

The Photooxidation of Polymers.

I. Experimental Methods

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Synopsis

The very early stages of the oxidation of polymers at ordinary temperatures must be studied if the ultimate reasons for oxidative instability are to be discovered. To this end apparatus which will allow the absorption of small amounts of oxygen to be measured with high precision has been designed and built. Its design is such that both photo-initiated oxidation and pure photolysis may be studied. Experimental manipulation of the apparatus and the calculation of results are discussed, as well as the preparation of polystyrene films for photooxidation and photolysis investigations.

I. INTRODUCTION

A very large amount of work has been carried out with a view to the improvement of the aging properties of commercial polymers. These investigations have often been specifically directed at relating aging to the deterioration of those physical properties of the materials which are of particular commercial importance. It is perhaps of little immediate concern to the producer, that the overall aging process is usually the consequence of the combined action of three principal agencies; namely oxygen, radiation, and heat. Nevertheless, for the ultimate complete understanding of the deterioration of a specific polymer it is necessary to simplify the systems experimentally by separating out the roles of these agencies and investigating their individual chemical consequences, in other words, to determine the fundamental chemical reactions which make up the overall aging process.

In this connection a great deal of detailed information is available about the action of heat on a number of polymers. In particular, the points of thermal instability, the influence of abnormalities in the polymer structure and the influence of the structure of the repeat unit have been given special attention. These thermal studies have recently been given additional impetus by the demands for the synthesis of high temperature resistant materials.

While a great deal of attention has also been paid to the individual effects of light radiation and oxygen, relatively less fundamental chemical

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information is available. The mechanism of the oxidation of simple olefins has been thoroughly investigated and the hydroperoxidation mechanism for these reactions put on a sound quantitative basis.¹ The hydroperoxides of saturated small molecular compounds are much less stable and their decomposition leads to a more complicated overall process, so strict quantitative work in this area has been more difficult. Nevertheless, it is clear that in the lower temperature ranges at least, the same hydroperoxidation process as occurs in olefins plays a major role.

The quantitative investigation of the oxidation of polymers proves much more difficult, however, for two main reasons. Firstly, it is often difficult to analyze small concentrations of oxidation products in the macromolecular environment. Thus it is tempting to carry the reaction so far that the chains are extensively broken down and volatile products, which are much more readily identified, begin to appear. These products, however, are usually the result of overwhelming secondary reactions involving the complex decomposition of the initially formed products and an extrapolation back to the initial stages of the overall reaction, which are so important if the ultimate reasons for oxidative instability are to be identified, is not always reliable. Secondly, the establishment in a solid polymer of a homogeneous oxidation reaction, which is desirable for quantitative investigations, is extremely difficult because in all but the thinnest films the rate of the reaction so readily becomes dependent upon the rate of diffusion of oxygen into the polymer film.

The present series of papers represents an attempt to clarify some fundamental relationships in the photolysis and oxidation of some relatively stable polymers. Photolysis and oxidation are studied together because photoinitiation of the oxidation reaction was necessary in order to achieve measurable rates without raising the temperature to such an extent that the secondary reactions, referred to above, overwhelmed the primary process. Polystyrene was specifically chosen as a starting point for these investigations because its thermal degradation is well understood and it is an important commercial material whose applications are strictly limited by the rapid deterioration of some of its useful physical properties in spite of the fact that, speaking in a relative chemical sense, it is not an unstable material.

This, the first paper in the series, is concerned with the development of apparatus and techniques for following these photolysis and photooxidation processes.

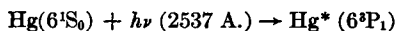
II. FACTORS INFLUENCING DESIGN OF APPARATUS

The oxidation of polystyrene is relatively slow, and since the early stages of the reaction were to be of particular interest it was necessary to develop apparatus which would allow the absorption of very small amounts of oxygen to be measured. Some of the more important factors which had an influence on the ultimate design of the apparatus are as follows.

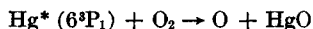
The rate of oxidation is very sensitive to the wavelength of the initiating radiation: 2537 Å. is found to be approximately forty times as effective as 3650 Å. radiation of similar intensity. Thus to achieve useful rates, 2537 Å. radiation had to be used and that part of the reaction vessel through which the sample is to be irradiated must be of silica.

It is important for two reasons that the atmosphere within the apparatus should be mercury-free and thus that an alternative manometric fluid should be used. Firstly, absorption of radiation by mercury vapor would cause considerable attenuation of the light intensity incident on the surface of the polymer. For example, it can be calculated² that a 1-cm. column of air containing mercury vapor at 25°C. (v.p. = 1.8×10^{-3} mm.) is sufficient to reduce the intensity of 2537 Å. radiation to 20% of its incident value. Secondly, the absorption of 2537 Å. radiation by mercury vapor in an atmosphere of oxygen results in the production of ozone.

Absorption of radiation gives excited atoms;



In absence of collisions these become deactivated by fluorescing, but oxygen quenches this fluorescence, atomic oxygen and ozone being formed.³



It is important that the overall reaction should not be complicated by the occurrence of ozonization.

Diocetyl sebacate was chosen as a manometric fluid because of its low vapor pressure, low absorption of 2537 Å. radiation, and low reactivity. Its low specific gravity also gives an increase, by a factor of approximately 16, in manometric sensitivity compared with mercury.

Close temperature control is clearly essential for the accurate determination of small pressure changes. With this in mind the apparatus was made as simple and small as possible yet capable of accommodating a relatively high area of film under conditions of uniform irradiation.

III. OXIDATION APPARATUS AND EXPERIMENTAL PROCEDURE

A. Apparatus

The apparatus, shown in Figure 1, consists essentially of two cells, C₁ and C₂, of equal volume joined by a differential manometer, M, and immersed to the level indicated (W.L.) in a water thermostat maintained at $28 \pm 0.01^\circ\text{C}$. The lower parts of the cells are constructed from B40 Pyrex cones and the upper parts are B40 fused silica sockets (Thermal Syndicate Limited) with optically flat ends through which the radiation is transmitted. Before assembly, the lower parts only of the cones were smeared with silicone high vacuum grease in order to avoid the presence of grease inside the cells and hence its possible oxidation. The cells are joined at P to the oxygen supply and high vacuum system and can be isolated

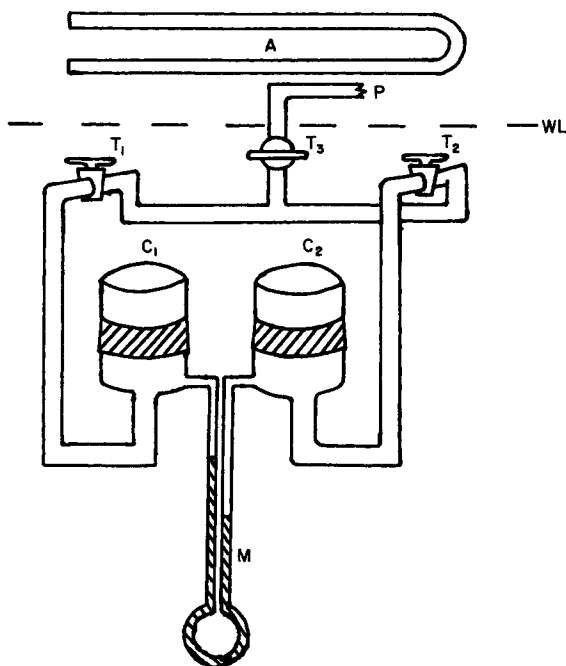


Fig. 1. Oxidation apparatus.

from these by using stopcock T_3 , and from each other by closing T_1 and T_2 . The films are oxidized in C_1 , while C_2 , which is under the same conditions of temperature, pressure and irradiation, acts as a compensating volume. In this way variations in pressure arising from small fluctuations in ambient temperature are balanced out. The manometer is constructed from heavy wall constant bore (Veridia) tubing having a volume of 0.165 cc./cm. The volumes of C_1 and C_2 including tubing to T_1 and T_2 , respectively, were both 130 ± 0.5 ml.

The arrangement of the film in C_1 is shown in Figure 2. It is placed between two brass rings which are screwed together, H , and placed on platform S , which consists of a brass disk, perforated to allow the oxygen to have free access to the underside of the film. The disk is in turn supported on a glass tube, G , round which the glass cup, C , is sealed. The purpose of the latter is to contain absorbents to remove the carbon dioxide and water produced during the reaction. Identical compensating equipment (with the exception of the film) is placed in C_2 .

The mercury vapor lamp, with its arc in a horizontal position (A in Fig. 1), is placed vertically and symmetrically above the apparatus.

Since the film is held rigidly, warping is impossible, and the surface area exposed to oxygen and radiation is accurately known. The position of the film is automatically fixed by means of the supports so that the intensity of radiation incident upon the film can be more easily held

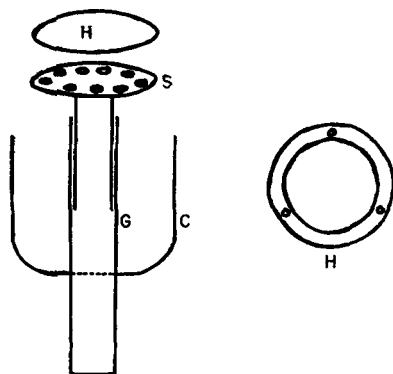


Fig. 2. Film arrangement in oxidation apparatus.

constant through a series of experiments. In addition the cells are fully compensated for spurious oxygen absorption or temperature effects.

B. Experimental Procedure

Evacuation and the supply of oxygen was achieved by using the system illustrated in Figure 3. A mercury vapor diffusion pump backed by a rotary oil pump was used, the pressure being observed on a vacuostat at V. Oxygen was supplied from the reservoirs, R_1 and R_2 , the former containing oxygen at 700 mm. and the latter about 20 mm. greater than that required in the oxidation apparatus. Pressurization of the oxidation apparatus was carried out as follows. With stopcocks, T_1 , T_2 , T_3 , T_4 , T_5 , T_7 , T_8 , and T_9 open, the whole system was evacuated to a pressure of

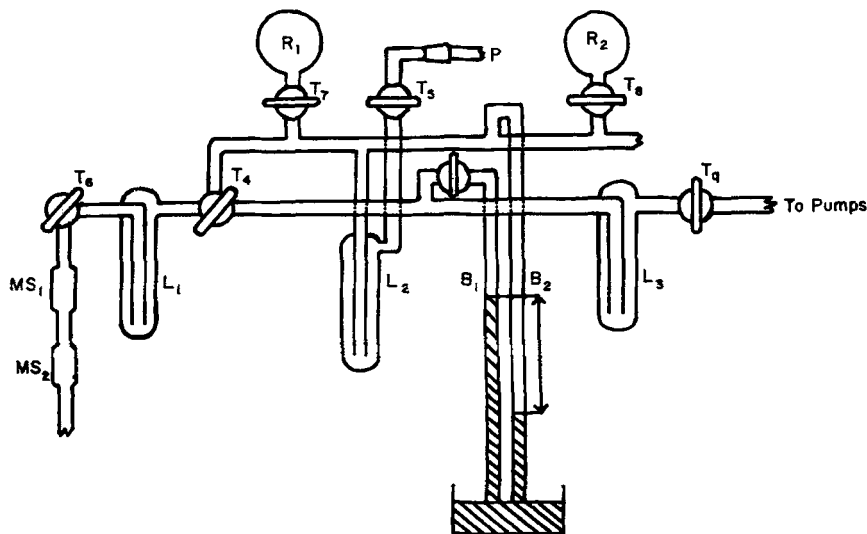


Fig. 3. Oxygen supply to oxidation apparatus.

10^{-5} mm. Hg. R_1 and R_2 were then filled to the appropriate pressures, observed on B_1 and B_2 , from an oxygen cylinder through tubes MS_1 and MS_2 containing respectively types 4A and 5A Linde molecular sieves (30 mesh) and a trap, L_1 , at -78°C . Thus H_2O and CO_2 were removed from the oxygen. A similar trap, L_2 , removes mercury vapor before the oxygen enters the reaction cells. With T_6 , T_7 , and T_8 closed, the apparatus was evacuated, and after closing T_4 the oxidation apparatus was pressurized to the working pressure, indicated by the difference in levels B_1 and B_2 , by appropriate manipulation of T_7 and T_8 . B_1 indicated the barometric height. After closing T_3 the apparatus is left for 30 min. to assume the temperature of the water bath. The cells were then isolated from one another by closing T_1 and T_2 , the lamp switched on taking care not to irradiate the films and the apparatus allowed to settle down for a further 30 min., before starting the reaction by exposing the cells. The resulting changes in levels in C_1 and C_2 were followed using a cathetometer.

C. Calculation of Extent of Reaction

1. Oxidation. The amount of oxygen absorbed is not linearly dependent upon the pressure difference measured by the levels in C_1 and C_2 , but may be calculated as follows, where V is the volume of C_1 and C_2 (cubic centimeters), P is the original pressure of oxygen in C_1 and C_2 (centimeters Hg), P_1 and P_2 are the new pressures in C_1 and C_2 , respectively (centimeters Hg), d and d_M are the density of manometric fluid and of mercury, respectively (grams/cubic centimeter), r is the radius of the manometer tubing (centimeters), $2h$ is the observed difference in levels (centimeters), and T is the reaction temperature (absolute). The original number of moles of oxygen (n_0) in C_1 and C_2 is given by

$$n_0 = PV/RT$$

Applying Boyle's Law,

$$PV = P_2(V + \pi r^2 h)$$

Therefore

$$P_2 = PV/(V + \pi r^2 h)$$

Thus

$$\begin{aligned} P_1 &= P_2 - (2hd/d_M) \\ &= [PV/(V + \pi r^2 h)] - (2hd/d_M) \end{aligned}$$

Also

$$V_1 = V - \pi r^2 h$$

The number of moles of oxygen, n_1 , left is given by

$$n_1 = P_1 V_1 / RT$$

and the extent of reaction by,

$$n_0 - n_1 = (PV - P_1V_1)/RT = \frac{1}{RT} \left[PV - \frac{PV^2}{V + \pi r^2 h} + \frac{PV\pi r^2 h}{V + \pi r^2 h} + \frac{2hdV}{d_M} - \frac{2h^2d\pi r^2}{d_M} \right]$$

The accuracy of the cathetometer (0.002 cm.) corresponds to an absorption of 1.9×10^{-8} moles of oxygen if the initial pressure is 600 mm. Hg. Since the weight of the sample is approximately 5×10^{-3} g., this represents an ultimate accuracy of approximately one molecule of oxygen per molecule of polystyrene of molecular weight 10^6 .

2. Photolysis in Vacuum. When photolysis is carried out in vacuum the amount of volatile material produced in C_1 is given by $(1/RT)[(2hd/d_M)(V + \pi r^2 h)]$.

IV. THE INITIATING RADIATION

A. Nature of Radiation Incident upon the Polymer Film

The photolysis and photooxidation of polystyrene is sensitive to the wavelength of the radiation. It is not feasible in work of this kind, however, to use monochromatic radiation. The range of particular interest lies in the near ultraviolet at wavelengths longer than those which are strongly absorbed by air but short enough and thus of high enough energy to affect the polymer. It was found possible to compare the effects of 2537 A. radiation with radiation of wavelength 3650 A. and longer by using (a) a Hanovia Chromatolite lamp, and (b) an Osram 125 w. M.B. which are, respectively, low and medium pressure mercury arcs.

According to the manufacturer's data, 8.4% and 84%, respectively, of the quantum output of the Hanovia lamp occurs at 1849 and 2537 A. and the remainder at longer wavelengths. From the Osram lamp 15% of the quantum output occurs at each of the wavelengths 3650 and 3663 A. with smaller amounts at various longer wavelengths. Since 1849 A. radiation is completely absorbed by 1 cm. of air at atmospheric pressure the Hanovia lamp yields largely monochromatic 2537 A. while the Osram lamp gives relatively high intensities from 3650/3663 A. upwards, with traces of radiation down to 3000 A. where the glass envelope becomes completely opaque.

By using the manufacturer's output data together with standard uranyl oxalate actinometric techniques^{2,4-6} the intensities of the various wavelengths from the lamps at the film have been computed and are presented in Tables I and II.

The transmissions of thicknesses of water and fused silica of the order of those encountered experimentally are illustrated in Figures 4 and 5 and show that the wavelengths which appear in Tables I and II will only be slightly attenuated in their passage to the film.

It is fortunate that the 1849 A. line is so strongly absorbed by the oxygen in the air, since photolysis of the oxygen in the cell would occur, yielding

TABLE I
 Output of Hanovia Lamp

λ , A.	Fraction of radiation emitted	Intensity at film (7.375 cm. from lamp), Einsteins/sec./cm. ²
1849	0.084	—
2537	0.84	2.54×10^{-9}
2652	0.0018	5.65×10^{-12}
2753	0.0010	3.14×10^{-12}
2893	0.003	9.42×10^{-12}
2967	0.001	3.14×10^{-12}
3021	0.0052	1.63×10^{-11}
3130	0.0052	1.63×10^{-11}
3650	0.0056	1.76×10^{-11}
3663	0.0056	1.76×10^{-11}
4046	0.0067	2.10×10^{-11}
4077	0.0067	2.10×10^{-11}
4339	0.0032	1.01×10^{-11}
4357	0.0080	2.52×10^{-11}
4358	0.016	5.03×10^{-11}

 TABLE II
 Output of Osram Lamp

λ , A.	Fraction of radiation emitted	Intensity at film, Einsteins/sec./cm. ²
3650	0.15	8.7×10^{-9}
3663	0.15	8.7×10^{-9}
4046	0.059	3.42×10^{-9}
4077	0.059	3.42×10^{-9}
4339	0.095	5.51×10^{-9}
4357	0.095	5.51×10^{-9}
4358	0.095	5.51×10^{-9}

ozone which could conceivably alter the course of the degradation reaction. The starch-potassium iodide test for ozone was applied and showed that the amount of ozone accumulating in the cell during 1 hr. irradiation was undetectable by this method and could therefore be assumed to be negligible.

B. Absorption of Radiation by Polystyrene

The ultraviolet absorption spectrum of a typical polystyrene film is illustrated in Figure 6, which shows that approximately 87% of incident 2537 A. radiation is absorbed.

Before attempting to obtain quantitative information from rates of oxidation of various thicknesses of film, Lambert's Law must be verified, that is, that the radiation is exponentially attenuated during its passage through the film or that $I_t = I_0 e^{-kl}$ in which I_0 and I_t are the incident and transmitted intensities and l is the film thickness. Figure 7 illustrates that this is so. The small intercept on the optical density axis can be as-

sociated with a 1.2% loss of incident radiation by scattering and reflection at the film surface and a corresponding correction must be made when quantum yields are calculated.

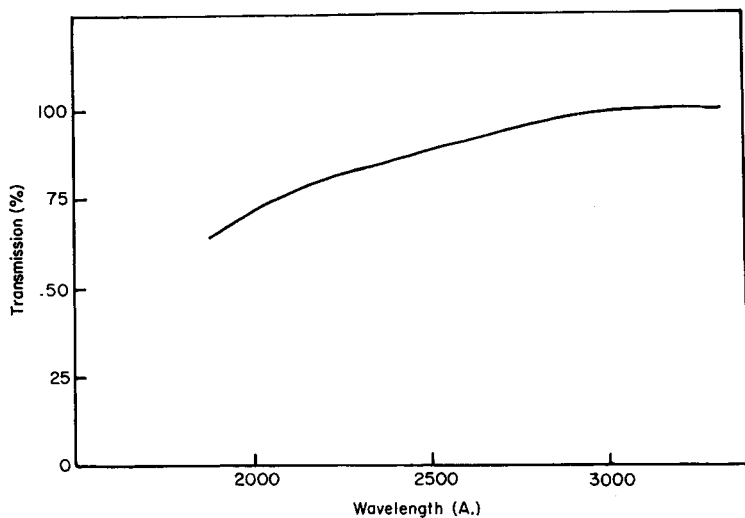


Fig. 4. Ultraviolet absorption of water (1 cm.).

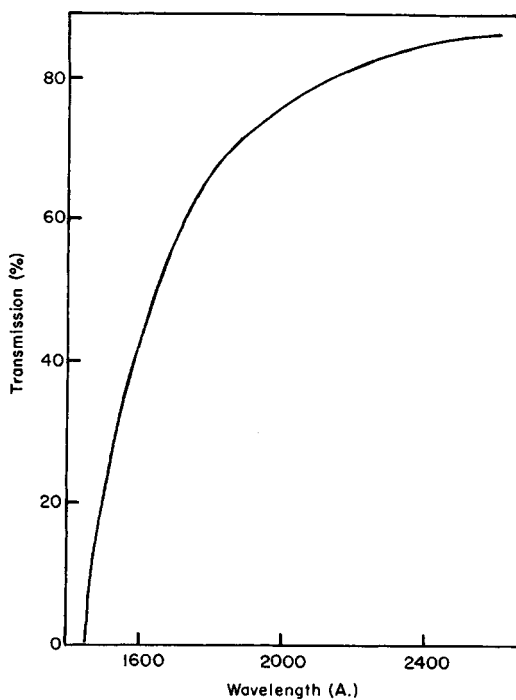


Fig. 5. Ultraviolet absorption of fused silica (2 mm.).

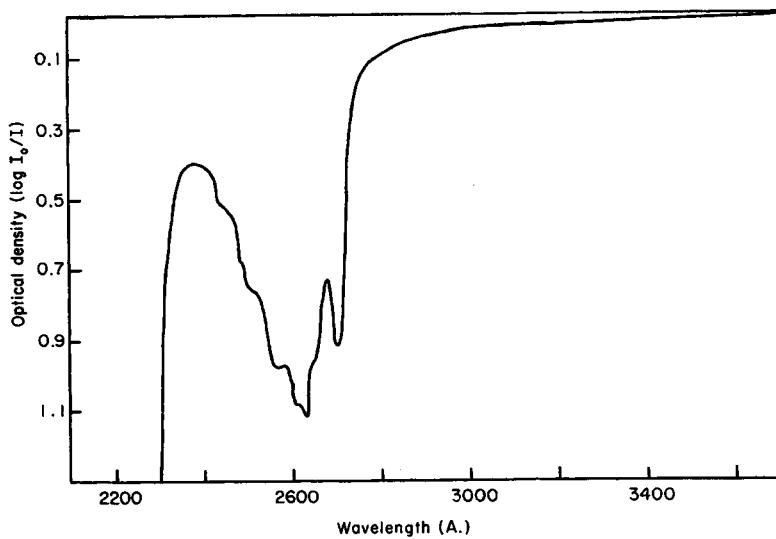


Fig. 6. Ultraviolet absorption of polystyrene film (0.0044 mm.).

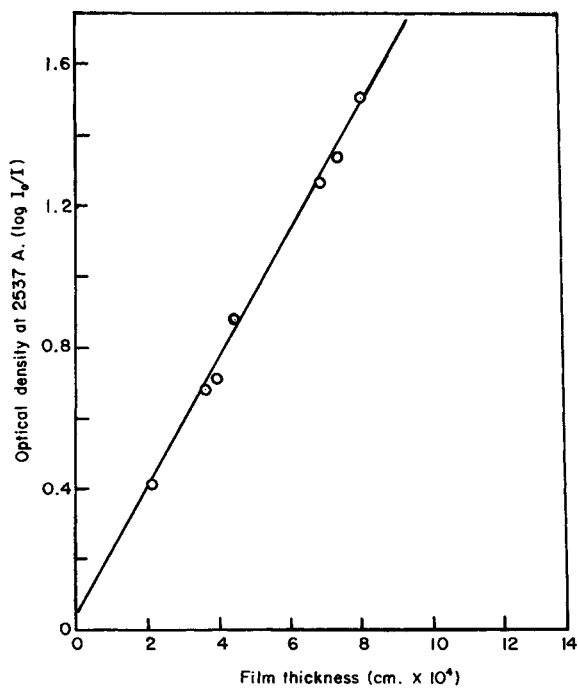


Fig. 7. Verification of Lambert's Law.

V. POLYMER FILMS

A. Choice of Film Thickness

The most appropriate thickness of the films to be used was decided by consideration of two properties of the polymer, namely, absorbance of 2537 Å. radiation and rates of diffusion of oxygen.

The intensity of 2537 Å. radiation is reduced to less than 1% by a 0.01 mm. film of polystyrene. It is clear therefore that even in the thinnest films the light intensity and hence the reaction rate can never even be approximately constant throughout the film.

Measurements by Barrer⁷ and Stannett⁸ indicate that the rate of diffusion of oxygen into polystyrene at 28°C. and 600 mm. is 7×10^{-7} cc./cm.²/mm./min. Thus for a film 0.01 mm. thick, that is, with a diffusion path of 0.005 mm., the rate of diffusion of oxygen is approximately 10^{-4} cc./cm.²/min. Early oxidation experiments indicated that this figure was greater than the rate of oxidation by a factor of at least five. The thinnest film which could be conveniently used consistent with reasonable mechanical strength was 0.0044 mm. In such material there should therefore be no question of the reaction rate being diffusion-controlled, and this thickness was therefore used as a standard throughout the present work.

B. Preparation of Films

Films were prepared by dissolving in chloroform the weight of polymer necessary to give the film thickness required, pouring the solution on mercury and allowing to evaporate slowly at room temperature for 24 hr. Clean distilled mercury was used but the possibility of contaminants on the mercury surface was reduced by rejecting six films before preparing the one to be studied.

In order to remove the last traces of chloroform the film was placed in a high vacuum system which was held evacuated until the chloroform absorption at 1218 cm.⁻¹ in the infrared spectrum had disappeared. It was found that this could be much accelerated by pressurizing the system with nitrogen at 300–600 mm., evacuating at intervals and warming to 45°C.

Film thicknesses were measured by weighing a known area and checked by measuring the absorption at 2537 Å. Good agreement between the two methods was achieved.

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Résumé

Il convient d'étudier les premiers stades d'oxydation des polymères aux températures ordinaires si l'on veut découvrir la cause de leur instabilité à l'oxydation. A cette fin, on a imaginé et réalisé un appareil permettant de mesurer avec précision l'absorption de petites quantités d'oxygène. Il a été conçu de façon à ce qu'on puisse y étudier aussi bien l'oxydation initiée par la lumière que la photolyse pure. On expose ici la technique expérimentale de manipulation de l'appareil, la méthode de calcul des résultats ainsi que la préparation de films de polystyrène utilisés pour les études de photooxydation et de photolyse.

Zusammenfassung

Wenn die wirklichen Gründe für die oxydative Instabilität aufgedeckt werden sollen, müssen die allerersten Stadien der Oxydation von Polymeren bei gewöhnlichen Temperaturen untersucht werden. Zu diesem Zweck wurde ein Apparat, welcher die Messung der Absorption kleiner Mengen von Sauerstoff mit grosser Genauigkeit gestattet, entworfen und gebaut. Er ist so eingerichtet, dass sowohl photochemische Oxydation als auch reine Photolyse untersucht werden kann. Die experimentelle Handhabung des Apparates und die Errechnung der Ergebnisse sowie die Darstellung von Polystyrolfilmen für Photooxydation und Photolyseversuche werden diskutiert.

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