Thermal-Oxidative Degradation of Poly(ethyl Acrylate)

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Saturated polymers are much more stable to oxidative degradation at moderate temperatures than those having residual unsaturation. In the absence of ultraviolet light, the degradation is usually quite slow, and not much attention has been given to this process.[1] We have studied the thermal-oxidative degradation of thin films of poly(ethyl acrylate) at 100° in air and found that oxygen absorption and chain scission reactions were surprisingly rapid.

Information on the degradation of polyacrylates is very meager. Madorsky and Strauss[2,3] have studied the pyrolysis of poly(methyl acrylate) *in vacuo* at 292–399°C. The polymer was broken down to a variety of relatively low molecular weight products, but in contrast to poly(methyl methyacrylate), only very small quantities of monomer were obtained. Wall and Florin[4] have included these results in a recent paper which discusses the degradation of polymers by a free radical chain mechanism. The degradation of poly(ethyl acrylate) by ultrasonic waves has been investigated by Schmid and Rommel,[5] and Larsen and Drickamer[6] have investigated the degradation which occurs when poly(ethyl acrylate) undergoes plastic deformation at high pressure. The effect of ionizing radiation on polyacrylates has been studied by a number of investigators.[7-11]

In the present work we have used emulsion-polymerized poly(ethyl acrylate) which has been purified and cast into films on the inside of glass tubes. The tubes were kept at the desired temperature while a stream of air was pulled through them, and the polymer degradation was followed by viscosity determinations and titration of the acidity which developed. Measurements were also made of the initial rate of oxygen absorption.

EXPERIMENTAL PROCEDURE

Poly(ethyl acrylate) was prepared by emulsion polymerization in the presence of an ammonium persulfate–sodium hydrosulfite redox catalyst system and with an octylphenol–ethylene oxide condensate as a dispersant. The emulsion was dialyzed overnight in regenerated cellulose tubing against running tap water before the films were cast. The dialysis removed catalyst residues and other low molecular weight materials which produced a brown discoloration when polymer films were heated. The dialyzed polymer did not discolor during degradation. Its molecular weight, as determined by viscosity measurements, was 1.2 × 10⁶.

The films were cast on the interior surface of cylindrical glass tubes such as shown in Figure 1. To prepare a film, dialyzed emulsion was pipetted into the part of the tube below the construction. The tube was then rotated horizontally while being evacuated. The film deposited by this procedure was not very uniform because the dispersion coagulated during the evaporation. However, the film could be made smooth, uniform, and transparent by dissolving it in a small amount of ethylene dichloride and then evaporating the solvent under
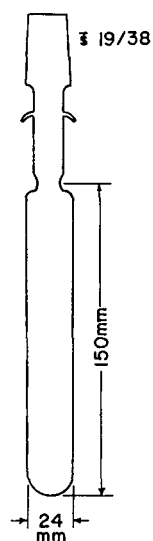

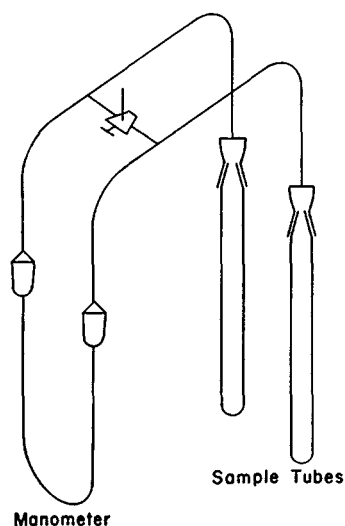Fig. 1. Sample tube for casting and degrading poly(ethyl acrylate) film.

of the manometer liquid was followed with a cathetometer. From these data, the dimensions of the manometer tube, and the total volume of the system, the oxygen sorption of the film could be calculated.

RESULTS AND DISCUSSION

Viscosity Changes and Oxygen Absorption

Viscosity changes during the degradation of poly(ethyl acrylate) at 100°C. are plotted in Figure 3. When heated in a vacuum of 0.1 mm. of mercury, the polymer degrades only very slightly. When a stream of air is passed through the tube, the film degrades rapidly and extensively, but this can be completely inhibited by the addition of 1% hydroquinone on the weight of the film. The hydroquinone was incorporated by dissolving it in the dialyzed emulsion before casting the film. Addition of benzoyl peroxide (in the ethylene dichloride used in the film-smoothing step) results in a more rapid decrease in viscosity whether air is present or not. The degraded peroxide-containing films were not completely soluble in ethanol. The yield of insolubles increased with time of heating, but did not make up more than 1% of the original polymer even for the longest times used.

Since the degradation apparently depended on the access of oxygen to the polymer, the degradation of films of different thickness was studied. The thickness was varied by adding different quantities of polymer to tubes of known size so that the thickness could be calculated from their dimensions. The data in Figure 4 show the intrinsic viscosity of these films after they were heated at 100° for 8 hours in air. For thicknesses from 10 to 70 μ the

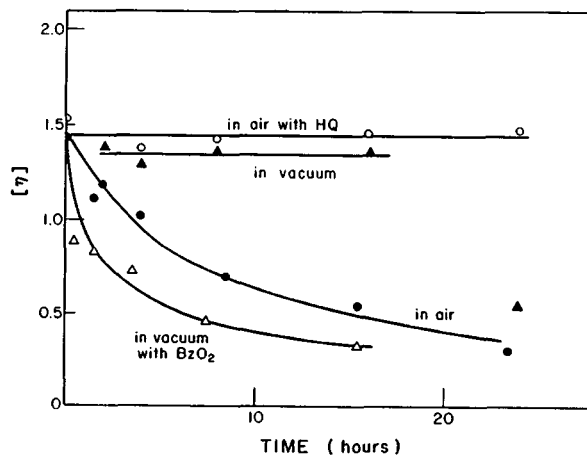Fig. 2. Oxygen absorption apparatus.

vacuum while the tube was rotated at 2700 rpm. Except when otherwise specified, the films were about 35 μ thick. The films were degraded by immersing the tubes in an oil bath controlled to within ±0.5°C., a separate film being prepared and degraded for each time period desired. The sample tubes in the bath could be connected to a vacuum manifold or fitted with an air inlet tube which reached near the bottom.

Degraded films were dissolved in 2B-ethanol, and their intrinsic viscosities were determined in a Cannon-Ubbelohde dilution viscometer. For acid content determinations, a portion of the alcoholic solution was titrated with sodium methoxide in methanol, a Beckman Model H-2 meter being used to detect the endpoint.

The apparatus used to measure oxygen absorption is shown schematically in Figure 2. It consisted essentially of two sample tubes connected together by a U-tube manometer containing dibutyl sebacate, with the upper arms of the U-tube joined through a three-way stopcock. One of the sample tubes held the experimental film, while the other served as a temperature compensator. To carry out a determination, the sample tubes were attached to the manometer, and the whole system was evacuated through the stopcock to about 0.1 mm. of mercury. The evacuation was continued while the sample tubes were immersed in the oil bath and allowed to come to temperature equilibrium, which required about 15 minutes. The apparatus was then filled with tank oxygen to atmospheric pressure, and the two arms of the manometer were isolated by closing the stopcock. The change in height

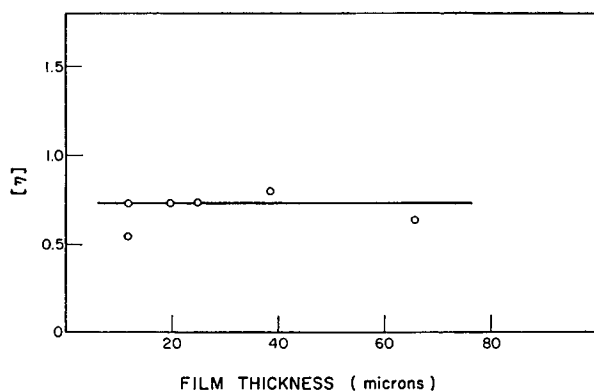Fig. 3. Degradation of poly(ethyl acrylate) film at 100°C

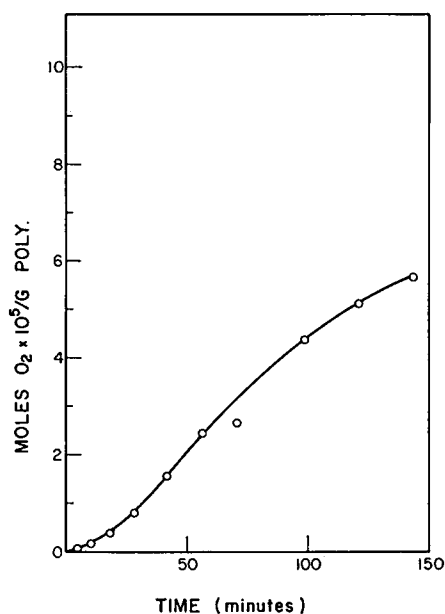Fig. 4. Effect of film thickness on degradation of poly(ethyl acrylate) at 100°C.

Fig. 5. Absorption of oxygen by poly(ethyl acrylate at 100°C.

extent of degradation in this time interval is the same. Over this range the diffusion of oxygen would not appear to be the limiting factor in the reaction.

The rate of oxygen absorption at 100°C. is shown in Figure 5. Only the initial part of the curve should be considered, since it was found that appreciable amounts of volatile products are soon produced and no provision was made for their removal. The beginning of the curve has the typical shape resulting from autocatalytic oxidation of polymers, and it seems reasonable to conclude that the oxidation of poly(ethyl acrylate) is a similar process. This process has generally been taken to involve the formation of hydroperoxides which decompose to yield fragments capable of further reaction with oxygen.

Temperature Effects and Rate

The intrinsic viscosities of poly(ethyl acrylate) films about 35 μ thick degraded in air at 80, 100, and 120°C. are shown in Figure 6. As the shape of these curves would indicate, the reciprocals of the viscosities plotted against time give straight lines. If the slopes of the latter are plotted against reciprocal temperature, as in Figure 7, an apparent activation energy of 28.6 kcal./mole may be calculated. As one would expect, this is lower than that calculated by Strauss and Madorsky[3] for the pyrolytic degradation of poly(methyl acrylate) (37 kcal./mole).

A measure of the change in molecular weight with time was obtained after estimating the constants of the Staudinger equation for alcohol solutions. The intrinsic viscosities of two different molecular weight fractions of poly(ethyl acrylate) were determined in 2B-ethanol, benzene, and acetone. From these
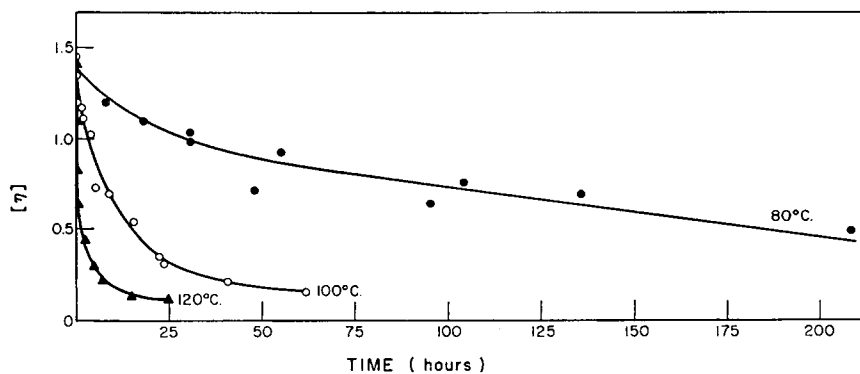

Fig. 6. Thermal-oxidative degradation of poly(ethyl acrylate) at different temperatures.
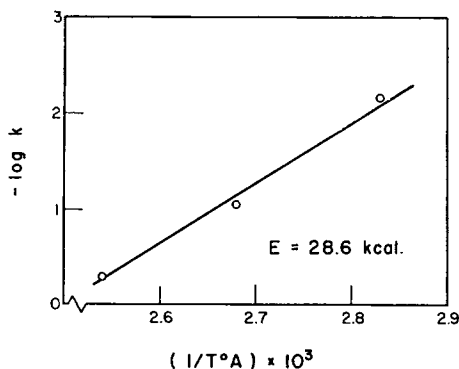
Fig. 7. Determination of apparent activation energy for thermal-oxidative degradation of poly(ethyl acrylate).

Fig. 8. Development of acidity in poly(ethyl acrylate) during thermal-oxidative degradation at 100°C.

data and the literature values of α and K for acetone and benzene,[13] the constants for 2B-ethanol were calculated to be $\alpha = 0.51$ and $K = 1.21 \times 10^{-2}$. The reaction rate constant at 100°C. becomes 1.1 × 10^{-3} (monomer units/polymer molecule)$^{-1/2}$ hour^{-1}.

Degradation Products

The products formed by the thermal oxidative degradation of poly(ethyl acrylate) are a heterogeneous mixture. Though changes in intrinsic viscosity are large, there are relatively small structural changes in the polymer, and only traces of nonpolymeric material are formed. After as much as a tenfold decrease in intrinsic viscosity, the weight loss was less than 0.05%. For the most part, we have made only a qualitative identification of products.

The infrared spectra of the films were examined before and after degradation with a Model 21 Perkin-Elmer infrared spectrophotometer. The only observable change in the degraded films was a new peak in the region where carboxylic acid groups would be expected to absorb. When the film was steeped in aqueous sodium hydroxide, washed, dried, and re-examined, the absorption was shifted into the region characteristic of the carboxylate ion. On the presumption that these changes indicated the creation of carboxylic acid groups on the polymer, acid contents of degraded films were determined as described above. Typical results are presented in Figure 8 for 35 μ films degraded at 100°C. in air.

In the oxygen absorption apparatus it had been recognized that volatile, condensable products were given off in the degradation. A small amount of condensate was obtained from the neck of a tube
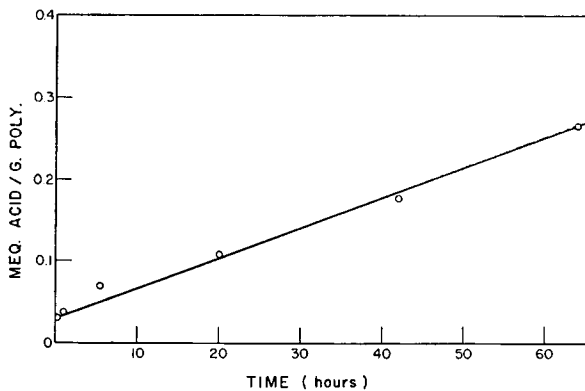
in which a film had been heated at 100°C. for 500 hours in air. Infrared examination of the condensate indicated the presence of water and other products containing at least two types of carbonyl groups probably ester and aldehyde carbonyl. Ketone or acid groups were not likely possibilities. There was no spectroscopic indication that ethyl acrylate or any other unsaturated compound was obtained. Some absorption was observed in the region where carbon-oxygen bonds in alcohols and ethers are expected.

A mass spectrometric analysis was made of the gas from another closed tube in which a polymer film had been degraded in air for 6 hours at 120°C. The consumption of oxygen was observed, and the following compounds were identified in the volume percentages shown.

Carbon dioxide	0.82%
Formic acid	0.46%
Ethanol	0.21%
Water	≤2.5%

These results are, for the most part, consistent with the infrared observations on the condensate. Water was found in both vapor and condensate, while carbon dioxide was in the vapor alone, as would be expected. Ethanol appeared to be in both vapor and condensate. It is surprising that formic acid was detected in the mass spectrum and not in the infrared unless relatively small amounts were produced. The carbonyl compounds tentatively identified in the condensate as aldehyde and ester must be high boiling.

Mechanism

Madorsky[3] indicated that the thermal degradation of poly(methyl acrylate) *in vacuo* at 292–399°C.

involved random chain splitting and not depolymerization. The rapid decrease in intrinsic viscosity, the insignificant weight loss, and the small yield of volatile products containing no identifiable monomer all lead to the conclusion that random scis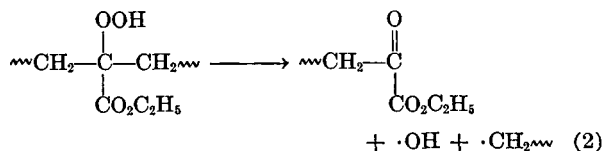sion is also involved in the thermal-oxidative degradation. The autocatalytic nature of the oxygen absorption and the character of the volatile products indicate that the mechanism is probably complex. However, the process resembles in a number of ways the thermal-oxidative degradation of other saturated vinyl polymers, and this has received some attention.
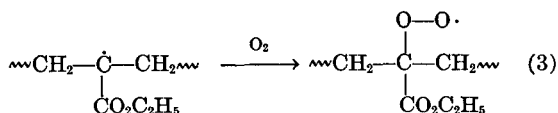
The initiating step in the oxidation of poly (styrene) in air at moderate temperatures is probably the attack of oxygen on the tertiary carbon[14-16] to yield a hydroperoxide. Analogously, for poly(ethyl acrylate), we would postulate the following reaction, which is slow compared to subsequent oxygen-consuming reactions.

$$\text{ⱭⱭCH}_2\text{—CH}\text{ⱭⱭ} \xrightarrow{\text{O}_2} \text{ⱭⱭCH}_2\overset{\overset{\displaystyle \text{OOH}}{|}}{\underset{\underset{\displaystyle \text{CO}_2\text{C}_2\text{H}_5}{|}}{\text{C}}}\text{ⱭⱭ} \quad (1)$$

with $\text{CO}_2\text{C}_2\text{H}_5$ below the CH.
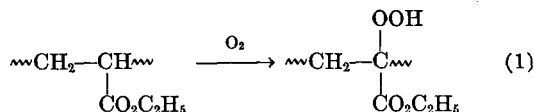
The decomposition of the hydroperoxide would be expected to result in chain scission.[17]

$$\text{ⱭⱭCH}_2\overset{\overset{\displaystyle \text{OOH}}{|}}{\underset{\underset{\displaystyle \text{CO}_2\text{C}_2\text{H}_5}{|}}{\text{C}}}\text{—CH}_2\text{ⱭⱭ} \longrightarrow \text{ⱭⱭCH}_2\overset{\overset{\displaystyle \text{O}}{\|}}{\underset{\underset{\displaystyle \text{CO}_2\text{C}_2\text{H}_5}{|}}{\text{C}}}$$

$$+ \cdot\text{OH} + \cdot\text{CH}_2\text{ⱭⱭ} \quad (2)$$

The free radicals produced in this reaction may abstract hydrogen from the polymer (most easily, again, at a tertiary carbon), combine with one another, or undergo further oxidation. Hydrogen abstraction would produce a polymer radical which would react with molecular oxygen much more easily than does the polymer itself.

$$\text{ⱭⱭCH}_2\overset{\cdot}{\underset{\underset{\displaystyle \text{CO}_2\text{C}_2\text{H}_5}{|}}{\text{C}}}\text{—CH}_2\text{ⱭⱭ} \xrightarrow{\text{O}_2} \text{ⱭⱭCH}_2\overset{\overset{\displaystyle \text{O—O}\cdot}{|}}{\underset{\underset{\displaystyle \text{CO}_2\text{C}_2\text{H}_5}{|}}{\text{C}}}\text{—CH}_2\text{ⱭⱭ} \quad (3)$$

The radical product can abstract a hydrogen to form the hydroperoxide and then decompose. This process would yield a main-chain scission and three radicals which would continue the process. This multiplicative character explains the autocatalytic feature of the reaction. The relatively high yield of water among the volatile products is accounted for by hydrogen abstraction by the hydroxyl radicals resulting from reaction (2). Recombination of polymer radicals is probably always

taking place, but is detected as a separate process only with difficulty.

It has been suggested, in the case of paraffin oxidation, that primary radicals such as $\cdot\text{CH}_2\sim$ react with oxygen to yield, after hydrogen abstraction, an unstable primary hydroperoxide which decomposes.[18] A similar mechanism in this case would give the products $\text{R}\cdot$, $\cdot\text{OH}$, and CH_2O. Subsequent oxidation[19,20] of formaldehyde produced in this way may account for the formic acid observed in the volatile products. The primary polymer hydroperoxide may also decompose to form an aldehyde,[21] and oxidation of this functional group can introduce acid functionality into the polymer. It seems likely that the carbon dioxide and ethanol generated arise from the further oxidation of moieties such as the ketoester product of reaction (2). It is unlikely that ethanol should be produced from the main chain by oxidative attack.

The inhibitory effect of hydroquinone is explained by its ability to stop the initiation reaction (1), either by scavenging oxygen as it diffuses into the film or, more probably, by reacting with a radical involved in the initiation steps. Benzoyl peroxide, by its thermal degradation, yields radicals which abstract tertiary hydrogen from the polymer
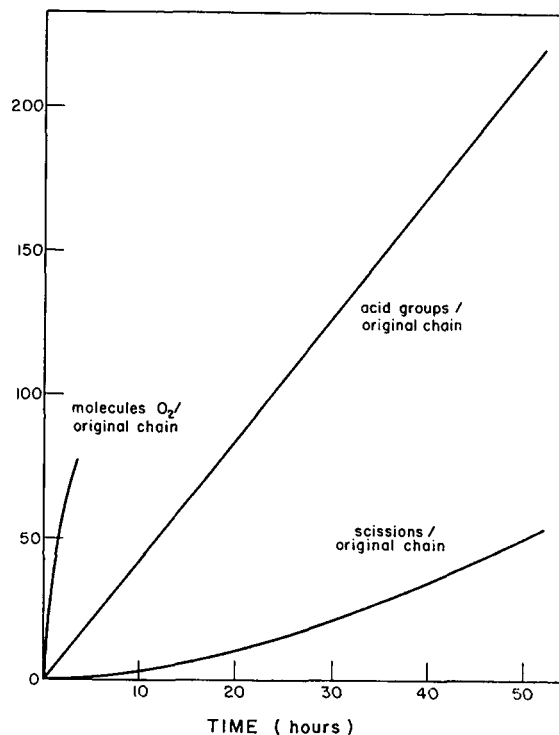

Fig. 9. Comparison of oxygen absorption, acid formation, and chain scission during thermal-oxidative degradation of poly(ethyl acrylate) at 100°C.

chain to produce odd electrons along the polymer chain. The observed degradation results from chain splitting at the radical sites.

This general picture of the mechanism indicates that oxygen will be consumed at a much faster rate than chain scission will be occurring. Since oxygenated groups other than carboxyls are produced, and since some of the acid formed is volatile, the consumption of oxygen will also be faster than the formation of titratable acid groups in the polymer. The observed rates of these processes may be compared in Figure 9 and are in the order expected.

CONCLUSION

Thin films of poly(ethyl acrylate) are degraded more rapidly and extensively in air at 100°C. than the saturated nature of this polymer would lead one to expect. Oxygen sorption measurements indicate that the reaction has the autocatalytic character observed in the oxidation of other polymers. The initiating step is probably the attack of molecular oxygen, which yields formation of a hydroperoxide. Degradation of the hydroperoxide results in chain splitting, and further oxidation of the new chain ends leads to acid groups in the polymer, together with small amounts of volatile oxygenated products.

The infrared and mass spectra were obtained for us by Mr. Earl Rector and Dr. Alan Weiss.

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Synopsis

The thermal-oxidative degradation of films of poly(ethyl acrylate) about 35 μ thick were studied in the temperature range of 80 to 120°C. The degradation was followed by determining intrinsic viscosity changes, absorption of oxygen, and production of titratable acidity in the polymer. From viscosity results an apparent activation energy of 28.6 kcal. was calculated. Only very slight degradation occurred when the polymer was heated in a vacuum. In air, the reaction is inhibited by the presence of hydroquinone, while the addition of benzoyl peroxide caused a rapid degradation even in a vacuum. The rate of oxygen absorption was found to be similar to that typical of autocatalytic oxidations. Oxygen diffusion did not appear to be the rate-determining factor in the degradation of films 10 to 70 μ thick. The weight loss during degradation was very small, but infrared and mass spectra indicated the presence of carbon dioxide, ethanol, formic acid, and water among the volatile products. A degradation mechanism based on hydroperoxide formation and decomposition is suggested.

Résumé

La dégradation thermique oxydative de films de polyacrylate d'éthyle de 35 μ d'épaisseur environ a été étudiée dans un intervalle de 80 à 120°C. La dégradation était suivie par mesure des variations de la viscosité intrinsèque, absorption d'oxygène, et production d'acide titrable dans le polymère. Au départ des résultats viscosimétriques on a calculé une énergie d'activation apparente de 28,6 Kcal. Il n'y a qu'une très faible dégradation si le polymère est chauffé sous vide. A l'air, la réaction est inhibée par la présence d'hydroquinone, alors que l'addition de peroxyde de benzoyle provoque une dégradiation rapide même sous vide. La vitesse d'absorption de l'oxygène a été trouvée semblable à celle des oxydations antocatalytiques typiques. La diffusion de l'oxygène ne semble pas être le facteur déterminant de la vitesse dans la dégradation de films de 10 à 70 μ d'épaisseur. La perte en poids durant le dégradation est très faible, mais la spectrographie infrarouge et la spectrographie de masse indiquent la présence d'anhydride carbonique, d'éthanol, d'acide formique et d'eau parmi les produits volatils. Un mécanisme de dégradation faisant intervenir la formation et la décomposition d'hydroperoxydes est suggéré.

Zusammenfassung

Der thermisch-oxydative Abbau von etwa 35 μ dicken Polyäthylacrylatfilmen wurde im Temperaturbereich von 80 bis 120°C. untersucht. Der Abbau wurde durch Bestimmung der Ändreung der Viskositätszahl, der Sauerstoffaufnahme und des entstandenen titrierbaren Säuregehaltes im Polymeren verfolgt. Aus den Viskositätsergebnissen wurde eine scheinbare Aktivierungsenergie von 28,6 kcal berechnet. Beim Erhitzen des Polymeren im Vakuum trat nur ein sehr schwacher Abbau ein. Unter Luft wird die Reaktion durch die Gegenwart von Hydrochinon verhindert, während der Zusatz von Benzoylperoxyd sogar im Vakuum einen schnellen Abbau hervorruft. Es wurde gefunden, dass die Geschwindigkeit der Sauerstoffaufnahme ähnlich, wie die für autokatalytische Oxydationen war. Die Diffusion des Sauerstoffs schien beim Abbau von 10 bis 70 μ dicken Filmen nicht der geschwindigkeitsbestimmende Faktor zu sein. Der Gewichtsverlust während des Abbaus war sehr klein. Infrarotanalytisch und massenspektroskopisch wurde die Gegenwart von Kohlendioxyd, Athanol, Ameisensäure und Wasser unter den flüchtigen Produkten nachgewiesen. Es wird ein Abbaumechanismus unter Annahme von Hydroperoxydbildung und -zersetzung vorgeschlagen.