also showed the rate-controlling step must involve the breaking of the tertiary C—H (or C—D) bond. Since in the present study, the volatilization process was actually monitored, the rupture of the chain again must be the rate determining step for the overall steps to give volatile products.

Substantiation of such a process was considered. It was felt that since the bulk phase of the polymer showed little or no observable changes besides the shift and intensity differences discussed for the 5.75  $\mu$  carbonyl band, an analysis of the volatile components would best offer a source of additional information.

Spectral examination of the residual material collected on the walls of the pyrolysis chamber indicated that this was highly oxidized polymer fragments. The spectrum of this material is shown in Figure 6. Of particular importance are the characteristic absorptions in the 3–4  $\mu$  region due to hydrogen-bonded, hydrogen-oxygen stretching vibrations of alcohol and carboxylic acid species. As well, changes in the 5.75  $\mu$  vibration (sharp and intense in the bulk phase) to a broad diffuse band indicate the complex functionality of this material. The volatile degradation products were collected in a Dry Ice-acetone trap and the noncondensable product (carbon dioxide) was collected in an Ascarite-filled tube. Using vapor-phase chromatographic techniques, the condensable products were identified as ethanol, water, and ethyl acetate.

All of the above-mentioned data indicate fairly conclusively that degradation proceeds via a random chain scission process. The independence of rate upon the polymer remaining is evidence for a reaction by which low polymer fragments volatilize from the surface of the film. The amount of polymer lost in this manner in any short time interval is negligible compared to the bulk of unreacted polymer remaining on the salt plate. Furthermore, the fact that the formation of highly oxygenated species can not





It remains a serious deficiency of the methods used here to establish concretely the mechanistic steps beyond the very early chain scission process. Since these secondary reactions will be dependent upon a number of molecular parameters of the oxidized polymer, such as volatility of the oxidized surface species and the extent of crosslinking, the determination of the specific nature of the extended degradation steps becomes difficult to establish with certainty. The use of isotopic labeling together with the synthesis and oxidation of model, low molecular weight, acrylic chains seem the only future pathway to gain additional information concerning these oxidations. Such approaches are presently being seriously considered.

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### Résumé

On a étudié la dégradation oxydante du polyacrylate d'éthyle par les techniques spectro-photométriques infra-rouges, et on a déterminé les produits volatils par analyse chromatographique en phase vapeur. Au cours de la dégradation, on ne détecte aucun changement dans le spectre du polymère, ce qui indiquerait la formation d'autres substances. Il y a seulement une diminution généralement uniforme dans toutes les bandes carbonyle-ester-détoxe de la région de 5.75 à 5.85 microns. Cette diminution d'absorption s'effectue à une vitesse appréciablement plus faible que celle observée précédemment pour la dégradation du polyacrylate d'éthyle. Il n'était pas essentiel de mentionner dans cette étude la formation des groupes acides carboxyliques dans le spectre du polymère dégradé. En contraste avec le polyacrylate d'éthyle dégradé, le polymère volatil formé par oxydation, de faible poids moléculaire, est fortement oxydé. En plus, on a identifié des produits très volatils de dégradation tels que l'anhydride carbonique, l'eau, l'acétate d'éthyle et l'alcool éthylique. Ni le monomère, ni l'acrylate d'éthyle ne sont détectés parmi les produits volatils. On a proposé un mécanisme sur la base de ces résultats. Initialement, il y a une attaque par l'oxygène moléculaire sur les atomes de carbone tertiaires de la chaîne polymérique pour former des groupes hydroperoxydes. La décomposition simultanée du groupe hydroperoxyde résulte dans la scission au hasard de la chaîne donnant éventuellement des unités polymériques de faible poids moléculaire. L'oxydation ultérieure des unités polymériques faibles conduit à la formation des produits observés.

### Zusammenfassung

Der oxydative Abbau von Polyäthylacrylat wurde mit Infrarotspektrophotometrie-methoden untersucht und die flüchtigen Abbauprodukte durch gaschromatographische Analyse bestimmt. Während des Verlaufs des Abbaues konnte keine für die Bildung anderer Stoffe sprechende Änderung im Spektrum des Polymeren festgestellt werden. Es trat lediglich eine allgemeine einheitliche Abnahme aller vorhandenen Absorptions-banden mit Ausnahme des 5,75-5,85  $\mu$  Ester-Ketoncarbonylbereichs auf. Diese Absorptionsabnahme verlief beträchtlich langsamer, als die früher für den Abbau von Polyäthylacrylat berichtete Geschwindigkeit. Die Bildung von Carbonsäuregruppen, die im Spektrum des abgebauten Polymeren gefunden worden waren, konnte in der vorliegende Untersuchung nicht bestätigt werden. Im Gegensatz zum abgebauten Polyäthylacrylat erwies sich das niedrigmolekulare, flüchtige, bei der Oxydation gebildete Polymere als hochgradig oxydiert. Zusätzlich wurden die hoch flüchtigen Abbauprodukte als Kohlendioxyd, Wasser, Äthylacetat und Äthylalkohol identifiziert. Monomeres Äthylacrylat konnte unter den flüchtigen Produkten nicht gefunden werden. Auf Grundlage dieser Ergebnisse wurde ein Abbaumechanismus aufgestellt. Die Reaktion wird eingeleitet durch einen Angriff von molekularem Sauerstoff am tertiären Kohlenstoffatom der Polymerkette unter Bildung von Hydroperoxydgruppen. Die darauffolgende Zersetzung des Hydroperoxyds führt zu einer statistischen Kettenspaltung, wobei niedrigmolekulare Polymereinheiten entstehen. Die weitere Oxydation der niedrigen Polymereinheiten führt zur Bildung der beobachteten Produkte.

Received March 30, 1964